EFFECT OF DIFFERENT NANOPARTICLES IN PMMA/PVC-BASED COMPOSITE POLYMER ELECTROLYTES

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Introduction

The development of secondary rechargeable battery is considered more important as compared to primary batteries. It's desirable to manufacture a smaller sized, high capacity and light weight battery which is environment friendly and renewable. In this paper, the attention has been focused on the polymer electrolyte due to its high ionic conductivity as well as good mechanical properties[1, 2]. In the recent years, there has been a tremendous interest in the preparation of polymer electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities because these polymer electrolytes play a major role in solid-state batteries, electro chromic windows, sensors, fuel cells etc.[3]. Polymer blends have been widely used in the industry because of their ability to combine unique material properties of their components at a relatively low cost when compared to the development of a new polymer. It is well-known that the properties of a polymer blends are greatly influenced by the morphology that is developed during the mixing process[4]. Earlier, electrolytes were consisted of polymers such as PEO and PPO or their blend complexes with suitable salts (LiClO$_4$, LiCF$_3$SO$_3$, *etc.*)[5]. However they showed poor room temperature conductivity ($\approx 10^{-8}$ Scm^{-1}). In the past two decades different polymer hosts, such as PMMA[6], PAN[7], PVC[8], PVdF[9] possess higher room temperature ionic conductivity (about 10^{-3} Scm^{-1}) comparing with other polymer electrolytes and could be useful for lithium and lithium-ion battery application.

Poly (vinyl chloride) (PVC) is one of the most common commodity plastics, which has been widely used in the automobile, building construction, packaging fields, etc., because of its low cost, easy method of preparation, and the broadening of the properties range[10].According to pita *et al.*[11] the addition of plasticizer to the PVC formulation decreases many mechanical properties such as hardness, tensile strength, modulus, etc., of PVC product. However, low temperature flexibility, elongation and ease of processing are all improved. Poly (vinyl chloride) (PVC) can act as a mechanical stiffener in the electrolyte due to its immiscibility with the plasticizer[12]. In general plasticizers are solids with relatively low melting point or liquid with relatively high melting point than solid plasticizers. They are well dispersed among plastic polymer molecules.

Thus the mobility of polymer molecules are increased, which is especially helpful to processing[11]. A PVC-based polymer electrolyte system plasticized with ethylene carbonate and propylene carbonate has been reported[13] to be applicable to lithium metal and lithium ion secondary batteries[14]. The addition of plasticizers also helps to reduce the glass transition temperature, Tg[15, 16] that enhanced the ionic conductivity by increasing the segmental motion of the polymer. The dielectric constant of the

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plasticizer is an important parameter that affects the ionic conduction. Higher dielectric constant results better dissociation of the salt as the number of free mobile charge carriers increased[17]. In addition, adding an appropriate amount of lithium salt into the polymer matrix significantly enhanced the ionic conductivity of the polymer electrolyte by increasing the number of charge carrier which provides free ions for conduction. The nano-sized filler particles such as SiO_2 and Al_2O_3 that integrated into the solid polymer electrolyte increase the mechanical strength and enhanced the ionic conductivity[18,19]. The increase in conductivity also attributed to the decrease in the level of crystallinity in polymers due to the presence of fillers[17]. Tetrahydrofuran (THF) is a strong aprotic solvent commonly used in the miscibility of polymers and also in the pharmaceutical industry due to its broad solvency for both polar and non-polar compounds[20]. In the present work, polymer electrolytes are prepared with different fillers for the constant weight percentage of PVC, PMMA, PC and $LiClO_4$.

Materials and methods

PVC, PMMA, the nano sized $BaTiO_3$, Al_2O_3, TiO_2 and the salt $LiClO_4$ (Aldrich Chemicals, USA) were dried under vacuum at 100° C about 12hours. The plasticizer propylene carbonate (PC) (Aldrich, USA) was used as received. All the composite polymer electrolytes were prepared using a simple solvent casting technique. The salt $LiClO_4$ and the polymers were first dissolved in Tetrahydrofuran (THF) separately and then mixed together. The given amounts of plasticizers were also added into the above polymer-salt mixtures. Finally, the nano filler $BaTiO_3$ was incorporated into the complex mixture and was stirred continuously about 24 hours for avoiding the fillers aggregation and to ensure the fine mixing. The obtained homogeneous viscous slurry was degassed to remove air bubbles and was poured into the Petri dish. The solvent was allowed to evaporate slowly from the complex at 60° C for 6 h. The composite polymer electrolyte films were harvested and stored in an evacuated desiccator.

Characterization

Ionic conductivity of the polymer composite electrolytes was estimated with the help of stainless steel blocking electrodes using a computer controlled micro-Autolab Type III Potentiostat/ Galvanostat electrochemical work-station of frequency range 1Hz-300 kHz. The ionic conductivity (σ) of the composite electrolytes was calculated using the following equation: $\sigma = t/R_b A$, where t, R_b and A are the thickness (cm), the bulk resistance (Ω) and the surface area (cm^2) of the membrane respectively. The ionic conductivity was found at different temperatures.

The XRD equipment used in this study is X-pert propanalytical diffractometer using Cu-K_α radiation as source and operated at 40 kV. The sample was scanned from 10 to 80° for 2 sec in the 2θ step scan mode. TG/DTA thermal analysis study of the membrane having maximum ionic conductivity was performed using Perkin Elmer Pyris-6 TG/DTA in an atmosphere containing nitrogen from ambient temperature to 86°C with the heating rate of 10°C min^{-1}.

Results and discussion
X-ray diffraction analysis

In order to investigate the effect of fillers such that Al_2O_3, TiO_2, $BaTiO_3$ in the PVC- PMMA system, XRD analysis has been performed. Their respective diffraction patterns are shown in Fig (1).
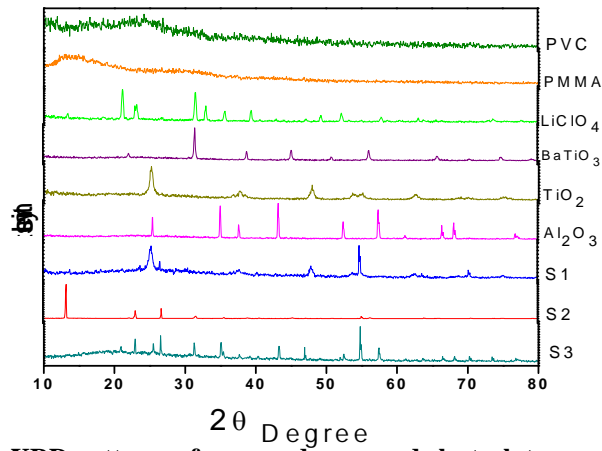

Fig. 1. XRD patterns of pure and prepared electrolyte membranes

Fig. 1 (Pure PVC–PMMA) is the diffraction pattern of the complex without fillers. In fig (S1, S2, S3) the peaks observed in the polymer complexes are due to the addition of fillers. This shows that the film containing Al_2O_3, TiO_2, $BaTiO_3$ as filler affects the diffraction pattern of the PVC –PMMA system. Peaks pertaining to pure PVC, pure PMMA, $LiClO_4$ are found to be absent in the complex polymer salt matrices. In addition to that,

the plasticizer PC also provides more amorphous phase and current carriers in the polymer-salt matrix. Thus the complexation in the polymer matrices has been confirmed from the above mentioned analysis.

Ionic conductivity studies

The ionic conductivity of a polymer electrolyte depends on the actual concentration of the conducting species and their mobility.
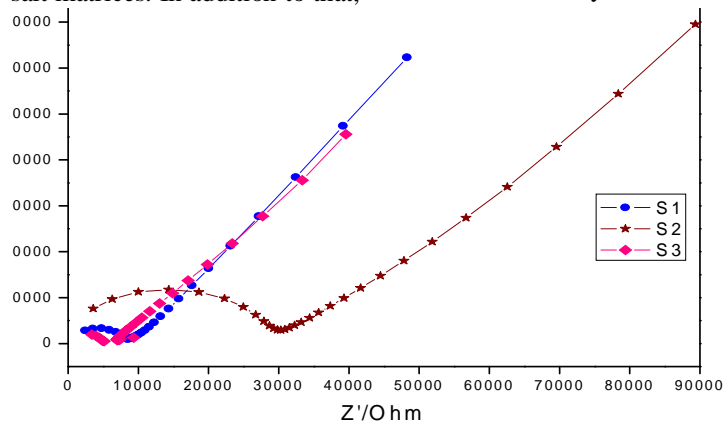

Fig. 2. Room temperature complex impedance plot of the prepared samples

Fig. 2 shows the impedance diagram of 8 wt% ratio of different fillers to PVC/ PMMA-LiClO$_4$-PC polymer electrolyte system at room temperature. In the impedance response the low frequency plot must be a straight line parallel to the imaginary axis, but the double layer at the blocking electrodes causes the curvature[21]. The intercept on the real axis gives the bulk resistance of the electrolyte. The conductivity of the polymer electrolyte was calculated from the measured resistance for the known area and thickness of the polymer film using the formula.

$$\sigma = t / (R_b \ A)$$

where t, R$_b$ and A are the thickness, bulk resistance and area respectively. The effect of BaTiO$_3$ on ionic conductivity of the prepared composite polymer electrolytes was measured. The conductivity values are listed in Table 1.

Table 1: Ionic conductivity values of PVC (17.5) / PMMA (7.5) / LiClO$_4$ (8) / PC (67) / 8 wt% of different fillers in the total polymer weight

Sample coding	PVC (17.5), PMMA (7.5), LiClO$_4$ (8), PC (67)	Ionic conductivity values $(\sigma) \times 10^{-3}$ Scm^{-1} at different temperatures (K)				
		303	313	323	333	343
S1	BaTiO$_3$ (8)	0.8011	0.8789	1.2120	1.4650	1.9900
S2	TiO$_2$ (8)	0.4210	0.5013	0.5987	0.6833	0.7641
S3	Al$_2$O$_3$ (8)	0.2641	0.3230	0.3910	0.4680	0.5410

Figure 3 shows the variation of ionic conductivities of the composite polymer electrolyte as a function of BaTiO$_3$ content at a temperature range 303K-343K.
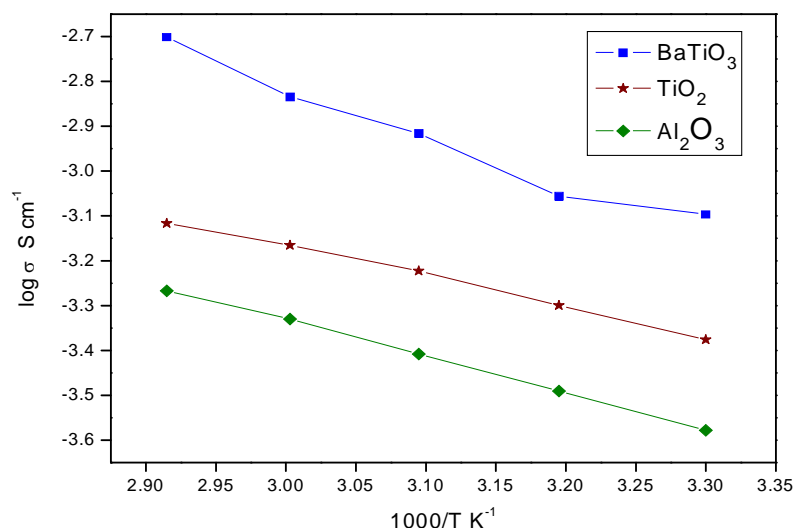

Fig. 3. Temperature dependent ionic conductivity plots of the prepared samples

A maximum ionic conductivity is found for the sample containing 8 wt% of $BaTiO_3$ at all temperatures studied. The highest ionic conductivity 0.8011×10^{-3} S/cm is obtained for the sample S1 at room temperature.

This behavior would be explained by Ferro electricity of the $BaTiO_3$ filler. $BaTiO_3$ filler is well known to be a ferroelectric material, and it shows strong Ferro electricity. Therefore at low filler contents, Ferro electricity of $BaTiO_3$ would contribute to dissociation of lithium salt, resulting in enhancement of total ionic conductivity. But at high filler contents, continuous non-conductive phase built up by large amount of filler as an electrically inert component would block up lithium ion transport, resulting increase in the total resistance of the composite polymer electrolyte[22]. It is reported for many composite polymer electrolytes formed by the addition of filler that ionic conductivity increases to reach its maximum value at 5-10 wt% of filler[23-25].

According to Croce *et al.*[26], the Lewis acid groups of the added inert filler may compete with the Lewis acid-lithium cations for the formation of complexes with PEO chains as well as the anions of the added lithium salt. Subsequently, this leads to a structural modifications on the filler surfaces due to specific actions of the polar surface groups of the inorganic filler. The Lewis acid-base interaction centers reacts with the electrolytic species, thus lowering the ionic coupling and promotes the salt dissociation via a sort of "ion-filler complex" formation.

In the present study, the filler $BaTiO_3$ which has a base center can react with the Lewis acid centers of the polymer chain and these interaction lead to the reduction in the crystallinity of the polymer host and indeed, this effect could be the reason for the observed enhancement in the ionic conductivity[27].

The temperature dependence of ionic conductivity of $PVC-PMMA-LiClO_4-PC$ with $BaTiO_3$, TiO_2, Al_2O_3, is shown in fig 3. The non-linearity in this plot indicates that the ionic conduction seems to obey the VTF relation which describes the transport properties in a viscous matrix[28-30].

It is found that as temperature increases, the conductivity values also increase for all the compositions. As the temperature increases, the polymer can expand easily and produce free volume. Thus ions, solvated molecules or polymer segments may move into the free volume. The resulting conductivity is represented by the free volume around polymer chain. The increase in free volume leads to the increase in ion mobility and segmental mobility that will assist the ion transport.

TG/DTA analysis

Fig. 4 shows the TG/DTA traces of PVC (17.5)-PMMA (7.5)-PC (67)-$LiClO_4$ (8)-$BaTiO_3$ (8 wt%) polymer composite which shows maximum conductivity value. An endothermic peak was observed at 75°C and corresponding about 7% of weight loss is attributed to the presence of moisture in the samples.

The film starts decomposing at 240°C followed by an endothermic peak, which indicates that the film is stable up to 240°C. The DTA trace shows an endothermic peak around 304°C, which corresponds to the melting point of PMMA polymer host.
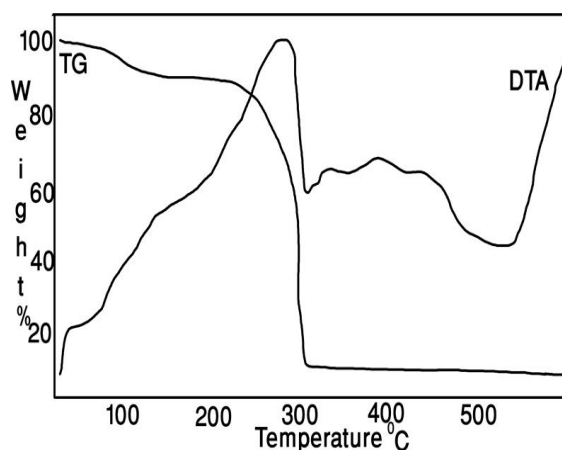
**Fig. 4. TG/DTA plots for PVC–PMMA-PC-LiClO$_4$ polymer complex
with different fillers**

It is clear from these observations, that the PMMA based composite polymer electrolytes, which contain LiClO$_4$ as salt can be operated up to 240°C.

Conclusions

PMMA based polymer electrolytes were prepared by solvent casting technique. The complex formation in PMMA-PVC-PC-LiClO$_4$ system has been confirmed from XRD. All electrolytes show appreciable conductivity even at room temperature. Maximum conductivity (0.8011 × 10^{-3} S cm^{-1}) at room temperature with good mechanical stability has been observed for PVC (17.5) - PMMA (7.5) - PC (67) - LiClO$_4$ (8) -BaTiO$_3$ (8 wt%) polymer matrix complex. Good thermal stability of these polymer electrolyte systems up to 240°C was confirmed by TG/DTA analysis. The addition of plasticizers such as propylene carbonate (PC) enhances the amorphous phase as well as the charge carrier dissolution in the matrix.

References

1. N. S. Choi, Y. G. Lee, J. K. Park, J. M. Ko, *Electrochim Acta*, 46 (2001) 1581.

2. A.M. Stephen, R. Trirunakaran, N.G. Renganathan, V. Sundaram, S. Pituchu mani, N. Muniyandi, R. Gangadharan, P. Ramamoorthy, *J. Power Sources*, 81-82 (1999) 752.

3. C. Vincent and B. Scrosati, Modern Batteries: An introduction to electrochemical power sources, John Wiley and sons, Inc, New York (1997).

4. Ticiane S. Valera, Augisto T. Morita and Nicole R. Demarquette, Study of morphologies of PMMA/PP/PS Ternary Blends,Macromolecules,39, 2663(2006).

5. C. Vincent, *Solid state ion.*, 134(2000)159.

6. K. S. Kim, K. S. Kum, H. W. Cho, B. Woncho, W. H. Rhee, *J.Power sources.*,124 (2003)221.

7. M. Watanabe, M. Kanba, Nagaoka, I. Shinohara, *J. Polym Sci Poly Phys Ed.,* 21(1983) 939.

8. A. M. Sukeshini, A. Nishimoto, M. Watanabe, *Solid State Ionics,* 86-88 (1996)385.

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9. E.Tsuchida, H.Ohno, E. Tsunemi, Electrochim Acta., 28(1983)833.

10. Jiliang Wang, Wanqing Yang and Jingxin Lei, Study on a Novel Ion-Conductive Compound Plasticizer for Soft and Antistatic PVC, Materials polymer engineering and science, 57-60 (2010).

11. Ramesh S, Tan Winie and Arof A. K., Investigation of Mechanical Properties of Polyvinyl chloride-Polyethylene Oxide (PVC-PEO) Based Polymer Electrolyte for Lithium Polymer cells, *European Polymer Journal*, 43,1963-1968(2007).

12. S. Rajendran, M. Ramesh Prabhu, M. Usha Rani, Characterization of PVC/PEMA Based Polymer Blend Electrolytes, *J. Electrochem Sci.,* 3(2008) 282-290.

13. A. M. Stephan, T. Premkumar, N. G. Renganathan, S. Pitchumani, R. Thirunakaran, N. Muniyandi, *J.Power sources*, 89(2000)80.

14. M. Alamgir, K. M. Abraham, J. Electrochem Soc., 140(1993)L96.

15. M. Kakihana, S. Schantz, L. M. Torell, *J. Chem Phys*, 92 (1990) 6271.

16. A. Bernson, J. Lindgren, *Solid State Ionics*, 60 (1993) 37.

17. K. W. Chew and K. W. Tan The Effects of Ceramic Fillers on PMMA-Based Polymer Electrolyte Salted With Lithium Triflate, LiCF$_3$SO$_3$ *J. Electrochem. Sci.,* 6 (2011) 5792 - 5801

18. Y. Tominaga, S. Asai, M. Sumita, S. Panero, B. Scrosati, *J. Power Sources*, 146(2005) 402.

19. Y. Liu, J. Y. Lee, L. Hong, *J. power sources* 109 (2002) 507.

20. Mudigoudra B.S.1, Masti S.P.2 and Chougale R.B.1 Investigation of Mechanical Properties of Ternary Polymer PVC/PVAc/PEG Blended Films, *Research Journal of Engineering Sciences* ISSN 2278-9472, Vol. 1(2), 63-65, August (2012) *Res. J. Engineering Sci.* International Science Congress Association.

21. C. Kim, G. Lee, K. Lio, K. S. Rhu, O. S. G. Kang, S. H. Chang, Solid State Ionics 123, 251(1999).

22. Takahito Itoh, Yosiaki Ichikawa, Takahiro Uno, Masataka Kubo, Osamu Yamamoto. Solid State Ionics 156(2003) 393-399.

23. Z. Wen, T. Itoh, M. Ikeda, N. Hirata, M. Kubo, O. Yamamoto, J. Power Sources, 90 (2000)20.

24. B. Scrosati, F. Croce, Polym. Adv. Technol. 4 (1993) 198.

25. D. Swierczynski, A. Zalewska, W. Wieczorek, Chem. Mater. 13 (2001) 1560.

26. F. Croce, L. Persi, B. Scrosati, F. Serriano-Fiory, E. Plichta, M. A. Hendrick, Electro Chim. Acta 46(2001) 2457.

27. W. Wieczorek, J. R. Steven, Z. Florjanczyk. Solid State Ionics 1996; 85: 67-72.

28. H. Vogel, Phys. Z. 22, 645(1922).

29. V. G. Tamman, H. Z. Hesse, An Org. Allg. Chem. 19, 245(1926).

30. G. S. Fulcher, J. Am. Ceram. Soc. 8, 339 (1925).

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