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Short communication

# Ionic conductivity studies in poly(methylmethacrylate)–polyethylene oxide hybrid polymer electrolytes with lithium salts

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## Abstract

The transport properties of gel-type ionic conducting membranes consisting of poly(methylmethacrylate) (PMMA), polyethylene oxide (PEO), LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>) and dimethyl phthalate (DMP) are studied. The polymer films are characterized by FTIR and impedance spectroscopic studies. At room temperature, the highest conductivity, viz.,  $0.64 \times 10^{-4} \text{ S cm}^{-1}$ , is obtained for a film of PMMA, PEO, LiBF<sub>4</sub> and DMP. Hybrid polymer electrolytes based on PMMA–PEO appear very promising for lithium battery applications. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Hybrid polymer electrolyte; FTIR; Conductivity; Lithium-ion battery; Impedance spectroscopy

## 1. Introduction

Polymer electrolytes are attracting increasing attention due to promising applications such as solid-state rechargeable lithium-ion batteries, supercapacitors, electrochromic windows, and sensors [1–3]. The main advantage of polymer electrolytes are favourable mechanical properties, ease of fabrication of thin films of desirable size and an ability to form effective electrode–electrolyte contacts. Armand et al. [4] have claimed that the crystalline complexes formed from alkali-metal salts with polyethylene oxide (PEO) are capable of demonstrating significant ionic conductivity and have highlighted their possible application as battery electrolytes. Nowadays, several types of polymer electrolytes have been developed and characterized such as those based on poly(ethylene oxide) (PEO) [5–7], poly (acrylonitrile) (PAN) [8–11], poly (methylmethacrylate) (PMMA) [12–14], poly (vinyl chloride) (PVC) [15–17] and poly(vinylidene fluoride) (PVdF) [18,19].

The electrolytes commonly exhibit conductivities which range from  $10^{-8}$  to  $10^{-4} \text{ S cm}^{-1}$  at temperatures between 40 and 100°C. Investigations have been focused primarily on the enhancement of the conductivity at room temperature via various approaches such as using blends, copolymers,

comb-branch polymers, and cross-linked networks. All improvements have been achieved either by reducing the crystallinity of the polymers or by lowering the glass transition temperature. It is generally observed, however, that high conductivity is achieved at the expense of good dimensional stability [20].

Blending of polymers is a useful method to develop new materials with improved mechanical stability. The problem in choosing polymer blends is the miscibility of the components. By careful selection of the support polymer, there may be the added advantage of lowering the degree of crystallinity. Combinations of proton-donating and proton-accepting polymers can form intermacromolecular complexes in aqueous or organic media. PMMA and PEO form one such couple [21,22]. Tsuchida et al. [23] discussed the ionic conductivity of hybrid films composed of lithium perchlorate and poly(methacrylic acid), PEO intermacromolecular complexes. Blends of PMMA and PEO have been reported [24–26]. These studies have shown clear evidence of the miscibility of PMMA and PEO. The crystallization and miscibility behaviour of PMMA–PEO blends have also been studied by means of techniques such as differential scanning calorimetry (DSC) [27,28] and dynamic mechanical analysis [24]. Studies on solid polymer electrolytes of PMMA, PEO and tetraalkylammonium salts have been reported by Ishikawa et al. [29].

In the present study, solid polymer electrolyte films consisting of PMMA, PEO, LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>)

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and dimethyl phthalate (DMP) are prepared and characterized by FTIR and ac impedance spectroscopy. It is found that the lithium salts have good solubility in the PMMA–PEO matrix and the resulting solid electrolytes exhibit good conductivity and mechanical stability.

## 2. Experimental

Three complexes of PMMA-based gel electrolytes have been examined in this work, namely, systems with the following mol% compositions:

S1: PMMA(17.5): PEO(7.5): LiCF<sub>3</sub>SO<sub>3</sub>(8): DMP(67)

S2: PMMA(17.5): PEO(7.5): LiBF<sub>4</sub>(8): DMP(67)

S3: PMMA(17.5): PEO(7.5): LiClO<sub>4</sub>(8): DMP(67)

The polymer composition PMMA(17.5)–PEO(7.5) is chosen since Bajpai et al. [30] and Bohnke et al. [31] reported that a PMMA content beyond 20 mol% develops a hardened PMMA–PEO polyblend.

In order to obtain homogenous samples, particular care was taken with respect to the purification of the components and the experimental procedure. LiCF<sub>3</sub>SO<sub>3</sub>, LiBF<sub>4</sub> and LiClO<sub>4</sub> were dried by annealing under vacuum at 150, 90 and 100°C, respectively, for 10 h. PMMA of average molecular weight  $1.7 \times 10^5$  (Aldrich) and PEO of molecular weight  $1 \times 10^5$  (Aldrich) were dried by heating under vacuum at 100 and 50°C, respectively, for 6 h. DMP (Aldrich) was used as received. All the components, i.e. the selected lithium salt, PMMA, PEO and DMP were dissolved in tetrahydrofuran (THF). The solution was stirred

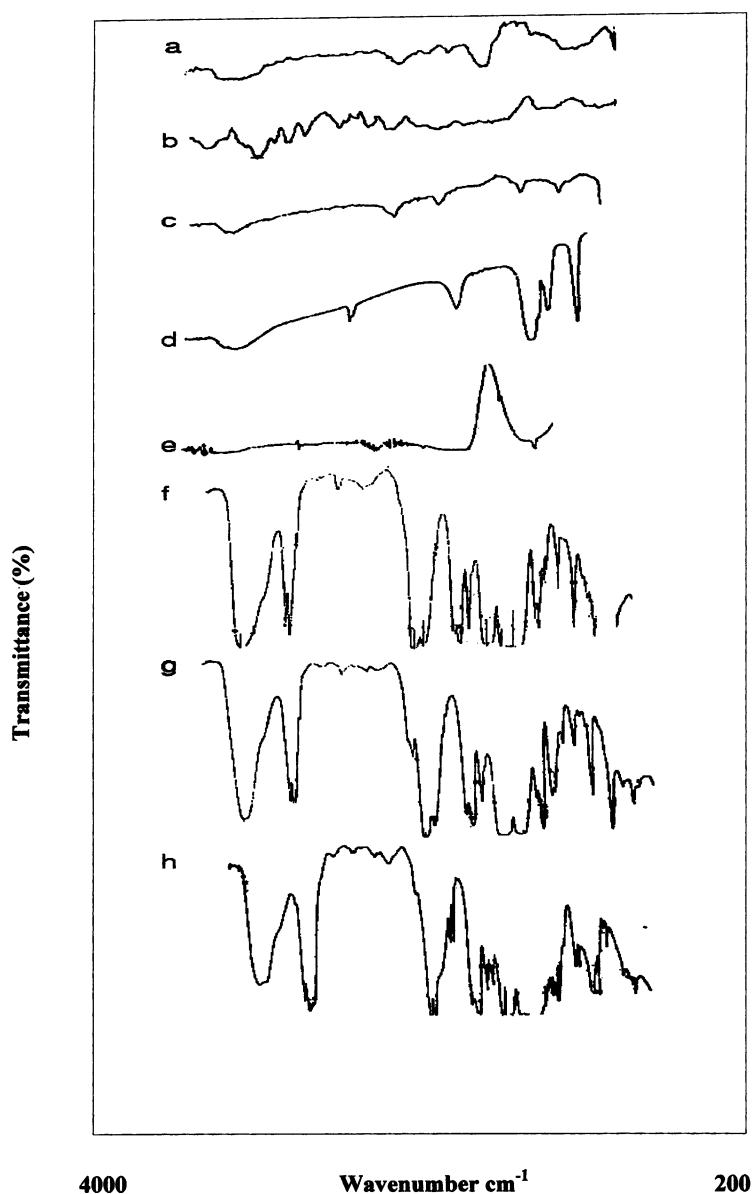


Fig. 1. FTIR plots for PMMA, PEO, LiClO<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiBF<sub>4</sub> and complexes: (a) PMMA; (b) PEO; (c) LiClO<sub>4</sub>; (d) LiCF<sub>3</sub>SO<sub>3</sub>; (e) LiBF<sub>4</sub>; (f) PMMA(17.5)–PEO(7.5)–LiClO<sub>4</sub>(8)–DMP(67); (g) PMMA(17.5)–PEO(7.5)–LiCF<sub>3</sub>SO<sub>3</sub>(8)–DMP(67); (h) PMMA(17.5)–PEO(7.5)–LiBF<sub>4</sub>(8)–DMP(67).

continuously for several hours until a homogeneous suspension was obtained. The film was cast on to a glass plate/polypropylene dish and then allowed to evaporate slowly at room temperature. The resulting film was visually examined for its dry and free-standing nature. FTIR measurements were made with a Perkin-Elmer 577 IR spectrophotometer in the range  $200\text{--}4000\text{ cm}^{-1}$ . The bulk electrical conductivities of the complex were evaluated from impedance plots in the temperature range  $273\text{--}333\text{ K}$  using a Keithley 3330 LCZ meter. The plots were recorded in the frequency range  $40\text{--}100\text{ kHz}$  with a signal amplitude of  $10\text{ mV}$ . The polymer film was sandwiched between stainless-steel electrodes for conductivity studies.

### 3. Results and discussion

#### 3.1. FTIR studies

The FTIR plots of pure PMMA, PEO,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiBF}_4$  and polymer electrolyte complexes are shown in Fig. 1. The C–H stretching frequency of PEO which appears at  $2900\text{ cm}^{-1}$  is shifted to  $2950\text{ cm}^{-1}$  in the complexes. The asymmetric stretching vibration at  $1950\text{ cm}^{-1}$  and the asymmetric bending vibration at  $1450\text{ cm}^{-1}$  of pure PEO are shifted to  $1985$  and  $1435\text{ cm}^{-1}$  in the polymer complex, respectively. The vibrational frequencies  $1485$ ,  $991$ ,  $842$ ,

and  $749\text{ cm}^{-1}$  of PEO are assigned to the  $\text{CH}_2$  scissoring, twisting, wagging and rocking modes. The peak at  $1731\text{ cm}^{-1}$  of PMMA is assigned to  $-\text{O}-\text{CH}_3$  deformation. Absorption peaks of pure PMMA ( $1745$ ,  $1152$  and  $500\text{ cm}^{-1}$ ) are shifted to ( $1731$ ,  $1149$  and  $504\text{ cm}^{-1}$ ) in the complexes. Vibrational bands of PMMA ( $1448$ ,  $964$  and  $988\text{ cm}^{-1}$ ) and PEO ( $1225$ ,  $1105$  and  $930\text{ cm}^{-1}$ ) are absent in the complexes. In addition to this, some new peaks at ( $2362$ ,  $1578$ ,  $706$  and  $670\text{ cm}^{-1}$ ) are found in the polymer complexes. If the alkali metal cations are coordinated to the ether oxygens, then one would expect to see large changes in the C–C and C–O–C stretching regions ( $1060\text{--}1150\text{ cm}^{-1}$ ) [32]. In the present work, the absorption peaks at  $1105$  and  $1130\text{ cm}^{-1}$  are shifted to values of  $1149$  and  $1039\text{ cm}^{-1}$ , respectively, in the complexes. The shift in the C–O–C stretching frequency is due to the association of  $\text{Li}^+$  with the ether oxygen.

The characteristic frequencies of  $\text{LiBF}_4$  ( $1633$ ,  $1305$  and  $1089\text{ cm}^{-1}$ ),  $\text{LiCF}_3\text{SO}_3$  ( $3564$ ,  $1646$  and  $1184\text{ cm}^{-1}$ ) and  $\text{LiClO}_4$  ( $1610$ ,  $1300$ ,  $920$  and  $470\text{ cm}^{-1}$ ) are shifted to ( $1600$ ,  $1350$  and  $1109\text{ cm}^{-1}$ ), ( $3545$ ,  $1671$  and  $1158\text{ cm}^{-1}$ ) and ( $1666$ ,  $1282$ ,  $931$  and  $486\text{ cm}^{-1}$ ) in the polymer complexes, respectively. This may be due to the change in environment for the  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$  and  $\text{ClO}_4^-$  ions in the complexes. The appearance of new peaks along with changes in the existing peaks in the FTIR spectra confirms the complexation.

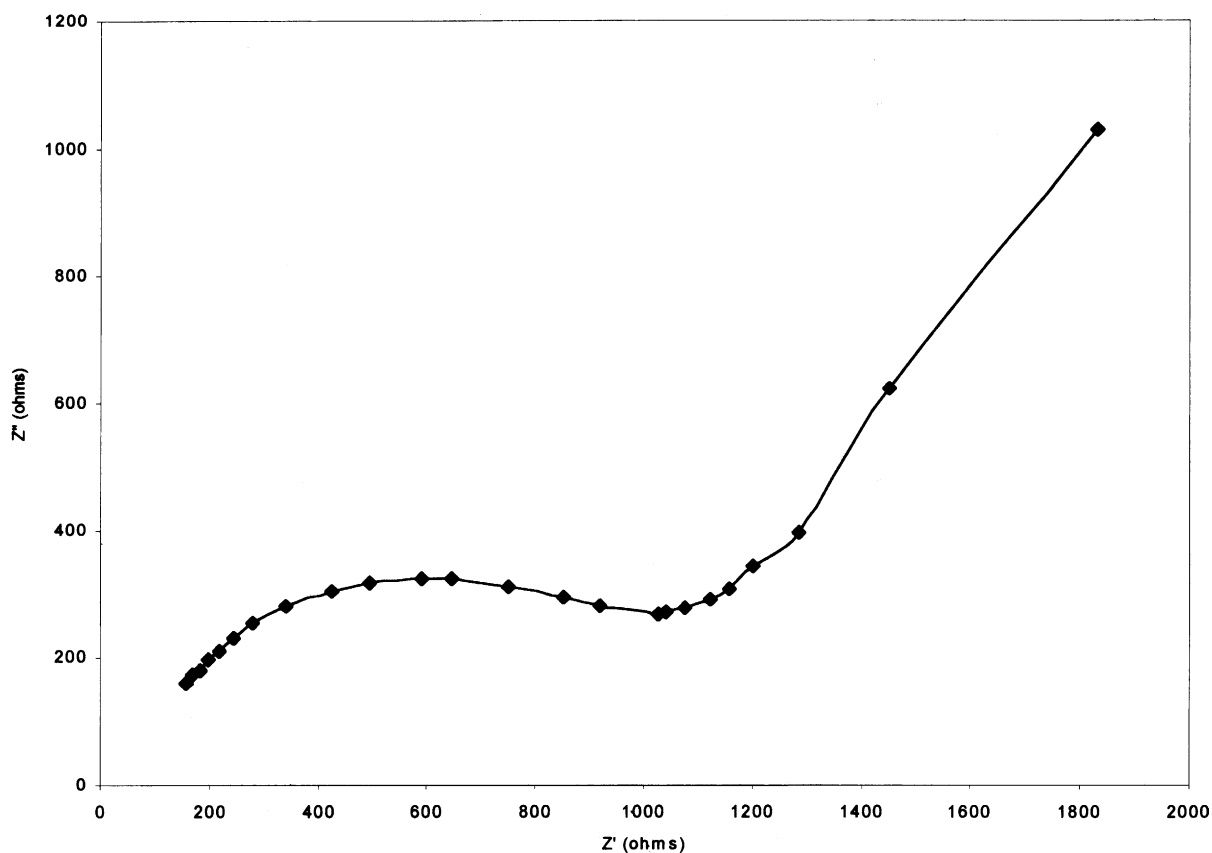


Fig. 2. Impedance diagram of PMMA(17.5)–PEO(7.5)– $\text{LiBF}_4$ (8)–DMP(67) at  $303\text{ K}$ .

Table 1  
Conductivity of PMMA–PEO–LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>)–DMP polymer electrolytes

Sample	Composition	Conductivity values $\times 10^{-4}$ S cm <sup>-1</sup>			
		303 K	313 K	323 K	333 K
S1	PMMA(17.5)–PEO(7.5)–LiCF <sub>3</sub> SO <sub>3</sub> (8)–DMP(67)	0.062	0.093	0.171	0.362
S2	PMMA(17.5)–PEO(7.5)–LiBF <sub>4</sub> (8)–DMP (67)	0.641	0.775	0.963	3.315
S3	PMMA(17.5)–PEO(7.5)–LiClO <sub>4</sub> (8)–DMP(67)	0.446	0.518	0.582	0.893

### 3.2. Conductivity studies

The ac impedance spectrum of the SS–SPE–SS (SPE: solid polymer electrolyte; SS: stainless-steel) system is given in Fig. 2. The intercept on the real axis gives the electrolyte bulk resistance. The conductivity of the polymer electrolyte was calculated from the measured resistance for the known area and thickness of the polymer film. The conductivity values obtained for dry plasticized films are summarized in Table 1. The value of  $6.4 \times 10^{-5}$  S cm<sup>-1</sup> for the PMMA–PEO–LiBF<sub>4</sub> and DMP complex at 303 K is comparable with the values reported by Borkowaska and Laskowski [33], viz.,  $6 \times 10^{-5}$  S cm<sup>-1</sup>, and Peled et al. [34], viz.,  $1 \times 10^{-5}$  S cm<sup>-1</sup> for PMMA–PEO based polymer electrolytes with lithium salts. The temperature dependence of the ionic conductivities of PMMA–PEO complexes containing different lithium salts is shown in Fig. 3. The data show that the conductivity can be well described by the familiar Arrhenius equation. The conductivity values of the LiCF<sub>3</sub>SO<sub>3</sub> electrolyte are lower than those of the LiClO<sub>4</sub>

and LiBF<sub>4</sub> electrolytes over the temperature range studied. This result may be due to the following reasons:

1. A smaller conductivity enhancement factor for the LiCF<sub>3</sub>SO<sub>3</sub> salt can be attributed to the larger anionic radius of the ion. Observed differences in the incremental conductivity for LiClO<sub>4</sub> and LiAsF<sub>6</sub> were correlated in a similar way by Tobishima and Yamaji [35]. This suggests that the ionic conductivity is affected by the diffusion rate of the ions, which in turn depends on the size of each ion.
2. This observation in (1) may be due to the lower degree of dissociation of the LiCF<sub>3</sub>SO<sub>3</sub> salt. The degree of dissociation of the various lithium salts has been previously compared by various authors in liquid electrolytes [36]. It was reported that the association tendency of the anions with Li<sup>+</sup> ions in non-aqueous aprotic solvents increases in the following order:

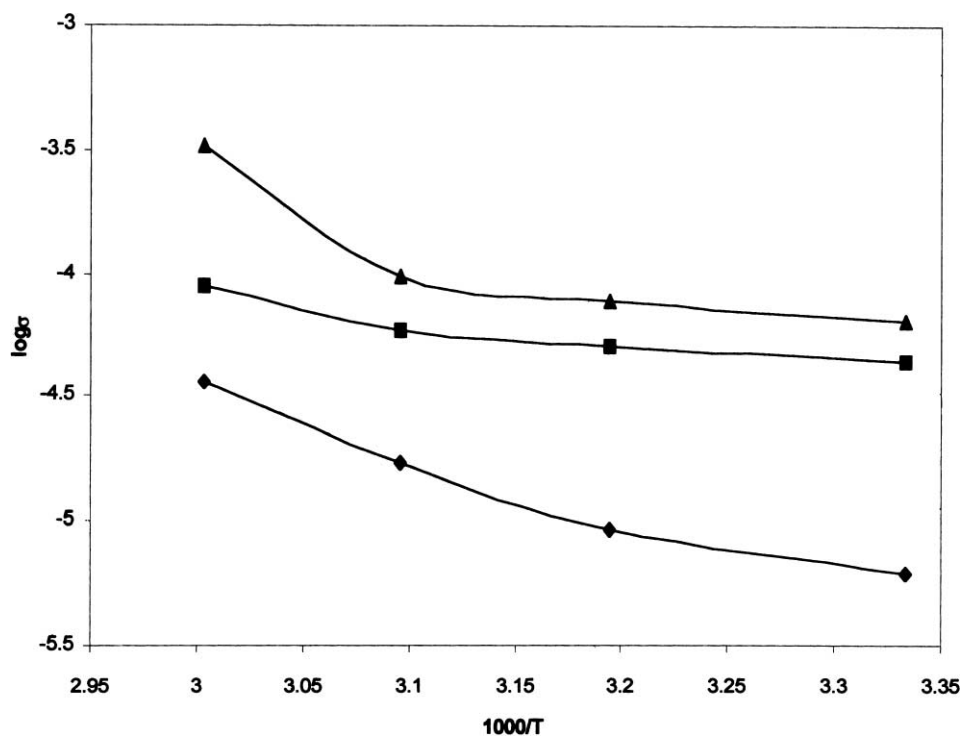
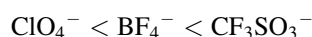


Fig. 3. Arrhenius plot of log conductivity against reciprocal temperature for PMMA–PEO–LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>)–DMP polymer complexes: (■) PMMA(17.5)–PEO(7.5)–LiClO<sub>4</sub>(8)–DMP(67); (◆) PMMA(17.5)–PEO(7.5)–LiCF<sub>3</sub>SO<sub>3</sub>(8)–DMP(67); (▲) PMMA(17.5)–PEO(7.5)–LiBF<sub>4</sub>(8)–DMP(67).

This result suggests that ion-pairing takes place to a lesser extent in the electrolytes containing  $\text{LiClO}_4$  or  $\text{LiBF}_4$  compared with the electrolyte which contains  $\text{LiCF}_3\text{SO}_3$ .

#### 4. Conclusions

Complex formation in PMMA–PEO–LiX–DMP ( $X = \text{ClO}_4, \text{BF}_4, \text{CF}_3\text{SO}_3$ ) system has been confirmed by FTIR studies. The maximum value of conductivity obtained for a PMMA (17.5)–PEO(7.5)– $\text{LiBF}_4$ (8)–DMP(67) polymer electrolyte system is  $6.4 \times 10^{-5} \text{ S cm}^{-1}$  at 303 K.

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