Effect Of Ceramic Oxide On The Ionic Conductivity Of Polymer Electrolytes

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ABSTRACT

Composite polymer electrolytes consisting of polymers poly (acrylonitrile)(PAN), poly (methyl methacrylate) (PMMA) with ethylene carbonate (EC) and propylene carbonate(PC) as plasticizers, lithium tetra fluoro borate ($LiBF_4$) as a salt and TiO_2 as an inert ceramic additive are prepared by solvent casting technique. The complex formation has been confirmed from XRD and FTIR studies and the thermal stability of the film is ascertained from TG/DTA studies. The maximum conductivity value is found to be 7.475×10^{-4} S/cm for PAN(15)-PMMA(5)-$LiBF_4$-(8)-EC(42)-PC(30)+15wt% TiO_2 film. The effect of TiO_2 concentration on ionic conductivity was studied using ac impedance spectroscopy and the results are discussed.   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

Polymer gel electrolytes have lately become of great interest for their use in secondary Lithium batteries. Polymer electrolytes have been studied for more than two decades since the first investigation reported by Armand and coworkers in 1979[1]. Composite electrolyte is a subset of polymer electrolytes with an idea of incorporating electrochemically inert fillers into polymer matrices[2-7]. Generally, high surface area particulate fillers such as ZrO_2, TiO_2, Al_2O_3 and hydrophobic fumed silica were incorporated into the polymer matrices and are called "Composite polymer electrolytes" or "Composite ceramic electrolytes"[8,9].

Thermal properties of various types of nano composite polymer electrolytes formed by dispersing ceramic powders having nano particle sizes into poly(ethylene oxide) PEO-LiX was already studied[10-13]. The addition of inorganic fillers, such as glasses, alumina, silica or other ceramics, to the polymer - lithium salt systems generally improves the transport properties, offers resistance to crystallization, and the stability of the electrode/electrolyte interface[14-16]. The conductivity enhancement depends on the filler used, and on its particle size[17].

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Several groups have resorted to the use of PAN/ PVC, PMMA/PEO, PVC/PMMA[18,19,20] polymer blend electrolytes. To the best of author's knowledge no work has been done on PAN/PMMA polymer blend electrolytes. Hence in the present investigation, PAN-PMMA-LiBF$_4$-EC-PC polymer electrolytes with different concentration of TiO$_2$ are studied and the results are reported here.

EXPERIMENTAL

Poly(acrylonitrile)(PAN), Poly(methyl methacrylate) (PMMA), ethylene carbonate (EC), propylene carbonate(PC) purchased from Aldrich, USA, and the inorganic salt LiBF$_4$ purchased from Lancaster, England were used in this study. PAN, PMMA and LiBF$_4$ were dried at 100°C for 10 hrs under vacuum (10^{-3}torr).

Appropriate quantities of PAN, PMMA, LiBF$_4$ were dissolved in distilled DMF and then stirred continuously after the addition of EC and PC until a homogeneous nature was evident. The ceramic filler TiO$_2$ was then added and the solution was stirred at 70^{0}C for about 3hrs till a jelly nature was obtained. The obtained mixture was cast onto Teflon bushes and glass plates. DMF was allowed to evaporate slowly at room temperature and then at 50^{0}C for the removal of the residual DMF content. The films were prepared for the constant weight ratio of PAN:PMMA:EC:PC:LiBF$_4$(15:5:8:42:30) with different weight ratios of TiO$_2$ (0,5,10,15& 20).

The XRD equipment used to study the polymer films in this study was JEOL, JDX 8030X-ray diffra ctometer. FTIR measurements were made in the range 400-4000cm^{-1} using a Jasco FTIR 460 plus IR spectrophotometer for complex confirmation. The bulk electrical conductivity of the polymer complexes were evaluated from the bulk resistance obtained from the impedance plots in the temperature range 301-373K. Instrument used for ac impedance measurement was Keithley 3330 LCZ meter. The plots were recorded in the frequency range 40Hz to 100KHz with a signal amplitude of 10mv. The polymer film was sandwiched between stainless steel electrodes for conductivity studies. TG/DTA analysis was carried out to find the thermal stability of the polymer electrolyte.
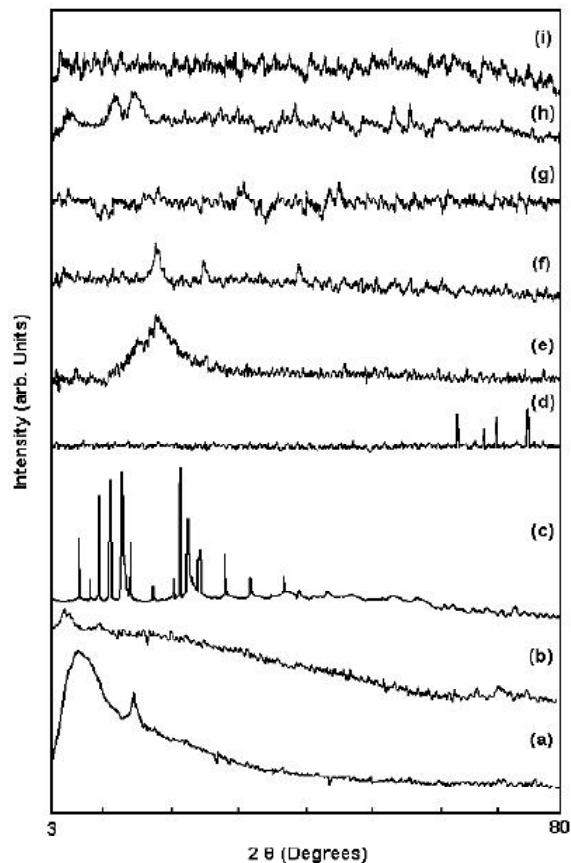

Figure 1 : XRD spectra of
(a)PAN b)PMMA c) LiBF$_4$ d)TiO$_2$,
(e) PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:0)
(f)PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:5)
(g)PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:10)
(h)PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:15)
(i)PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:20)

RESULTS AND DISCUSSION

XRD studies

XRD patterns of pure PAN, PMMA, LiBF$_4$, TiO$_2$ and the complexes are shown in figure 1. XRD of pure PAN and PMMA reveal the amorphous nature of the polymers. The diffraction peaks appearing at 2θ values 20^0 and 23^0 indicate the crystalline phase of LiBF$_4$ (Figure1c). The above mentioned LiBF$_4$ peaks are almost found disappearing in the polymer electrolyte system figure 1(e-i). This shows that the inorganic salt is thoroughly mixed with the host polymers.

The XRD patterns obtained for PAN-PMMA-LiBF$_4$-EC-PC-TiO$_2$ polymer electrolyte films exhibit
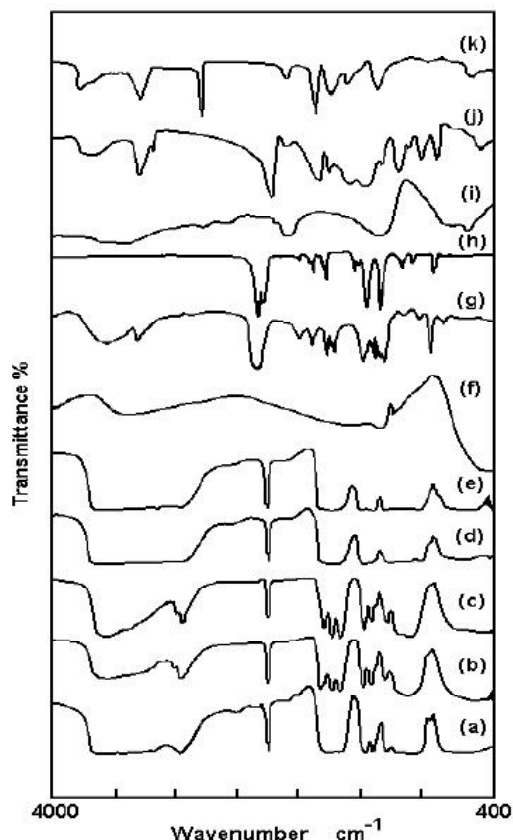
Figure 2 : FTIR spectra of
(a)PAN b)PMMA c) LiBF$_4$ d)EC e)PC f)TiO$_2$
(g) PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:0)
(h)PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:5)
(i)PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:10)
(j)PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:15)
(k)PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$(15:5:8:42:30:20)

TABLE 1 : Conductivity values of PAN:PMMA:Li BF$_4$:EC:PC:TiO$_2$(TiO$_2$- 0,5,10,15,20) at different temperatures

Films	Conductivity values (×10^{-3} S/cm)				
	303K	318K	333K	353K	373K
S$_1$	0.153	0.253	0.496	0.795	0.960
S$_2$	0.181	0.420	0.802	0.993	1.157
S$_3$	0.200	0.643	1.110	1.505	1.810
S$_4$	0.748	1.145	2.580	3.169	4.968
S$_5$	0.352	0.849	1.450	1.982	2.482

crystalline peak at 2θ value around 25⁰ indicating the presence of TiO$_2$ in the polymer matrix. Upon increasing the concentration of TiO$_2$, the intensity of the corresponding peak is also found to increase. The polymer electrolyte film figure 1(e) bereft of TiO$_2$ exhibits the amorphous phase[21].

FTIR spectroscopic studies

FTIR spectra of the prepared samples were recorded in the transmittance mode. FTIR of starting materials PAN, PMMA, EC, PC, LiBF$_4$ and polymer complexes are given in figure 2(a-j). Complexation may shift in the polymer cage peak frequencies. Figure 2(f) shows the FTIR spectrum of the film bereft of ceramic oxide. The C=N stretching frequency at 2245cm^{-1} and a band at 1250cm^{-1} assigned to C-O stretching in the pure PAN are found to be shifted to 2241cm^{-1} and 1247cm^{-1} respectively which shows the interaction of PAN with the plasticizers. The band at 2952 cm^{-1} assigned to C-H stretching frequency of PMMA is shifted to 2948cm^{-1} and also the vibrational peaks of PAN and PMMA at 640cm^{-1} and 1389cm^{-1} respectively are shifted in the complex. The peak corresponding to C=O stretching frequencies of EC at 1801cm^{-1} and PC at 1789cm^{-1} are shifted to a higher frequency of 1803cm^{-1} in the complex. The vibrational peaks at 2952cm^{-1} assigned to C-H stretching of PMMA and 2942cm^{-1} assigned to asymmetrical CH$_2$ stretching of PAN are shifted to an intermediate frequency with reduced intensities in the complexes with ceramic additives. The group frequencies of PAN(2245, 1455, 1250, 640cm^{-1}) and PMMA(2952, 1733, 1388cm^{-1}) are found to be shifted in the polymer complexes. In addition to the above, some new peaks at(3578, 3289, 2995, 1782, 1665, 1483, 1113, 454, 421cm^{-1}) are also observed. Hence, from the above discussion, we can conclude that the complexation between PAN, PMMA, EC, PC and LiBF$_4$ has occurred.

Conductivity studies

The conductivity values of the polymer complexes were calculated from the bulk resistance obtained from the intercepts of the typical impedance plots for various temperatures. TABLE 1 shows the conductivity values of the complexes in the range 303-373K. It is observed that the conductivity increases with an increase in temperature for all the complexes and this behavior is in agreement with the theory established[1]. The plot between log σ and 1000/T is shown in figure 3. The non linearity in Figure 3 indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion. Thus the result may be described by VTF relation which describes the trans-
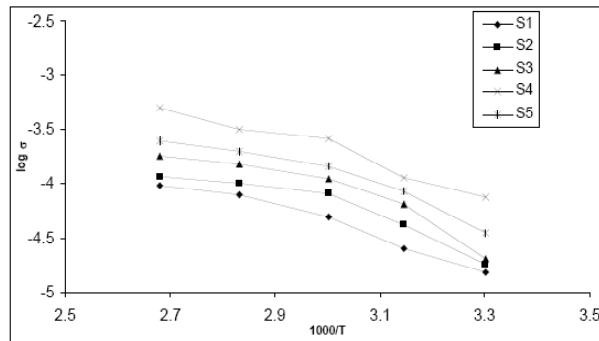
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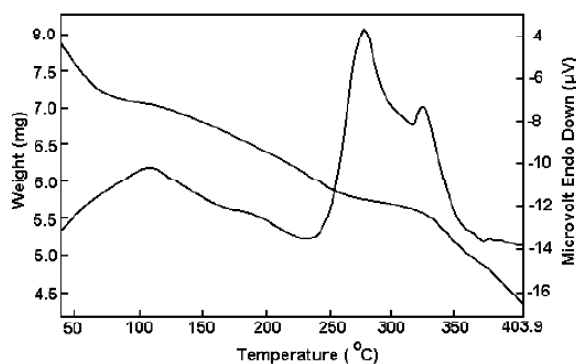**Figure 3 : Arrhenius plot of log σ against reciprocal temperature of PAN:PMMA:LiBF$_4$:EC:PC:TiO$_2$**

Figure 4 : TG/DTA curve for PAN:PMMA:LiBF$_4$:EC: PC:TiO$_2$(15:5:8:42:30:15)

port properties in a viscous matrix[22].

Among the five films prepared in this work, the conductivity value of PAN-PMMA-LiBF$_4$-EC-PC with 15wt% of TiO$_2$ has the maximum conductivity value(7.475×10^{-4} S/cm) at room temperature. This value is higher than that of the system bereft of TiO$_2$. It is interesting to note that the conductivity of the system increases with the concentration of TiO$_2$ to an extent(i.e. in our case 15wt%) and decreases, this may be due to ion association or grouping above this concentration. The increase in conductivity has been attributed to **(i)** the ceramic particles acting as nucleation centers for the formation of minute crystallites[1,23,24], **(ii)** the ceramic particles aiding in the formation of amorphous phase in the polymer electrolyte[25,26,27], **(iii)** to the formation of a new kinetic path via polymer-ceramic boundaries.

TG/DTA studies

In order to ascertain the thermal stability of the polymer electrolyte having maximum conductivity value(Film S$_3$), was subjected to TG-DTA analysis. TG-DTA analysis of PAN-PMMA-LiBF$_4$-PC-EC with 15wt% of TiO$_2$ is shown in figure 4. A small endothermic peak at 63.6^0C is noted. An exothermic peak is observed at 280^0C indicating the decomposition of polymer electrolytes which is followed by an endothermic peak at 326^0C. From the TG curve, it can be seen that, with the increase in the temperature, the film S$_3$ looses its weight gradually upto 300^0C. It is found that there is an abrupt weight loss of the film beyond 300^0C. Thermal stability of polymer electrolyte film S$_3$ is estimated as 300^0C. The first, second and third decompositions of the film take place in between 50-90, 225-250 and 320-350^{0}C respectively. The weight losses of the polymer electrolyte at 100, 200 and 300^0C are found as 12, 19 and 28% respectively.

CONCLUSION

Polymer electrolyte films are prepared using the solvent casting technique. Complexation is confirmed from XRD & FTIR studies. Among the five films prepared, the polymer electrolyte(film S$_3$) is found to be the best film on the basis of both conductivity and mechanical stability. The conductivity of the polymer electrolyte PAN (15)-PMMA (5)-LiBF$_4$ (8)-EC (42)-PC (30)-TiO$_2$(15) is found as 7.475×10^{-4} S/cm. The thermal stability of the film is estimated as 300^0C. Hence the properties of PAN-PMMA-LiBF$_4$-EC-PC-TiO$_2$ polymer electrolyte look very desirable and promising for Li battery applications.

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