Materials Science

Trade Science Inc.

An Indian Journal

Full Paper

Investigations on polyvinylidene fluoride-co-hexa fluoropropylene blended polymer electrolytes

Ravi Shanker Babu[1]*, M.Usha Rani[1], S.Rajendran[2]
[1]School of Advanced Sciences, VIT University, Vellore- 632 014, (INDIA)
[2]School of Physics, Alagappa University, Karaikudi – 630 003, (INDIA)
E-mail : ravina2001@rediffmail.com

ABSTRACT

Polymer blend electrolyte comprising of poly (vinylidene fluoride-co-Hexa fluoro propylene) (PVdF-HFP), poly (methyl methacrylate) (PMMA) as host polymers and lithium per chlorate (LiClO$_4$) as the complexing salt were prepared by solution casting technique. The polymer ratio conducive for preparing polymer electrolytes for lithium battery applications is optimized based on the characterization studies Viz. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Differential scanning calorimetry(DSC) and electro chemical impedance analysis. These studies confirm the formation of polymer- salt complex and miscibility of polymers PVdF-HFP and PMMA. The room temperature electrical conductivity is found to be of the order of 10^{-5} S cm^{-1} and temperature dependence of ionic conductivity of polymer electrolyte films is elucidated.
© 2011 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Booming microelectronic industry and the electric/ hybrid car market that depend on power packs with high energy and power densities paved the way towards the improvement in energy sources[1-4]. Secondary batteries based on lithium represent an excellent choice for electrochemical power sources characterized by its high energy densities, good cyclability and reliability[5,6]. Lithium polymer batteries were found as potential candidate for the aforesaid applications, as the use of polymer electrolyte makes the battery highly safe and flexible[7]. Technological significance of polymer electrolytes reported by Fenton in 1973 was unappreciated until the findings reported by Armand et al.[8]. Pioneering work based on dry solid polymer electrolytes offer appreciable ionic conductivity only above 80ºC[9,10], the poor ionic conductivity of such electrolytes at ambient temperature limits their practical usage. However most of the solid –state polymer electrolytes (SPE) have low ionic conductivities (less than 10^{-5} S cm^{-1} at room temperature) effected by low mobility of the charge carriers in the polymer matrices. This magnitude of conductivity is far from the adequate level for practical room temperature applications. The most promising alternative is gel-type electrolytes prepared by the immobili-
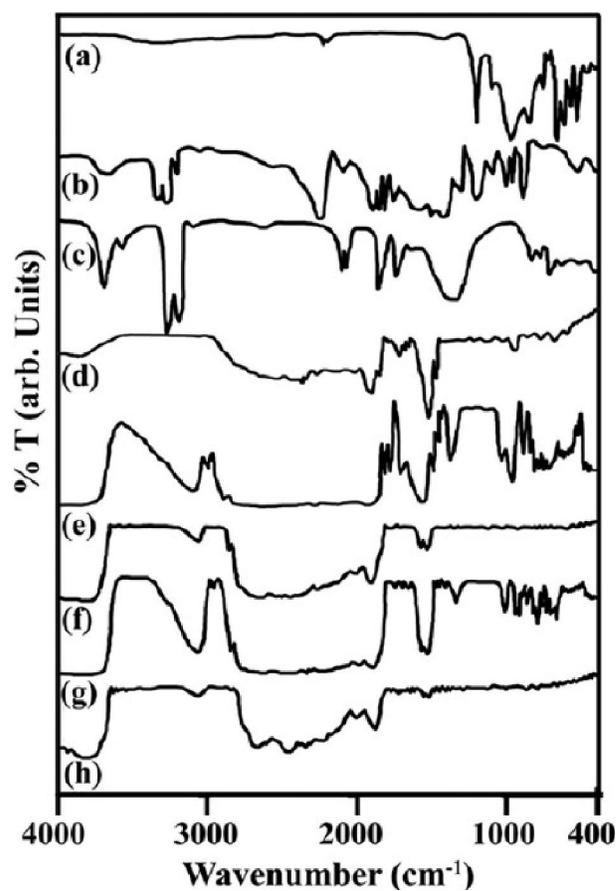
Full Paper
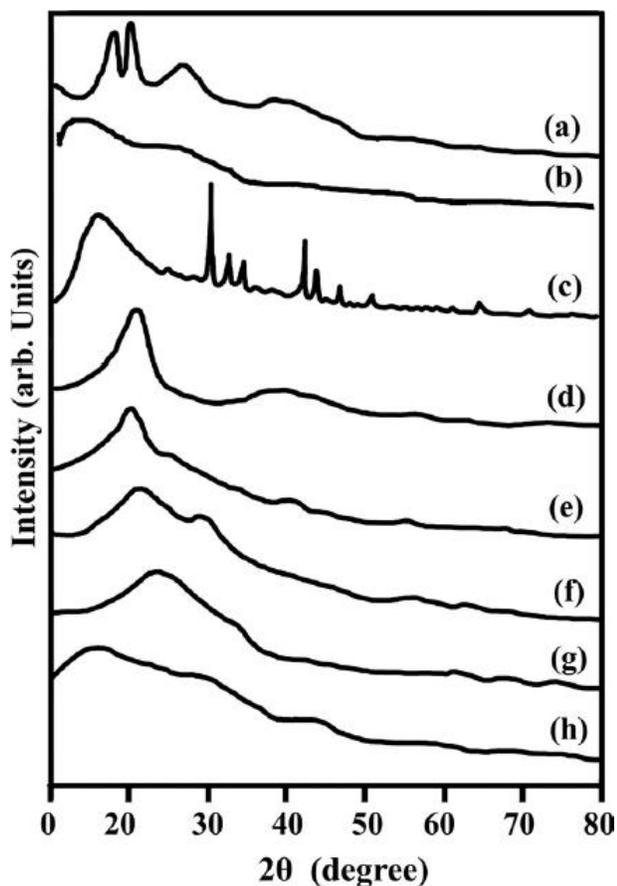
Figure 1 : XRD Spectra of (a) PVdF-HFP (b) PMMA (c) LiClO₄. (d) PVdF-HFP(100)–PMMA(0)–LiClO₄(8), (e) PVdF-HFP(75)–PMMA(25)–LiClO₄(8), (f) PVdF-HFP(50)–PMMA(50)–LiClO₄(8), (g) PVdF-HFP(25)–PMMA(75)–LiClO₄(8), (h) PVdF-HFP(0)–PMMA(100)–LiClO₄(8)

Figure 2 : FTIR Spectra of (a) PVdF-HFP (b) PMMA (c) LiClO₄. (d) PVdF-HFP(100)–PMMA(0)–LiClO₄(8), (e) PVdF-HFP(75)–PMMA(25)–LiClO₄(8), (f) PVdF-HFP(50)–PMMA(50)–LiClO₄(8), (g) PVdF-HFP(25)–PMMA(75)–LiClO₄(8), (h) PVdF-HFP(0)–PMMA(100)–LiClO₄(8)

zation of an aprotic liquid solution of a lithium salt in a polymer matrix. The resulting gel polymer electrolytes have ionic conductivities of the order of 10^{-3} S cm^{-1} at room temperature, almost as high as that of liquid electrolytes[11].

A variety of polymers, such as poly(ethylene oxide) (PEO)[12,13], poly(acrylonitrile) (PAN)[14], poly(methyl methacrylate) (PMMA)[15], poly(vinyl chloride)[16], poly(vinylidene fluoride) (PVdF)[17] etc. has been used as the polymer matrix to lodge the liquid electrolyte. Further, various approaches have been made to modify the structure of polymer electrolytes in order to improve their electrical, electrochemical and mechanical properties. These approaches include: synthesizing new polymers[18]; cross-linking two polymers[19]; blending of two polymers[20]; addition of plasticizers[21]; inorganic fillers etc.[6].

Amid the various polymers, PVdF and its copoly-

mers are very important because of their high strength and good stability[17,22-24]. Most impressive results have been obtained on poly(vinylidene fluoride-co-Hexa fluoro propylene) (PVdF-HFP). Of the two different blocks, VDF block has a stronger tendency than HFP block to undergo crystallization. The amorphous HFP phase aids ionic conduction deemed due to the entrapping liquid electrolyte, whereas the crystalline regions maintain freestanding films[25]. Authors have made series of studies on PVdF-HFP membranes prepared by phase inversion technique with different non-solvents as porogenic agents[26,27]. However the morphology and cycling performance of the membranes are found to be poor. In order to circumvent the above said drawback and increasing the ionic conductivity, blending PMMA to PVdF-HFP was carried out. Blending is more useful because of ease of preparation and can control the properties of polymer electrolytes by changing the compo-

Full Paper

sition of blended polymer matrix. There are several reasons for choosing PMMA to blend with PVdF-HFP: (i) PMMA is one among the widely used polymer matrix for gel electrolytes[28,30] as it is compatible with most liquid electrolytes; (ii) PMMA-based gel electrolytes have shown excellent interfacial stability towards lithium metal[28], and may improve the interfacial stability of (PVdF-HFP)-based systems; (iii) PMMA is an amorphous polymer that could decrease the crystalline phase in (PVdF-HFP) and in turn benefit ionic conductivity. On the basis of conductivity PMMA based polymer gel electrolytes are found to have high ionic conductivity, close to that of a liquid electrolyte, but difficult to form a polymer membrane with stable dimensions and good physical properties[31].

In the present work, solvent free polymer electrolytes consisting of PVdF-HFP and PMMA at five different weight ratios and with constant weight of $LiClO_4$ as the complexing salt were prepared so as to optimize the appropriate blend ratio which could suit well for lithium battery applications. This optimization is being substantially ascertained by XRD, FTIR, Impedance spectroscopy and DSC studies.

EXPERIMENTAL PROCEDURE

All polymer electrolyte samples were prepared by solution casting technique[32,33]. The polymer poly(vinylidene fluoride – Hexafluoro propylene) (PVdF-HFP) (average molecular weight 4×10^5), poly(methyl methacrylate (PMMA) (average molecular weight 12×10^4); alkali metal salt : lithium per chlorate ($LiClO_4$) all bought from Aldrich USA were used. The polymers and the Li salt were annealed under vacuum at 90°C, 120°C respectively for 10 hrs and each component was dissolved in pre-distilled Acetone (E-Merck, Germany). The dissolved polymer and salt were stirred continuously for 24 hrs at room temperature and at 50°C until homogeneous slurry was obtained. The thus obtained slurry was cast on to Teflon bushes and Teflon covered glass plates. The cast films were allowed to dry under argon atmosphere at room temperature for 3 hrs and then they were dried under vacuum at 60°C for 3 hrs for the evaporation of residual solvents if any. The thicknesses of the obtained films were about 0.1mm. The phase analysis of the poly-

mer was performed with X-ray diffractometer (XRD) [Bruker (D8 Advance)] at room temperature. The Fourier transform infrared (FTIR) spectrum in the range 4000–400 cm^{-1} was recorded using Jasco FTIR 460 plus (Japan) spectrophotometer.

The conductivity measurements were carried out with thus obtained films obtained by the casting technique. The electrolyte film was placed between the stainless steel electrodes with a spring load arrangement of a specially designed conductivity jig to ensure proper electrode-electrolyte contact. Electrical conductivity measurement was carried out using Aurbin FRA2 μAutolab-III with signal amplitude of 10mV in the frequency range 100Hz–500 kHz. Variation in conductivity with increase of temperature is recorded 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

XRD studies

X-ray diffraction pattern of pure PVdF-HFP, PMMA, $LiClO_4$ and complexes are shown in figure 1a-h. The following observations are made

Figure 1a-c shows the diffraction patterns of pure PVdF-HFP, PMMA and $LiClO_4$. The sharp crystalline peaks at 18º, 20º and broad diffraction peaks at 26º and 38º in figure 1a is due to the presence of the crystalline PVdF in PVdF-HFP[34-36] and the sharp peaks in figure 1c depicts the crystalline nature of the alkali metal salt. Absence of sharp peaks in figure 1b shows complete amorphous nature, diacritic to PMMA.

Figure 1d-h shows the diffractograms of (PVdF-HFP)-PMMA-$LiClO_4$ complexes at constant salt content with different polymer ratio. Figure 1d shows the XRD spectrum of (PVdF-HFP)-$LiClO_4$ complex where the crystalline peak corresponding to PVdF-HFP is found to reduce to a single peak indicating the reduction of crystallinity in the system. Figure 1e-h shows a chronological increase in amorphicity as the concentration of PMMA is increased. The highest amorphicity is seen for the film bereft of PVdF-HFP (i.e. film with PMMA-$LiClO_4$) but does not show highest conductivity which could be due to the fact of the difference in
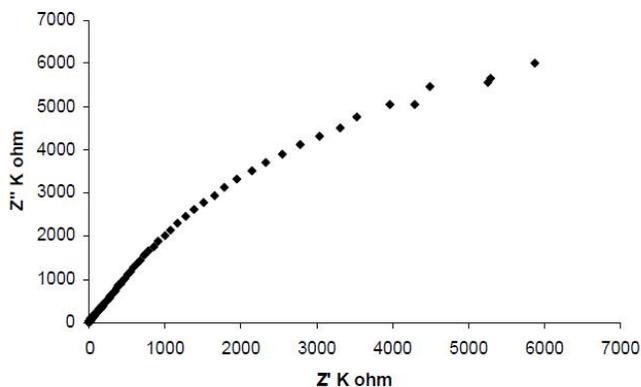
Figure 3 : Impedance diagram for PVdF-HFP –PMMA–LiClO₄ (75 – 25 – 8 wt.%) at 302 K
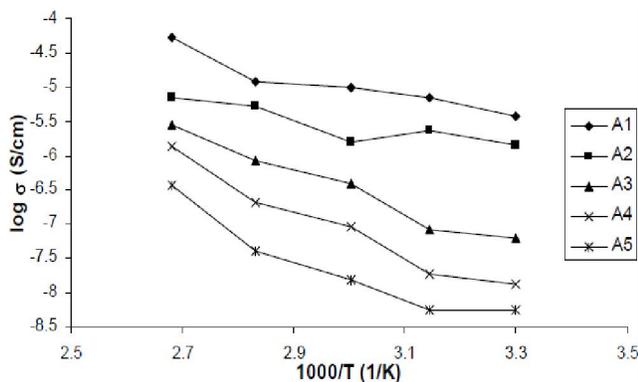
Figure 4 : Arrhenius plot of the conductivity for PVdF-HFP-PMMA-LiClO₄ polymer complexes for different concentrations

dielectric constant of the polymers ie. PVdF-HFP having higher dielectric constant than PMMA, further more, higher concentration of PMMA reduces the ionic conductivity in polymer electrolytes which is also observed by others[37]. From the aspect of conductivity the film with 75% of PVdF-HFP and 25% of PMMA is found to exhibit higher conductivity when compared with other complexes even though the film has a bit higher crystallinity than the others. The higher conductivity despite its crystallinity could be attributed to the presence of larger amount of PVdF-HFP.

The sharp crystalline peaks pertaining to LiClO₄ (Figure 1c) are found to be absent in the complexes which indicates the complete dissolution of lithium salts in the polymer matrices.

The XRD studies confirmed the fact that there exist a definite complex coordination between PVdF-HFP, PMMA and LiClO₄.

FTIR studies

Infra-red spectrum is an indispensable record which gives sufficient information about the structure of the compound. In the present study FTIR technique is used as a tool to identify the interaction between the host polymers and the lithium salt. FTIR spectra were recorded in the range 400-4000 cm⁻¹ at room temperature. The data are analyzed on the basis of the literature available for the lithium salt, C-H stretching of PVdF, C-F, CF_2 stretching regions of PVdF-HFP, scissoring vibration of the vinyl group and C-H rocking vibrations.

Figure 2a-c & 2d-h shows the FTIR spectra of pure PVdF-HFP, PMMA, LiClO₄ and complexes (TABLE 1) respectively. The vibrational bands in figure 2a at 1072, 976, 763 (α phase), 614 are characteristic of the crystalline phase of PVdF-HFP, and bands at 879, 841 cm⁻¹ (β phase) corresponds to amorphous phase of PVdF-HFP[31]. The group frequencies at 1403 is attributed to CH_2 deformation which has moved to higher frequency region around 1412 cm⁻¹ in the complexes indicating the weakening of interaction between H atoms of CH_2 group and F atoms of CF_2 groups[38]. The band corresponding to 1278 cm⁻¹ assigned to symmetrical stretching of CF_2 is found to be shifted to a lower side in all the complexes which could be due to the interaction of polymer and lithium salt. This result is in accordance with the result obtained by Saika et al.[34]. This shift may be attributed to the ionic association through redissociation of charge accompanying the formation of ionic pairs and aggregates and is in close agreement with other workers[34,35,39,40]. The vibrational frequency at 1179 cm⁻¹ assigned to asymmetrical stretching vibrations of CF_2 is found absent in the complexes.

The characteristic frequencies at 2952, 1733, 1437, 1388, 1242, 1195, 988, 752 cm⁻¹ assigned to CH_3 asymmetric stretching, C=O stretching, O-CH_3 deformation, CH_3 symmetrical bending, C-C-O vibrations, CH_2 twisting, CH_2 wagging, CH_2 rocking of PMMA is found to undergo changes due to the addition with PVdF-HFP and LiClO₄. The peak corresponding to CH_3 stretching is found to undergo a hierarchical increment in frequency as the concentration of PMMA is increased in the complex. The C=O stretching frequency suffers a change in frequency to 1722 cm⁻¹ which could be due to the interaction of this carbonyl group between PVdF and PMMA in the binary blend. This result is being substantially supported by the findings of Colemann et al.[41], CH_2 wagging and CH_2 rocking vi-

Full Paper

TABLE 1 : Conductivity values of PVDF-HFP-PMMA-LiClO$_4$ systems with different polymer ratio

Sample	Concentration PVdF-HFP-PMMA-LiClO$_4$	Conductivity σ (× 10^{-5} S cm^{-1})				
		302K (RT)	318K	333K	353K	373K
A$_1$	100-0-8	5.248	9.997	23.450	38.025	77.690
A$_2$	75-25-8	2.341	3.387	7.080	11.487	26.890
A$_3$	50-50-8	0.537	1.000	2.531	4.467	11.213
A$_4$	25-75-8	0.208	0.331	0.812	1.656	4.898
A$_5$	0-100-8	0.089	0.151	0.347	0.631	1.660

brations of PMMA are found to be shifted around 982 and 750 cm^{-1} in the complexes indicating the interaction between the polymers and the salt. The vibrational bands corresponding to C-C-O vibration and CH$_2$ twisting are found to be absent in the complexes.

The characteristic absorption peaks of LiClO$_4$: 1150, 1080, 941 cm^{-1} and 627 cm^{-1} assigned to symmetrical vibration of ionic pairs between Li$^+$ and ClO$_4^-$ and stretching vibrations of ClO$_4^-$ respectively.

Apart from the above there are some new peaks appearing in the spectra for the complexes (434, 718, 883, 1557, 2048, 2299, 2596, 3028 cm^{-1}). The above analysis establishes the formation of polymer salt complex[42-45].

Conductivity studies

Assiduous use of ac impedance studies is to establish the conductivity mechanism; participation of the polymer chain mobility and carrier generation process. The impedance studies of PVdF-HFP – PMMA blend polymer electrolytes for different compositions were carried out at different temperatures. Figure 3 shows the ac impedance spectrum of polymer electrolyte with highest conductivity.

The conductivity of the polymer electrolyte was calculated using the formula σ = l/R$_b$A, where R$_b$ is the bulk resistance obtained from the isotherm (Z' vs Z") for the film with known area 'A' and thickness 'l'. The disappearance of semicircular portion in the impedance curve leads to a conclusion that the current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction[46]. Conductivity values of the complexes in the temperature range 302K to 373K are elucidated in TABLE 1. It is evident from the table that as the concentration of PMMA increases above 25% the conductivity is found
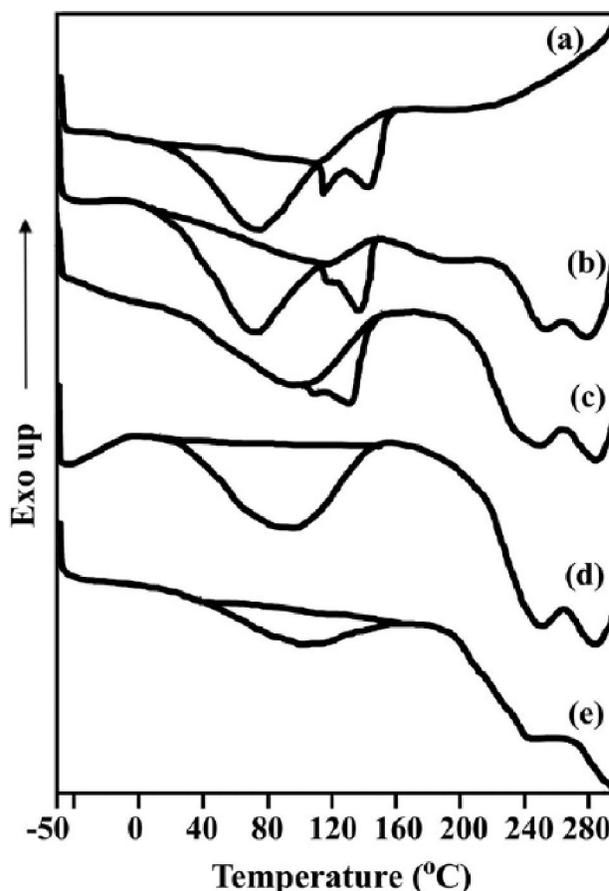
Figure 5 : DSC spectra of (a) PVdF-HFP(100)–PMMA(0)–LiClO$_4$(8), (b) PVdF-HFP(75)–PMMA(25)–LiClO$_4$(8), (c) PVdF-HFP(50)–PMMA(50)–LiClO$_4$(8), (d) PVdF-HFP(25)–PMMA(75)–LiClO$_4$(8), (e) PVdF-HFP(0)–PMMA(100)–LiClO$_4$(8)

to decrease which is in accordance with the findings of Agnihotry et al.[47].

The impedance plot for the PVdF-HFP – PMMA - LiClO$_4$ (film A$_2$) is shown in figure 3 and the conductivity of this system is found to be 2.341×10^{-5} S cm^{-1} at 302 K and 2.689×10^{-4} S cm^{-1} at 373 K. It is evident from TABLE 1 that, there is an incremental change in conductivity with the raise in temperature, for which Free-volume model[43] could be considered the rationale. As the temperature increases, the polymer can expand easily and produce free volume. Thus, ions, solvated molecules, or polymer segments can move generously into the free volume. This leads to an increase in ion mobility and segmental mobility that assist in ion transport and virtually compensate for the retarding effect of the ion clouds.

Figure 4 shows the Arrehenius plot of the ionic conductivity for all compositions. The temperature depen-

Full Paper

dence on the ionic conductivity is not linear which suggest that the ion conduction follows the William-Landell-Ferry (WLF) mechanism[48], that is, ion transport in polymer electrolytes is correlated with polymer segmental motion[49]. This result ascertains that the polymer electrolytes prepared are bereft of plasticizer and the residual solvents.

DSC studies

In the present investigation the miscibility of the polymers and the complexing salt is confirmed from the DSC measurement. The DSC data of the complex systems containing PVdF-HFP - PMMA in different weight ratios (TABLE 1) is shown in figure 5. The inability in determining the T_g (the glass transition temperature) of PVdF-HFP due to its semi-crystalline nature is evident. However, the position and intensity change of the melting peak of the samples can be observed. The fact of marginal shift in T_g of polymer salt complex to a higher side due to the addition of lithium salt[50,51] is substantial from the thermogram. Figure 5a & 5e and figure 5b-d shows a gradual increase in T_g which could be due to the increase in PMMA concentration in the complex. The melting temperatures of the polymer matrices suffer the same kind of strategy because of the effect of salt on physical property of the polymer. It is evident that the melting temperature of the polymer electrolytes has receded from its original melting temperatures. The combined single T_g and negative-shift of melting peak indicates the compatibility of the polymer hosts, which is in accordance with the results published[52].

CONCLUSION

Complex formation and miscibility of PVdF-HFP-PMMA-LiClO$_4$ polymer complex has been confirmed from FTIR, XRD and DSC studies. The film with the concentration PVdF-HFP (75): PMMA (25): LiClO$_4$ (8) is optimized to have high ionic conductivity 2.341×10^{-5} S cm^{-1} (at room temperature) with appreciable mechanical stability. The temperature dependence of ionic conductivity is explained on the basis of free volume model. Hence it is ascertained from the aforesaid properties the polymer electrolyte based on PVdF-HFP – PMMA – LiClO$_4$ could be utilized in the fabrication of lithium batteries.

REFERENCES

[1] J.M.Trascon, M.Armand; Nature, **414**, 359 **(2001)**.
[2] S.T.Myung, M.H.Lee, S.Komaba, N.Kumagai, Y.K.Sun; Electrochim.Acta, **50**, 4800 **(2005)**.
[3] N.Tamura, Y.Kato, A.Mikami, M.Kamino, S.Matsudta, S.Fujitami; Electrochem.Soc., **153**, A1626 **(2006)**.
[4] M.Green, E.Fielder, B.Scrosati, M.Wachtler, J.S.Moreno; Electrochem.Solid State lett., **6**, A75 **(2003)**.
[5] W.H.Meyer; Adv.Mater., **10**, 439 **(1998)**.
[6] F.Croce, G.B.Appetecchi, L.Perci, B.Scrosati; Nature, **394**, 456 **(1998)**.
[7] Y.K.Sun, S.H.Jin; J.Mater.Chem., **8**, 2399 **(1998)**.
[8] M.B.Armand, J.M.Chabagno, M.Ducolt; In: P.Vashista, J.M.Mundy, G.K.Shenoy, (Eds.); Fast Ion Transport in Solids, Elsevier, Amsterdam, 131 **(1979)**.
[9] A.Manuel Stephan; Eur.Polym.J., **42**, 21 **(2006)**.
[10] A.Manuel Stephan, K.S.Nahm; Polymer, **47**, 5952 **(2006)**.
[11] Y.Liu, J.Y.Lee, L.Hong; Solid State Ionics, **150**, 317 **(2002)**.
[12] C.Berthier, W.Gorecki, M.Minier, M.B.Armand, J.M.Chabagno, P.Rigaurd; Solid State Ionics, **11**, 91 **(1983)**.
[13] R.Borkowska, J.Laskowski, J.Plocharski, J.Przyluski, W.J.Weiczorek; Appl.Alectrochem., **23**, 991 **(1993)**.
[14] F.Croce, B.Scrosati; J.Power Sources, **44**, 9 **(1993)**.
[15] G.B.Appetecchi, F.Croce, B.Scrosati; Electrochim.Acta, **40**, 991 **(1995)**.
[16] A.Mary Sukeshini, A.Nishimoto, M.Watanabe; Solid State Ionics, **86-88**, 385 **(1996)**.
[17] Z.Jiang, B.Carroll, K.M.Abraham; Electrochim. Acta, **42**, 2667 **(1997)**.
[18] Q.Z.Xu, G.Wang; J.Power Sources, **41**, 315 **(1993)**.
[19] W.Wieczorek, Z.Florjancyk, J.R.Stevens; Electrochim.Acta, **40**, 2251 **(1995)**.
[20] D.W.Kim, J.K.Park, H.W.Rhee; Solid State Ionics, **83**, 49 **(1996)**.
[21] G.Nagasubramanian, A.I.Attia, G.J.Halpert; Appl. Electrochem., **24**, 298 **(1994)**.
[22] H.S.Choe, J.Giaccai, M.Alamgir, K.M.Abraham; Electrochim.Acta, **40**, 2289 **(1995)**.
[23] Y.Saito, C.Capiglia, H.Kataoka, H.Yamamoto, H.Ishikawa, P.Mustarelli; Solid State Ionics, **136/ 137**, 1161 **(2000)**.

Full Paper

[24] P.Periyasami, K.Tatsumi, M.Shikano, T.Fujieda, Y.Saito, T.Sakai, M.Mizuhata, A.Kajinami, S.Deki; J.Power Sources, **88**, 269 **(2000)**.

[25] A.Manuel Stephan, Y.Saito; Solid State Ionics, **148**, 475 **(2002)**.

[26] Y.Saito, H.Kataoka, A.Manuel Stephan; Macromolecules, **34**, 6955 **(2001)**.

[27] A.Manuel Stephan, Dale-Teeters; Electrochim Acta, **48**, 2143 **(2003)**.

[28] G.B.Appetecchi, F.Croce, B.Scrosati; Electrochim. Acta, **40**, 991 **(1995)**.

[29] C.S.Kim, S.M.Oh; Elecrochim.Acta, **46**, 1323 **(2001)**.

[30] J.Vondrak, M.Sedlarikova, J.Velicka, B.Klapste, V.Novak, J.Reiter; Electrochim.Acta, **46**, 2047 **(2001)**.

[31] Z.Li, G.Su, X.Wang, D.Gao; Solid State Ionics, 176, 1903 **(2005)**.

[32] H.S.Kim, B.W.Cho, K.S.Yun, H.S.Chun; Theories and Application of Chemical Engineering, KIChE, **1**, 49 **(1995)**.

[33] A.Manuel Stephan, R.Thirunakaran, N.G.Renganathan, S.Pitchumani, N.Muniyandi, P.Ramamoorthy; J.Power Sources, **81&82**, 752 **(1999)**.

[34] D.Saikia, A.Kumar; Electrochim.Acta, **49**, 2581 **(2004)**.

[35] S.Abbrent, J.Plestil, D.Hlavata, J.Lindgren, J.Tegenfeld, A.Wendsjo; Polymer, **42**, 1407 **(2001)**.

[36] A.Tawansi, A.H.Oraby, H.I.Abdelkader, M.Abdelaziz; J.Magn.Magn.Mater., **262**, 203 **(2003)**.

[37] From Kankan.

[38] S.Rajendran, O.Mahendran, R.Kannan; Mater. Chem.Phys., **74**, 52 **(2002)**.

[39] D.Battisti, G.A.Nazri, B.Klassen, R.Aroca; J.Phy. Chem., **97**, 5826 **(1993)**.

[40] A.M.Stephan, T.Prem Kumar, N.G.Renganathan, S.Pitchumani, R.Thirunakaran, N.Muniyandi; J.Power Sources, **89**, 80 **(2000)**.

[41] M.M.Coleman, J.Zarian, D.F.Varnell, P.C.Painter; J.Polym.Sci.Polym.Lett., **15**, 745 **(1977)**.

[42] M.M.E.Jacob, S.R.S.Prabaharan, S.Radhakrishnan; Solid State Ionics, **104**, 267 **(1997)**.

[43] T.Miyamoto, K.Shibayana; J.Appl.Phy., **44**, 5372 **(1973)**.

[44] G.S.Fulcher; J.Am.Ceram.Soc., **8**, 339 **(1925)**.

[45] H.J.Rhoo, H.T.Kim, J.K.Park, T.S.Hwang; Electrochim.Acta, **42**, 1571 **(1997)**.

[46] S.Izuchi, S.Ochiai, K.Takeuchi; J.Power Sources, **68**, 37 **(1997)**.

[47] S.A.Agnihotry, C.Pradeep, S.S.Shekon; Electrochim.Acta, **44**, 3121 **(1999)**.

[48] M.L.Williams, R.F.Landel, J.D.Ferry; J.Am.Chem. Soc., **77**, 3701 **(1955)**.

[49] Y.Okamoto, T.F.Yeh, H.S.Lee, T.A.Skotheim; J.Polym.Sci., Part A: Polym.Chem., **31**, 2573 **(1993)**.

[50] P.M.Blonsky, D.F.Shriver, P.Austin, H.R.Allock; Solid State Ionics, **18&19**, 258 **(1986)**.

[51] S.Rajendran, Ravi Shanker Babu, P.Sivakumar; Journal of Applied Polymer Science (Online).

[52] Y.X.Jiang, Z.F.Chen, Q.C.Zhuang, J.M.Xu, Q.F.Dong, L.Huang, S.G.Sun; J.Power Sources, **160**, 1320 **(2006)**.