



## Short communication

## Ionic conduction in poly(vinyl chloride)/poly(ethyl methacrylate)-based polymer blend electrolytes complexed with different lithium salts

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## ABSTRACT

Poly(vinyl chloride)/poly(ethyl methacrylate)-based polymer blend electrolytes comprising propylene carbonate as a plasticizer and a lithium salt LiX ( $X = \text{BF}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) are prepared by a solvent casting technique. The electrolytes are subjected to characterization by ionic conductivity, X-ray diffraction, Fourier transform infrared spectroscopy and thermogravimetric/differential thermal analysis. The electrolytes that contain  $\text{LiBF}_4$  exhibit maximum conductivity and are thermally stable up to 254 °C.

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## 1. Introduction

There has been tremendous interest in the preparation of polymer electrolytes with high ionic conductivity, good mechanical strength and good thermal stability for application in solid-state batteries, electrochromic windows, sensors, fuel cells, etc. [1,2]. Whereas there have been many reports of the physical and electrochemical properties of poly(ethylene oxide)-based electrolytes [3–5], very few studies have been made on other polymer hosts like poly(acrylonitrile) (PAN) [6,7], poly(methyl methacrylate) (PMMA) [8], poly(vinyl chloride) (PVC) [9,10] and poly(vinylidene fluoride) (PVdF) [11].

Very recently, poly(ethyl methacrylate) (PEMA) as a host has drawn the attention of researchers by virtue of its promising properties. It has an ionic conductivity of the order of  $10^{-3} \text{ S cm}^{-1}$  and electrochemical stability up to 4.3 V. A prototype battery gave 92% of the initial capacity after 100 cycles upon repeated charge–discharge at the 1C rate [12].

Generally, gel polymer electrolytes are obtained by dissolving a low molecular weight plasticizer, and polymer host along with a lithium salt in a low boiling solvent (e.g., tetra hydrofuran, THF) and the resultant solution is cast as film after the evaporation of the

solvent. These electrolytes, however, lose their mechanical strength because of the addition of plasticizers [13–15]. The films have to be hardened by either chemical or physical curing, which results in high processing costs. The problem of poor mechanical strength can be circumvented by blending PEMA with a polymer such as PVC which, because of its poor solubility in the plasticizer medium, manifests itself in phase separated morphology to provide a rather rigid framework in the polymer electrolyte film [16].

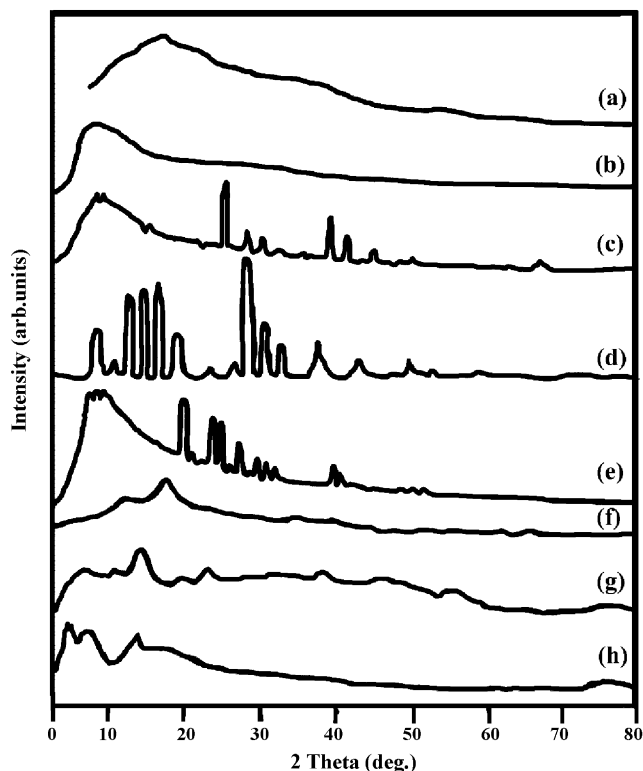
In the present study, an attempt has been made to determine the role of different anions, namely,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$  and  $\text{CF}_3\text{SO}_3^-$ , on the ionic conductivity of PVC/PEMA-based polymer electrolyte. The thermal stability of these polymer electrolytes is also reported.

## 2. Experimental

The PVC and PEMA employed in this study were obtained from Aldrich, USA. The plasticizer PC (also from Aldrich) was used as supplied. Lithium perchlorate ( $\text{LiClO}_4$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ) and lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) were dried by annealing under vacuum at 120, 70 and 80 °C, respectively, for 24 h. The polymer electrolytes were prepared by dissolving appropriate amounts of the corresponding constituents in anhydrous THF and casting them as films using a solvent casting technique. The THF was allowed to evaporate at room temperature to yield mechanically stable films (free standing). The films were further dried in a temperature-controlled oven at 50 °C for 12 h to remove traces of THF, if any. The ionic conductivities of the polymer electrolytes

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**Fig. 1.** X-ray diffraction patterns of: (a) pure PVC; (b) pure PEMA; (c)  $\text{LiCF}_3\text{SO}_3$ ; (d)  $\text{LiClO}_4$ ; (e)  $\text{LiBF}_4$ ; (f) PVC (5)-PEMA (20)- $\text{LiCF}_3\text{SO}_3$  (8)-PC (67); (g) PVC (5)-PEMA (20)- $\text{LiClO}_4$  (8)-PC (67); (h) PVC (5)-PEMA (20)- $\text{LiBF}_4$  (8)-PC (67).

were evaluated from complex impedance plots in the temperature range 301–341 K using a Keithley 3330 LCZ meter in the frequency range 40 Hz–100 kHz. X-ray diffractograms were obtained with a Bruker (D8 Advance) diffractometer. Fourier transform infrared (FTIR) studies were conducted with a PerkinElmer (Paragon 500 grating) IR spectrophotometer. The thermal stability of the films was characterized by thermogravimetric/differential thermal analysis (TG/DTA) at a heating rate of  $10^\circ\text{C min}^{-1}$  from room temperature to  $400^\circ\text{C}$ .

### 3. Results and discussion

#### 3.1. X-ray diffraction studies

Fig. 1 shows the X-ray diffraction patterns for pure PVC, PEMA,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$  and their complexes of PVC (5)-PEMA (20)-PC (67)-LiX (8) where ( $\text{X}=\text{CF}_3\text{SO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ). The patterns of pure  $\text{LiBF}_4$ ,  $\text{LiClO}_4$  and  $\text{LiCF}_3\text{SO}_3$  show several diffraction peaks due to the crystalline nature of the compounds. These peaks completely disappear in the complexes, which demonstrates the absence of excess salt in all the complexes. A diffraction peak appears at  $2\theta = 13^\circ$  and corresponds to pure PVC which is found to be absent in the complexes. This reveals that a structural modification has occurred in the system [17]. The diffraction peak of PEMA is markedly reduced in all the complexes. The shift and decrease in the relative intensity of the peaks suggest that complexation has occurred between the salts and the polymers.

#### 3.2. FTIR analysis

The FTIR spectra of the polymer complexes are presented in Fig. 2. The peak at  $1725\text{ cm}^{-1}$  represents the carbonyl stretching vibration of PEMA. The peaks at 2982, 2939 and  $2910\text{ cm}^{-1}$  are

due to the methylene, (C)  $\text{CH}_3$ , and ethylene, (O)  $\text{C}_2\text{H}_5$ , groups which overlap [18]. Peaks at  $2963$  and  $1329\text{ cm}^{-1}$  are assigned, respectively, to asymmetric C–H methylene group vibration and in-plane CH deformation of PVC. The peaks at  $954$  and  $630\text{ cm}^{-1}$  are assigned to trans-CH rocking and cis-CH wagging of PVC. The peak at  $1777\text{ cm}^{-1}$  represents the  $\text{CH}_3\text{—C—}$  vibration of propylene carbonate. The frequency of  $\text{C=O}$  at  $1785\text{ cm}^{-1}$  indicates the interaction of the plasticizer with  $\text{LiClO}_4$ . The weak intensity peaks appearing at  $1027$ ,  $930$  and  $507\text{ cm}^{-1}$  are assigned to the  $\text{SO}_3^-$  stretching mode [19],  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  [20], respectively.

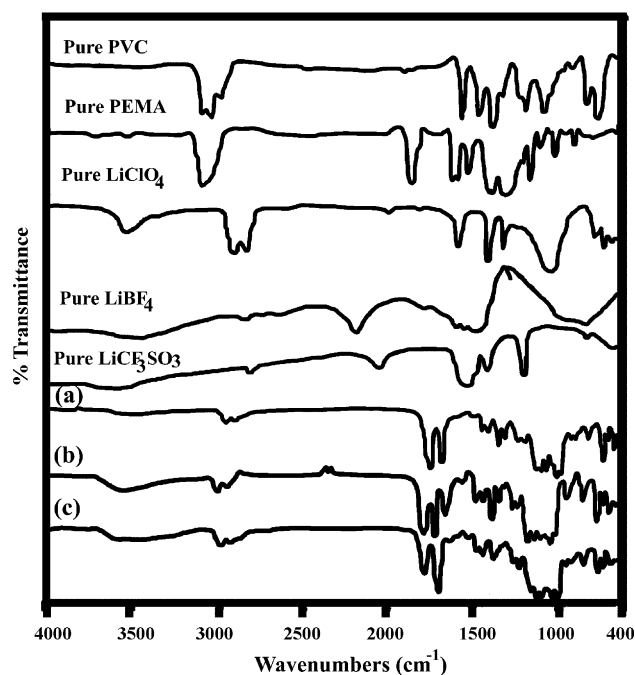
The vibrational peaks at  $1776$ ,  $1382$ ,  $1035$ ,  $959$ ,  $923$ ,  $771\text{ cm}^{-1}$  of pure PVC;  $1157$ ,  $1032$ ,  $850$ ,  $646\text{ cm}^{-1}$  of pure PEMA;  $2924$ ,  $1652$ ,  $1378$ ,  $1366\text{ cm}^{-1}$  of pure  $\text{LiClO}_4$ ;  $1545$ ,  $1450\text{ cm}^{-1}$  of pure  $\text{LiBF}_4$ ;  $3497$ ,  $1266$ ,  $768\text{ cm}^{-1}$  of pure  $\text{LiCF}_3\text{SO}_3$  are shifted to  $1785$ ,  $1387$ ,  $1053$ ,  $967$ ,  $940$ ,  $775$ ,  $1144$ ,  $1624$ ,  $860$ ,  $660$ ,  $2942$ ,  $1662$ ,  $1387$ ,  $1355$ ,  $1531$ ,  $1447$ ,  $3491$ ,  $1269$  and  $749\text{ cm}^{-1}$ , respectively.

It is also found that some of the peaks appearing in the pure polymers and salts disappear in the complexes, i.e., those at  $1807$ ,  $1545$ ,  $1250$ ,  $1192$ ,  $1184$ ,  $1087\text{ cm}^{-1}$ . In addition to this, new peaks are observed at  $2987$ ,  $1227$  and  $1114\text{ cm}^{-1}$  in the polymer complexes. The shifting of peaks and the formation of new peaks in the electrolyte systems indicate polymer–salt interaction in PVC/PEMA-based polymer blend electrolytes.

#### 3.3. Conductivity measurements

The ionic conductivity ( $\sigma$ ) of PVC/PEMA-based gel polymer electrolytes containing different lithium salts, namely,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$ , were calculated from  $\sigma = l/R_bA$ , where 'l' and 'A' represent the thickness and area of the film, respectively, and  $R_b$  is the bulk resistance of the gel electrolyte obtained from complex impedance measurements [21,22].

Fig. 3 shows the room temperature complex impedance spectra of a PVC (5)-PEMA (20)-PC (67)-LiX (8) wt.% (where  $\text{X}=\text{CF}_3\text{SO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ) polymer electrolyte system. According to the theoretical analysis given by Watanabe and Ogata [23], two semicircles



**Fig. 2.** FTIR spectra of: (a) pure PVC; (b) pure PEMA; (c)  $\text{LiCF}_3\text{SO}_3$ ; (d)  $\text{LiClO}_4$ ; (e)  $\text{LiBF}_4$ ; (f) PVC (5)-PEMA (20)- $\text{LiCF}_3\text{SO}_3$  (8)-PC (67); (g) PVC (5)-PEMA (20)- $\text{LiClO}_4$  (8)-PC (67); (h) PVC (5)-PEMA (20)- $\text{LiBF}_4$  (8)-PC (67).

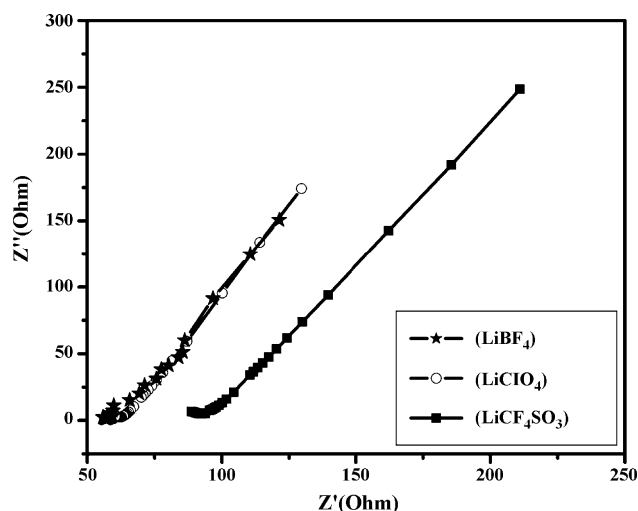


Fig. 3. Impedance diagram for PVC-PEMA-LiX-PC (5–20–8–67 wt.%) (where X =  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ) at 301 K.

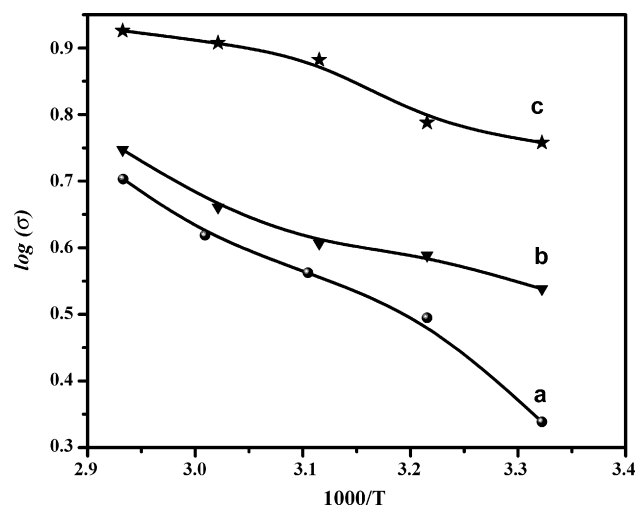


Fig. 4. Arrhenius plot of PVC-PEMA-LiX-PC (5–20–8–67 wt.%) complexes: (a) X =  $\text{CF}_3\text{SO}_3^-$ , (b) X =  $\text{BF}_4^-$  and (c) X =  $\text{ClO}_4^-$ .

should appear in the impedance spectrum for a symmetric cell, i.e., one at high frequencies corresponding to the bulk electrolyte impedance and the other at low frequencies related to the interfacial impedance. It has also been reported [24–26] that the high-frequency semicircle does not appear in practical impedance plots for plasticized polymer electrolyte membranes. This feature indicates that the conductivity is mainly due to ions.

Conductivity versus inverse temperature plots of PVC-PEMA-PC-LiX (where X =  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ )-based hybrid polymer electrolytes are given in Fig. 4. The overall features of these Arrhenius plots are quite similar for the electrolytes with different Li salts. The curvatures indicate that ionic conduction appears to obey the VTF relation, which describes transport properties in a viscous matrix. It supports the idea that the ion moves through the plasticizer-rich phase.

Conductivity data for hybrid polymer electrolytes containing different salts are presented in Table 1.  $\text{LiBF}_4$  offers the highest conductivity ( $6.726 \times 10^{-3} \text{ S cm}^{-1}$ ) among the lithium salts. Since all the anions are counter ions of strong acids, the difference in conductivity is presumably due to the difference in lattice energies of

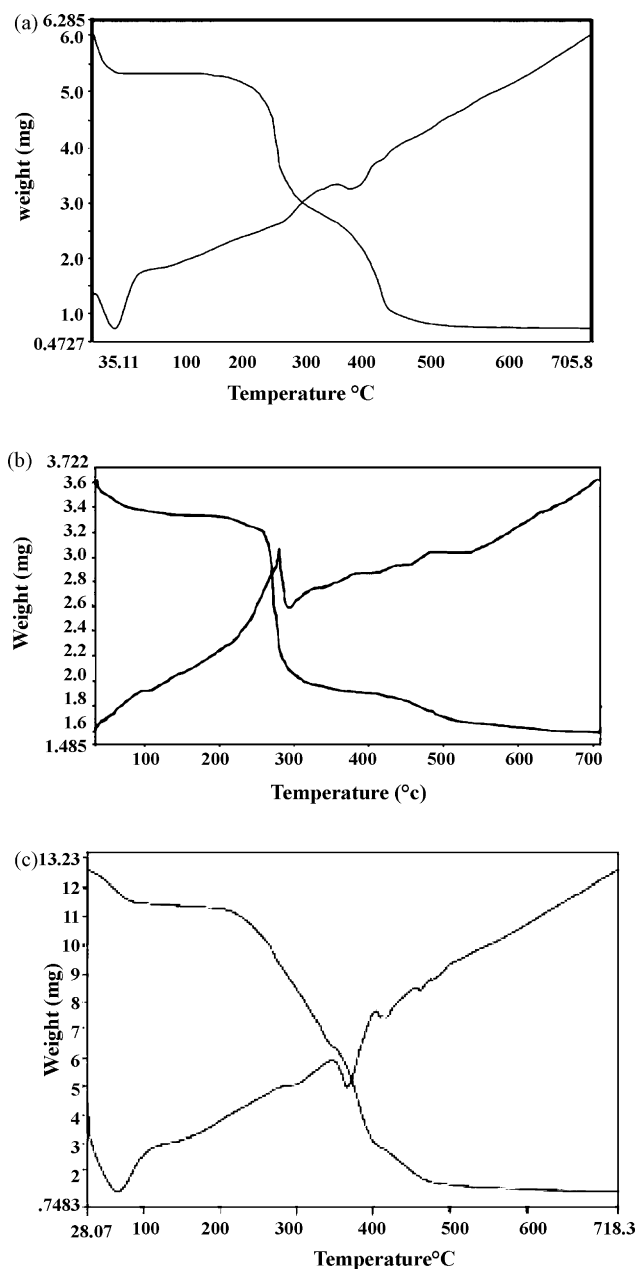


Fig. 5. TG/DTA curves of PVC (5)-PEMA (20)-LiX (8)-PC (67) complexes: (a) X =  $\text{BF}_4^-$ , (b) X =  $\text{ClO}_4^-$  and (c) X =  $\text{CF}_3\text{SO}_3^-$ .

the salts [27].  $\text{LiBF}_4$  has the lowest lattice energy ( $699 \text{ kJ mol}^{-1}$ ) and therefore allows easier solvation of  $\text{Li}^+$  ions by the polymer matrix, which facilitates a higher ionic conductivity. A similar observation has been reported by Immanuel et al. [28].

Table 1  
Ionic conductivity values of PVC-PEMA-PC-LiX (where X =  $\text{CF}_3\text{SO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{BF}_4^-$ ) polymer electrolyte systems

Film	Li salt	Ionic conductivity ( $10^{-3} \text{ S cm}^{-1}$ )				
		301 K	311 K	321 K	331 K	341 K
C1	$\text{LiCF}_3\text{SO}_3$	2.181	3.125	3.651	4.157	5.046
C2	$\text{LiClO}_4$	3.454	3.878	4.043	4.578	5.588
C3	$\text{LiBF}_4$	6.726	7.139	7.626	8.088	8.429

### 3.4. TG/DTA analysis

TG/DTA analyses of polymer electrolytes containing  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ , or  $\text{LiCF}_3\text{SO}_3$  are given in Fig. 5(a)–(c), respectively. In Fig. 5(a), the film starts decomposing at  $35^\circ\text{C}$  with a weight loss of 3–5%. This is attributed to the presence of moisture at the time of loading of the samples. A second decomposition takes place at  $254^\circ\text{C}$  with a rapid weight loss of 80 wt.%. This indicates that the film is stable up to  $254^\circ\text{C}$ . The DTA trace shows an endothermic peak at around  $280^\circ\text{C}$ , which corresponds to the melting point of the PEMA polymer host.

Similar endothermic peaks are observed at around  $38$  and  $50^\circ\text{C}$  with a weight loss of about 2–5% in Fig. 5(b) and (c), respectively. The gradual decomposition of the films start at  $231$  and  $248^\circ\text{C}$ , respectively. It is clear from these observations that the hybrid polymer electrolytes with  $\text{LiBF}_4$ ,  $\text{LiClO}_4$  and  $\text{LiCF}_3\text{SO}_3$  as salt can be operated up to  $254$ ,  $231$  and  $248^\circ\text{C}$ , respectively.

### 4. Conclusions

Complex formation in a PVC/PEMA system has been confirmed by XRD and FTIR studies. All electrolytes show appreciable conductivity, even at room temperature. A maximum conductivity ( $6.726 \times 10^{-3} \text{ S cm}^{-1}$ ) at room temperature with good mechanical stability has been observed for a PVC (5)-PEMA (20)-PC (67)- $\text{LiBF}_4$  (8 wt.%) system. The good thermal stability of this polymer electrolyte system up to  $254^\circ\text{C}$  is confirmed by TG/DTA analysis. There are prospects that this system can be used as an electrolyte in lithium batteries and other electrochemical devices.

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