PVDF-HFP Based Porus Polymer Electrolyte For Lithium Battery Applications

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Abstract-In order to develop the Solid Polymer Electrolyte (SPE) for lithium ion battery applications, P(VdF-HFP) and PEMA blend polymer with ethylene carbonate (EC), propylene carbonate (PC) and lithium perchlorate ($LiClO_4$) based SPEs were prepared by facile solution casting technique. AC conductivity of the SPEs was found as 5.49X10^{-3} Scm^{-1} at room temperatures and 8.13 X10^{-3} Scm^{-1} at 348 K. The crystallinity and complexation behavior of the SPEs were confirmed by XRD and FTIR analysis. The surface morphology of the electrolyte was studied by SEM analysis.

Keywords: Solid Polymer Electrolyte (SPE), P(VdF-HFP)/ PEMA, Ionic conductivity, Lithium ion battery.

1. Introduction

Polymer Electrolytes having better strength in the electrochemical devices such as Super Capacitor [1], Fuel Cell [2], Electrochromic devices [3], and Rechargeable Batteries [4] etc. Many researchers passing across the difficulties of the properties of polymer electrolytes in secondary batteries such as lighter weight, safer and more flexible in shape as compared with their liquid electrolytes and its electrochemical properties in order to make them possible for power storage application, Especially enhancement of ionic conduction of polymer electrolytes are involved an important role in the rechargeable batteries. However it is difficult to balance the required parameters of polymer electrolytes, such as high ionic conductivity and poor mechanical strength [1].

Many kinds of polymer have been selected as the matrix of poly (ethylene oxide) PEO, poly (acrylonitrile) PAN [5], poly (methyl methacrylate) PMMA [6], poly (vinylidene fluoride) P(VdF-HFP) [7], poly (ethyl methacrylate) PEMA [8] etc. PVdF-HFP contains both amorphous (HFP) and crystalline (PVdF) phases which provides plasticity and mechanical strength, respectively. PVdF-HFP based membranes tend to be opaque or translucent [9], while PEMA based membranes are transparent. Both PEMA and PVdF-HFP contains electron pairs that can coordinate with cations from inorganic salts, i.e. Li^+, H^+, to form polymer-salt complex and hence produces ionic conduction. Blend host matrices also help to increase the ionic conductivity.

The highest ionic conductivity of PVdF-HFP/PEMA complex was observed by Arof et al [10] as 1.05 X 10^{-4} Scm^{-1} and Ulaganathan et al [11] as 0.918 X$10^{-3}$$Scm^{-1}$ at room temperature. In order to further increase the ionic conductivity of PVdF-HFP/PEMA based polymer blend electrolytes, an attempt has been taken to incorporate the $LiClO_4$, EC & PC as plasticizer with the host polymer. The prepared electrolytes membranes were subjected into various studies, such as a.c. impedance measurement, FTIR, XRD and SEM.

2. Experimental

Poly (vinylidene fluoride – co – hexafluoropropylene) (PVdF-HFP), MW ~ 455,000, Sigma Aldrich) in pellet form, Poly (ethyl methacrylate) (PEMA, average MW ~ 515,000, Sigma Aldrich) in powder form, Ethylene Carbonate (EC, FW=88.06, purity 99%, Alfa Aesar), Propylene Carbonate (PC, FW=102.09, purity 99%, Alfa Aesar), Lithium Perchlorate ($LiClO_4$, MW = 106.39, battery grade, purity 99.99%, Sigma Aldrich) in powder were used as received. PVdF – HFP and PEMA blend based polymer electrolytes are prepared by Solution casting technique. Two different weight ratios of PVdF-HFP and PEMA are dissolved in volatile solvent such as acetone separately follow as Table 1. The $LiClO_4$ (8) was dissolved in the mixture of EC and PC (41 and 21) in appropriate amount of acetone. PVdF-HFP based polymer mixture was stirred continuously until obtained complete homogeneous solution. Further, polymers and salt mixture was stirred about 24 h and then kept at 60°C – 70°C until get the transparent resultant solution, the homogeneous gelled complex solution was cast on cleaned glass plate and dehydrated at 45°C in an oven for several hours to allow the complete evaporation of the acetone until solvent – free polymer electrolyte membranes were formed. Upon cooling at room temperature, the mechanically stable and transparent membranes were carefully peeled from the glass plates and stored in the vacuum desiccators for further drying before characterizations.

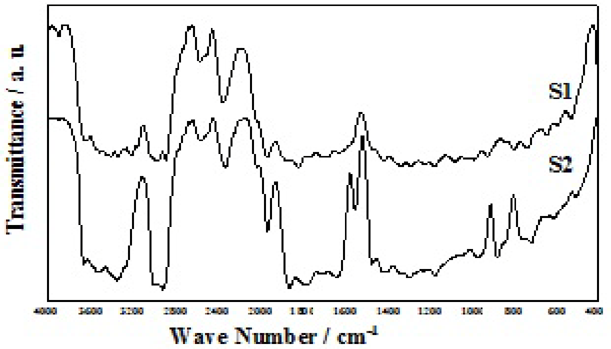

Figure 1: FTIR Spectrum of (S1) PVdF-HFP/PEMA (10:20), and (S2) PVdF-HFP/PEMA (06:24).

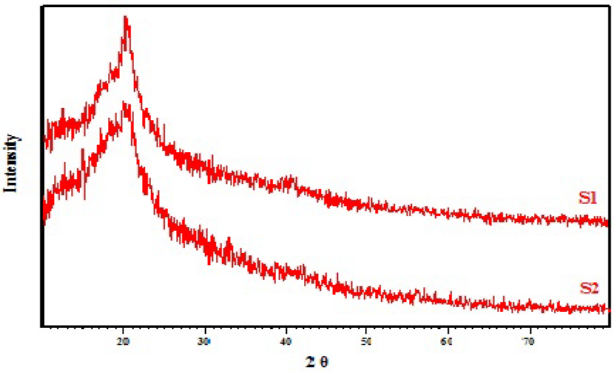

Figure 2: X-ray Diffraction for (S1) PVdF-HFP/PEMA (10:20), and (S2) PVdF-HFP/PEMA (06:24).

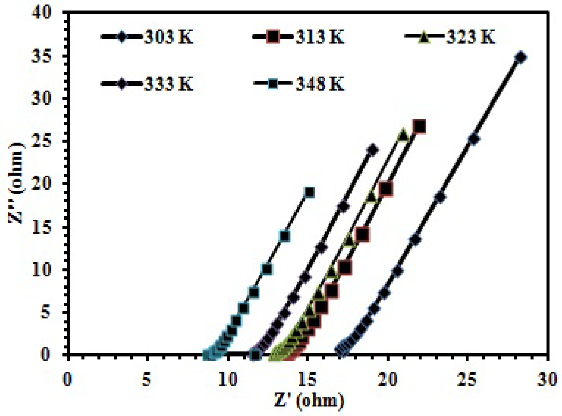

Figure 3: a.c. impedance of (S1) PVdF-HFP/PEMA (10:20)-EC (41)-PC (21)-$LiClO_4$ (8)

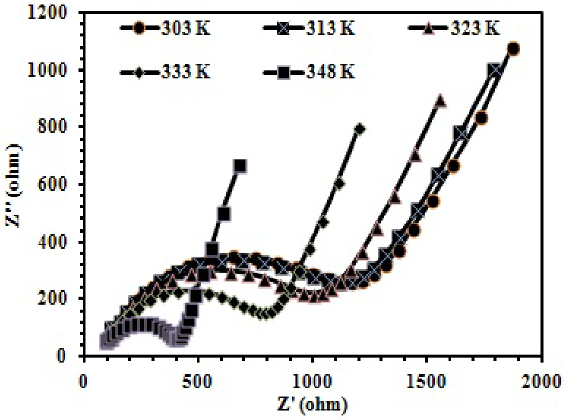

Figure 4: a.c. impedance of (S2) PVdF-HFP/PEMA (06:24)-EC (41)-PC (21)-$LiClO_4$ (8)

3. Results and Discussion

3.1 Studies of FTIR Spectroscopy

Infrared spectroscopy has been used to characterize the chain structure of polymer and has led the way in interpreting the reaction of multifunctional monomers [12]. The complex formation of PVdF-HFP and PEMA blend polymers and it's interaction with lithium salt and plasticizers are confirmed by FTIR analysis. Fig.1 shows the prepared samples declare as S1 and S2 respectively. The vibrational peaks at 499 cm^{-1} and 450 cm^{-1} are assigned to the bending and wagging vibration of – CF_2 respectively, the crystalline phase of the PVdF – co – HFP polymer is identified by the vibration bands at 986 cm^{-1}, 775 cm^{-1} and 615 cm^{-1}. The peak at 1178 cm^{-1} and 1399 cm^{-1} are assigned to the symmetrical stretching of – CF_2 and – CH_2 groups [13]. The peaks at 886 cm^{-1} and 888 cm^{-1} are assigned to the vinylidene group of the polymer. The frequency 3021cm^{-1} of C –H stretching vibration of PVdF crystalline phase of PVdF-HFP is shifted to 3047cm^{-1}. The bending vibration at 1790 cm^{-1} is assigned to PVdF-HFP, which is shifted to 1781 cm^{-1} in S1. The single bond bending vibration at 1483 cm^{-1} is assigned to – CH_3 asymmetric bending vibration of propylene carbonate , which is shifted to 1478 cm^{-1} in S1. The vibrational band at 1292 cm^{-1} is assigned to – C – F – stretching vibration of PVdF-HFP, which is shifted to 1289 cm^{-1} in S1 and 1076 cm^{-1} in S2. Frequency 888 cm^{-1} is assigned to the vinylidene group of polymer, which is shifted to 871 cm^{-1} in S1. Frequency at 844 $cm^{-1}$is assigned to C – Cl stretching vibrations of perchlorate. The crystalline region of PVdF in PVdF-HFP polymer 1797 cm^{-1}, 1417 cm^{-1}, 882 $cm^{-1}$and 839 cm^{-1} are shifted to 1790 cm^{-1}, 1418 cm^{-1} and 844 cm^{-1} in the polymer complexes.

The FTIR spectrum of PEMA shows the vibrational peaks at 2985 cm^{-1} and 2955 cm^{-1} which are attributed to the asymmetric and symmetric C-H stretching of the ethylene group of PEMA. The vibrational peaks corresponding to the –CH_2 Scissoring, –CH_2 wagging and –CH_2 rocking are observed at 1480 cm^{-1}, 921 cm^{-1} and 752 cm^{-1}. The C-H bonding due to C=CH_2 group is observed at 915 cm^{-1} , PEMA has lone pair electron at the oxygen atoms located at the carbonyl (C=O) and C – O – C group while PVdF-HFP contains free electron pairs at the fluorine atoms of CF_2 and CF_3 groups. The C=O stretching band of PEMA are located about 1707cm^{-1} in S2 and 1718 cm^{-1} in S1. The vibrational peaks of PEMA at 645 cm^{-1} in S2 and 844 cm^{-1} in S1 are identified. In the region, 2900 – 3000 cm^{-1} to be exact at 2982 cm^{-1},2939 cm^{-1}, 2910 cm^{-1} are due to the C – H stretching vibration of the methylene, (C) CH_3 and ethylene (O) C_2H_5 groups which overlap [14]. These frequencies are shift to 2961 cm^{-1} and 2969 cm^{-1} in S2 and S1 respectively. The skeletal vibration is shifted to 1478 cm^{-1} in S1, which is assigned to – CH_3 asymmetric bending of plasticizer such as propylene carbonate. The vibrational peaks at 775 cm^{-1} in S1 are belonging to the anion and cations are coordinated with the carbonyl carbon and carboxylic oxygen (C=O) presence in the polymer complexes. The vibrational peaks of $LiClO_4$ at 1630 cm^{-1} in S1 identified, which is shifted to 1645 cm^{-1} in S2. Shifting and formation of new peaks imply the polymer salt interaction in PVdF-HFP and PEMA blend based polymer electrolytes systems.

3.2 Studies of X-ray Diffraction

Fig. 2 shows the X-ray diffraction pattern for S1 and S2. The peak found at $2\theta = 20.4$ of PVdF – co – HFP reveals the partial crystallization of the PVdF units present in the copolymer, giving on overall semi crystalline morphology of PVdF – co – HFP [11]. The presence of broad hump in the pattern of PEMA confirms the amorphous nature of the polymer. The broad and lower intensity peak observed at $2\theta = 21$ degree represents the amorphous phase of PVdF-HFP/PEMA complex. No diffraction peaks identified to $LiClO_4$ is observed, that the salt is completely dissolved and trace of plasticizer also were absent in all electrolyte systems, which confirms the complete dissolution of the salt and plasticizer in the complex matrix and salt does not have any separate phases in the electrolytes.

3.3 Studies of Ionic Conductivity

The ionic conductivity of the each sample was calculated using the equation $\sigma = t/R_b*A$ (Scm^{-1}), where t is thickness of the electrolyte, R_b is the bulk resistance and A is the area of the electrolyte – electrode contact. The imaginary impedance (Z'') was plotted against the real impedance (Z') and the bulk resistance was obtained from the intercept with the real-axis [15]. Fig.3 and 4 shows the complex impedance spectra of P(VdF-HFP) – PEMA – EC – PC – $LiClO_4$ for the various concentrations of polymer blend based electrolyte system at different temperature with enlarged view of each complex impedance spectra. According to the theoretical analysis given by Watanabe and Ogata [16], as shown in Fig. 4 two semi circles should be appear in an impedance spectrum for a symmetric cell. i.e., one at higher frequency related to bulk electrolyte impedance and other at lower frequencies related to the interfacial impedance. It is also reported [17] that high frequency semi circle does not appear in our useful impedance plots for blend polymer membrane as shown in Fig.3. This phenomenon is quite reasonable since the too unproblematic mobility in this solid electrolyte system, when compared with liquid and gel polymer electrolytes. These complexes obey the temperature dependant ionic conduction is good agreement with Vogel – Tamman – Fulchar (VTF) relations, which describes the transport in a viscous matrix [18]. It supports to initiative the ions movements through the plasticizer rich phase, which is the conducting medium and involved with lithium salt. The samples are having improved ionic conductivity to higher temperature from ambient temperature, which could be credited to the enhance the free volume of the polymer electrolyte membrane, hence the free volume in a solid polymer electrolyte increases as a result and the segmental motion also permit the ions to hope from one site to another site or given the pathway to ion migration. Table.2 shows the a.c conductivity at different temperatures of two different complexes. S1 achieved the higher ionic conductivity as 5.49X10^{-3} Scm^{-1} at room temperatures and 8.13 X10^{-3} Scm^{-1} at 348 K in the complexes. When the addition of both polymer ratios as 1:2 those polymer amorphous region helps to given this maximum ionic conductivity at room temperature with flexible nature of electrolyte membranes. When PEMA increases with decreasing of P(VdF – HFP) in the complex, its overall amorphous phase become reduced and hence low ionic conduction with poor mechanical strength.

3.4 SEM Analysis

The Scanning Electron Microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure characteristics of solid objects. Fig.5 reveals the surface morphology of the polymer electrolytes depend upon the mixture of polymer blend ratios at various concentrations of PVdF-co-HFP and PEMA. It is common knowledge that a porous structure is essential for ionic transport from one site to another site. Hence, large porosity and small pore size are fundamental for a good separator. When PVdF-HFP and PEMA are taken as 1:2 wt %, the surface shows enormous number of pores and hence higher ion migration. The higher percentage of PEMA shows lower conductivity is due to fewer pores which evident from sample S2.

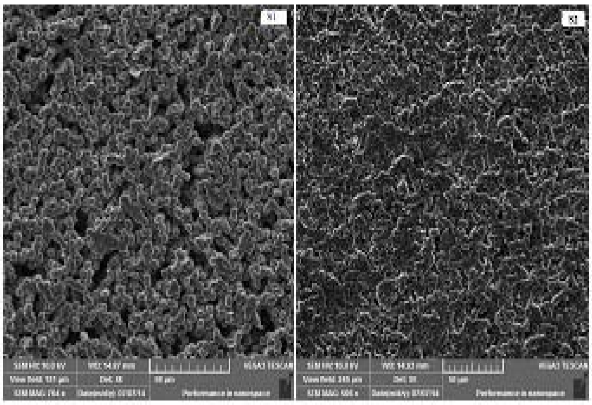

Figure 5: SEM image of PVdF-HFP/PEMA S1 (1:2), S2 (1:4)

Table 1: Description of Composition

Sample ID	P(VdF-FP)/wt.%	PEMA/wt.%
S1	0.10	0.20
S2	0.06	0.24

Table 2: Conductivity Values At Different Temperature

Sample ID	303 K	313 K	323 K	333 K	348 K
S1	X10^{-3} Scm^{-1}				
	5.49	6.90	7.33	8.03	8.13
S2	X10^{-5} Scm^{-1}			X10^{-4} Scm^{-1}	
	8.11	8.10	8.75	1.16	2.32

4. Conclusions

PVdF-HFP based polymer electrolytes prepared by solvent casting technique. The structural and complex formation in PVdF-HFP/PEMA-EC-PC-$LiClO_4$ system has been confirmed from XRD and FTIR studies. All electrolytes show appreciable ionic conductivity even at room temperature. Maximum conductivity as 5.49X10^{-3} Scm^{-1} at room temperature with good mechanical stability has been observed in PVdF-HFP (10) – PEMA (20) – EC (41) – PC

(21) – $LiClO_4$ (8) based system. Higher conductivity in this composition could be attributed to the higher amorphicity. The porosity of polymer electrolytes is also analyzed.

5. Acknowledgements

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References

[1] J Gamby., P.L Taberna, P Simon, J.F Fauvarque, M Chesneau, "Studies and characterizations of various activated carbons used for carbon/carbon super capacitors." Journal of Power Sources 101(1), pp.109-116, 2001.
[2] Jari Ihonen, Frédéric Jaouen, Göran Lindbergh, Göran Sundholm, "A novel polymer electrolyte fuel cell for laboratory investigations and in-situ contact resistance measurements."Electrochimica Acta 46(19) , pp.2899-2911, 2001.
[3] Diogo F. Vieira, César O. Avellaneda, Agnieszka Pawlicka, "Conductivity study of a gelatin-based polymer electrolyte." Electrochimica Acta 53(4), pp. 1404-1408, 2007.
[4] Manuel Stephan, Kee Suk Nahm, T. Prem Kumar, M. Anbu Kulandainathan, G. Ravi, J. Wilson, "Nanofiller incorporated poly(vinylidene fluoride–hexafluoropropylene) (PVdF–HFP) composite electrolytes for lithium batteries."Journal of Power Sources, 159 (2), pp.1316-1321, 2006.
[5] Prasanth Raghavan, Xiaohui Zhao, Chorong Shin, Dong-Ho Baek, Jae-Won Choi, James Manuel, Min-Yeong Heo, Jou-Hyeon Ahn, Changwoon Nah, "Preparation and electrochemical characterization of polymer electrolytes based on electrospun poly(vinylidene fluoride-*co*-hexafluoropropylene)/polyacrylonitrile blend/composite membranes for lithium batteries."Journal of Power Sources 195 (18), pp. 6088-6094, 2010.
[6] Hyung-Sun Kim, Kyong-Soo Kum, Won-Il Cho, Byung-Won Cho, Hee-Woo Rhee, "Electrochemical and physical properties of composite polymer electrolyte of poly(methyl methacrylate) and poly(ethylene glycol diacrylate)
[7] Chun-Guey Wu, Ming-I. Lu, Chung-Chih Tsai, Huey-Jan Chuang, "PVdF-HFP/metal oxide nanocomposites: The matrices for high-conducting, low-leakage porous polymer electrolytes."Journal of Power Sources 159(1), pp. 295-300, 2006.
[8] Jakub Reiter, Jiří Michálek, Jiří Vondrák, Dana Chmelíková, Martin Přádný, Zdeněk Mička, "Poly(ethyl methacrylate) and poly(2-ethoxyethyl methacrylate) based polymer gel electrolytes."Journal of Power Sources 158 (1), pp.509-517,2006.
[9] Hae-Sook Han, Hyo-Rang Kang, Sun-Wook Kim, Hee-Tak Kim, "Phase-separated polymer electrolyte based on poly(vinyl chloride)/poly(ethyl methacrylate) blend." Journal of Power Sources 112(2), pp.461-468, 2002.
[10] A.K. Arof, L.N. Sim, S.R. Majid, "Characteristics of PEMA/PVdF-HFP blend polymeric gel films incorporated with lithium triflate salt in electrochromic device."Solid State Ionics, pp.209–210, 15-23, 2012.
[11] M. Ulaganathan, Chithra M. Mathew, S. Rajendran, "Highly porous lithium-ion conducting solvent-free poly(vinylidene fluoride-co hexafluoropropylene) /poly(ethyl methacrylate) based polymer blend electrolytes for Li battery applications."Electrochimica Acta 93,pp.230-235, 2013.
[12] D.L. Pavia, G.M.Lapman, G.S. Kriz, introduction to spectroscopy, Harcourt College Publication, USA, 2001.
[13] Chi S Kim, Seung M Oh, "Importance of donar number in determining solvating ability of polymers and transport properties in gel-type polymer electrolytes."Electrochimica Acta 45 (13), pp.2101-2109,2000.
[14] R.M Silverstein, G.C. Bassler, T.C. Morill, spectroscopic identification of organic compounds, 5th edition john willy & sons, inc., USA 1991.
[15] Yong-Zhong Bao .Lin-Feng Cong, Zhi-Ming Huang. Zhi-Xue Weng, "Preparation and proton conductivity of poly(vinylidene fluoride)/layered double hydroxide nanocomposite gel electrolytes." J Mater Sci 43, pp.390–394, 2008.
[16] M.Watanabe, N.Ogata, in: J.R. MacCallum, CA. Vincent (Eds.), Polymer Electrolyte Review, Vol. 1, Elsevier, New York, 1987.
[17] D. Saikia, A. Kumar, "Ionic conduction in P(VDF-HFP)/PVDF–(PC+DEC)–$LiClO_4$ polymer gel electrolytes."Electrochimica Acta 49(16) , pp.2581-2589, 2004.
[18] S. Rajendran, Ravi shanker Babu, P.Sivakumar, "Investigations on PVC/PAN composite polymer electrolytes." Journal of Power Sources, 164(2), pp.815-821, 2007.