

# Studies on the Effect of Anions of Various Lithium Salts in PEMA Gel Polymer Electrolytes

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Received 19 April 2008; accepted 11 November 2008

DOI 10.1002/app.29710

Published online 20 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Polyvinylidene fluoride (PVdF)–polyethyl methacrylate (PEMA) based electrolytes comprising a binary mixture of solvents (EC and PC) (ethylene carbonate and propylene carbonate) and lithium salts LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>) have been prepared using solvent casting technique. The prepared electrolytes were subjected to ionic conductivity, XRD, SEM, and FTIR analysis to understand the salt contribution. Comparison of conductivity studies of the electrolytes with the three salts has also been made. These electrolytes exhibited good electrochemical properties, because they have

an ionic conductivity of the order of 10<sup>-3</sup> S cm<sup>-1</sup>, an electrochemical window exceeding 4.5 V and lithium ion transference number averaging above 0.75. Because, the complex containing LiClO<sub>4</sub> exhibited maximum conductivity among the other complexes studied, DMA and CV analyses were also been performed and the results are reported. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1–6, 2011

**Key words:** PEMA; lithium salts; impedance studies; DMA; CV

## INTRODUCTION

Alkali metal ion conductive electrolytes with high ionic conductivity at ambient temperature have been extensively studied because of the stringent need for such materials in high energy density devices. A considerable interest is presently devoted to the development of lithium ion conducting polymer electrolyte membranes to be used in plastic-like lithium ion batteries. Polymers like Polyvinylidene fluoride (PVdF), Poly(methyl methacrylate) (PMMA), Poly(vinyl alcohol) (PVA), etc. formed homogeneous composites with various lithium salts and showed good ionic conductivity. The small size of cation and large size of anion have dictated the choice of the metal salts.<sup>1–3</sup>

Conductivities of 10<sup>-7</sup> to 10<sup>-4</sup> S cm<sup>-1</sup> at temperature between 40 and 100°C have been reported for PEO based electrolytes containing low lattice energy lithium salts such as LiClO<sub>4</sub>, LiBF<sub>4</sub>, and LiCF<sub>3</sub>SO<sub>3</sub>. Kanbara et al.<sup>4</sup> reported that PVA formed transparent and homogeneous electrolytes with lithium salts and showed good ionic conductivity of the order of

10<sup>-4</sup>–10<sup>-3</sup> S cm<sup>-1</sup> at room temperature. The ionic conduction in these electrolytes occurs in the amorphous regions of the polymer, via large-amplitude segmental motion of the polymer chains.<sup>5</sup> Recent works<sup>6,7</sup> in polymer electrolytes has yielded conductivities >10<sup>-3</sup> S cm<sup>-1</sup> at room temperature. These electrolytes comprise polymer blends, plasticized with low molecular weight organic solvents. The liquid electrolytes are most often a mixture of two or more solvents for e.g., EC, PC, Dimethyl carbonate (DMC), Diethyl carbonate (DEC), and a lithium salt. Mixture of EC and PC<sup>8</sup> provide one of the highest conductive solutions with lithium salts as the dissociation may be strengthened. The small size of cation, large size of anion, and low dissociation energy has dictated the choice of the metal salts. Salt like LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>) are stable, dissolve, and dissociate easily and give high conductivities. We have previously reported the preparation of new blend based polymeric electrolytes composed of polyethyl methacrylate (PEMA)–PVdF–LiClO<sub>4</sub> and showed its high ionic conductivity and good mechanical stability.<sup>9</sup> The anionic part of the lithium salt plays an vital role in contributing towards the conductivity and stability of the resultant electrolyte. In the view of this, an attempt has been made to find the role of different salts with respect to the ionic conductivity. In this investigation, PVdF-PEMA blend based electrolyte with a range of lithium salts viz LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub> and using EC+PC as a

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Contract grant sponsor: National Science Council of Republic of China; contract grant number: NSC 94-2214-E-002-003.

**TABLE I**  
**Conductivity,  $E_a$ , and  $t_+$  Values of PVdF-PEMA-LiX-EC + PC Based Electrolytes**

Sample code	Compositions			
	PVdF(27)-PEMA(3)-LiX(5)-EC + PC(67)	$\sigma$ ( $\times 10^{-3}$ S cm $^{-1}$ at 301 K)	$E_a$ (eV)	$t_+$
A1	X = ClO $_4$	1.34	0.15	0.76
A2	X = BF $_4$	0.73	0.22	0.88
A3	X = CF $_3$ SO $_3$	0.22	0.33	0.77

common mixture of plasticizer. The characteristics and electrochemical performance of these polymer electrolytes were examined and the results are reported.

### EXPERIMENTAL

The materials used in this work are PEMA ( $M_w \sim 515,000$ ), PVdF ( $M_w \sim 534,000$ ), LiClO $_4$ , and EC obtained from Aldrich, PC obtained from Fluka. Polymers and Li salt were used after drying in the vacuum oven below their corresponding melting points for 24 h. Plasticizers were used without further purification. All the electrolytes were synthesized using solvent casting technique. The stoichiometric ratios of the prepared electrolytes were listed in Table I. As mentioned in Table I, polymers, salts, and EC+PC mixture were dissolved individually in distilled Tetrahydrofuran (THF) and then mixed together. Solution thus obtained was then mechanically stirred continuously for 12 h and the homogeneous solution was poured on to absolute flat glass petri plates for slow evaporation at 40°C about 12 h. Traces of the residual solvent in the films were removed at 60°C under 10 $^{-3}$  Torr pressure. This procedure provided mechanically stable, freestanding, and flexible thin films (approximate thickness about 100  $\mu$ m). The as prepared electrolytes were subjected for various characterizations. All the preparation, stirring, casting, and cell assembling for characterization were carried out in a dry room having a dew point between 228 and 233 K (−45 and −40°C).

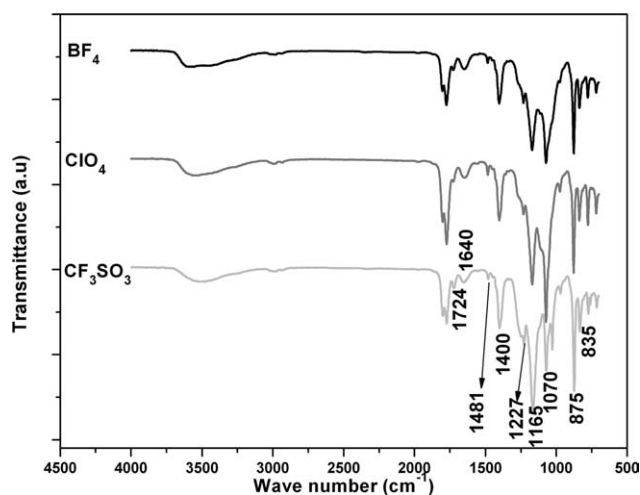
The impedance studies were carried out by sandwiching the electrolytes between stainless steel (SS) electrodes, and the impedance was measured with the signal amplitude of 10 mV in the temperature range 301–373 K. The electrochemical studies of the electrolytes were performed using ECO CHEMIE PGSTAT 30. The interfacial resistance was also measured using the same impedance technique for lithium symmetric cell. The electrochemical stability of the electrolytes was determined using the linear sweep voltammetry (LSV) for SS/GPE/Li cell assemble at 1 mV s $^{-1}$  from its OCP to 6 V. The lithium symmetric cell couple was used for lithium ion

transference number measurement by polarization technique for constant DC voltage of 5 mV. The surface morphology of the prepared electrolytes was examined by JEOL JSM-5310 scanning electron microscope (SEM). The samples were sputtered with Pt coating and then examined under vacuum. The X-ray diffraction (XRD) analysis of the electrolytes was carried out by Philips' X'pert X-ray diffractometer. The Fourier transform infra red (FTIR) spectroscopy measurements were made in the range 4000–400 cm $^{-1}$  using Perkin-Elmer-Paragon IR spectrophotometer (Model 500). Dynamic mechanical analysis of the samples were performed using DMA 2980 dynamic mechanical analyzer (TA Instruments) under rectangular tension mode at frequency 1 Hz and heat rate of 2°C min $^{-1}$  between −75 and 200°C. The effective sample dimensions used in this analysis were maintained as 33  $\times$  13.25  $\times$  0.3 mm for sample A1. The cyclic voltammetric analysis has been performed in the same ECO CHEMIE PGSTAT 30, for the sample possessing maximum ionic conductivity (A1) with the cell couple LiFePO $_4$ /GPE/Li at the scan rate of 5 mV min $^{-1}$ .

### RESULTS AND DISCUSSION

#### FT-IR

FT-IR is a useful tool for understanding the physical or chemical environment of a group in a molecule in the electrolyte. The plasticizer EC has carbonyl group in its molecule, which is known to be very sensitive to its environment in FT-IR spectra.<sup>10</sup> Two peaks in the region appeared in all complexes containing the three lithium salts (Fig. 1), which were thought to be the frequencies of the carbonyl group of EC. That is EC in the mixtures is exposed to two different environments, one is the interaction with the polymers corresponding to 1775 cm $^{-1}$  and the other is the interaction with itself (1806 cm $^{-1}$ ). The splitting into 1770 and 1800 cm $^{-1}$  bands were considered to be Fermi resonance of the C=O stretching mode. Thus the peak at 1806 cm $^{-1}$  is assigned to the  $\gamma_{C=O}$  region of carbonate groups.<sup>11</sup> The carbonyl stretching vibration observed at 1725 cm $^{-1}$  in pure PEMA is shifted to 1724 cm $^{-1}$  in the complexes containing LiBF $_4$  and LiCF $_3$ SO $_3$  salts and gets

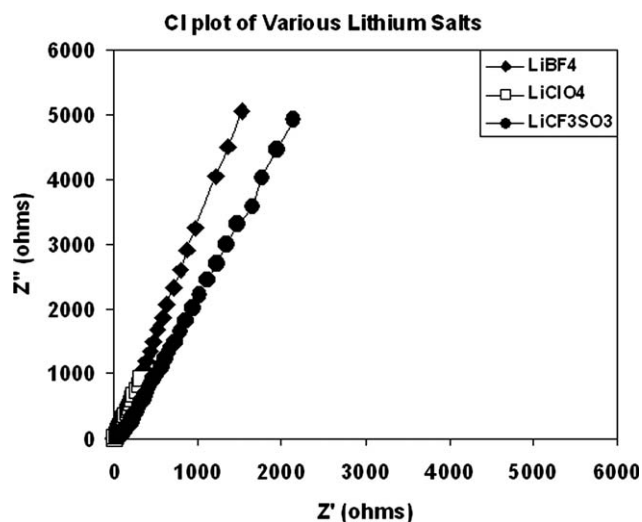


**Figure 1** FT-IR spectra of PVdF-PEMA-LiX ( $X = \text{ClO}_4$ ,  $\text{BF}_4$ ,  $\text{CF}_3\text{SO}_3$ )-EC+PC based electrolytes.

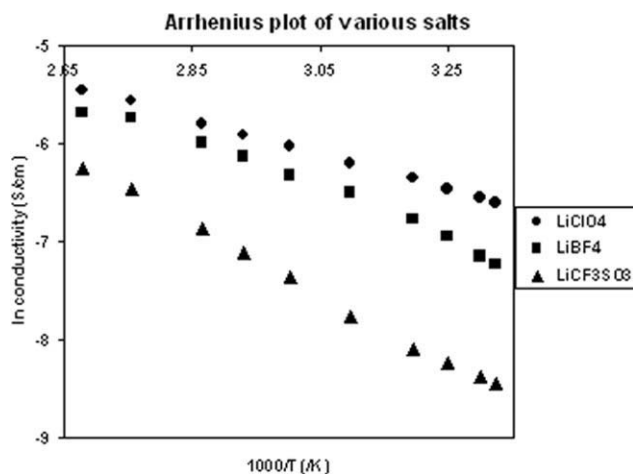
disappeared in  $\text{LiClO}_4$  complex. Peak at  $1483 \text{ cm}^{-1}$  is assigned to  $\text{CH}_2$  scissoring of PEMA and is shifted to 1482, 1487, and  $1481 \text{ cm}^{-1}$  in the complexes containing  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ , and  $\text{LiCF}_3\text{SO}_3$  complexes, respectively. Frequencies  $1640 \text{ cm}^{-1}$  and  $1400 \text{ cm}^{-1}$  are assigned to  $>\text{C}=\text{O}$ ,  $>\text{C}=\text{C}<$ , and vibrational peaks of PVdF and are slightly shifted in all the complexes. The bands at  $1240 \text{ cm}^{-1}$  are associated with different vibrations of ester group<sup>12</sup> and appears at 1233, 1230, and  $1227 \text{ cm}^{-1}$  in the complexes comprising  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ , and  $\text{LiCF}_3\text{SO}_3$ , respectively. Frequencies  $1172\text{--}1066 \text{ cm}^{-1}$  are assigned to C–F and  $\text{CF}_2$  stretching and frequencies  $837\text{--}624 \text{ cm}^{-1}$  are assigned to C–Cl stretching vibrations of PVdF and are shifted to 1169, 1172, and  $1165 \text{ cm}^{-1}$  and 838, 838, and  $835 \text{ cm}^{-1}$  in  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ , and  $\text{LiCF}_3\text{SO}_3$  complexes, respectively. The presence of peak at  $874 \text{ cm}^{-1}$  is assigned to C–O–C symmetric stretching of PEMA and vinylidene group of PVdF ( $880 \text{ cm}^{-1}$ ) is shifted to 879, 878, and  $875 \text{ cm}^{-1}$  in  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ , and  $\text{LiCF}_3\text{SO}_3$  electrolytes, respectively. The absorption band appearing at  $940 \text{ cm}^{-1}$  is assigned to the totally symmetric vibration of  $\text{ClO}_4^-$ <sup>13</sup> and is found to be absent in  $\text{LiClO}_4$  complex. The vibrational peak of perchlorate anion at  $976 \text{ cm}^{-1}$  is shifted to  $977 \text{ cm}^{-1}$  in the complex. Some peaks appear at 940 and  $756 \text{ cm}^{-1}$  in  $\text{LiCF}_3\text{SO}_3$  system corresponding to wagging and rocking modes of PEMA and are absent in the rest. The  $\text{CF}_3$  stretching frequency is appeared at  $1031 \text{ cm}^{-1}$  and is shifted to  $1029 \text{ cm}^{-1}$  in film A3. Also a new peak appears in the region  $1070 \text{ cm}^{-1}$  in all complexes. From the above analysis, shifting and absence of peaks in complexes pertaining to the individual components and existence of new peaks corroborated the complex formation of polymer, salt, and plasticizers in the matrices.

### Impedance and microstructure analyses

Ionic conductivity measurements of the electrolytes help us to assess the role of the conducting species and their mobility. The complex impedance plots of the electrolytes containing various salts were plotted and analyzed for the conductivity values. The AC impedance spectra for the three electrolytes at 301 K are given in Figure 2. The plots were obtained from a SS/GPE/SS cell assemble and display two well-defined regions. One is a high frequency range, which is related to the ionic conduction process in the bulk of the polymer electrolyte; another is a low frequency region, with a straight line parallel to the imaginary axis that is attributed to the effect of blocking electrode. Since a blocking electrode was used in impedance analysis, the film/electrode interface can be regarded as a capacitance. When the capacitance is ideal, it should show a vertical spike in the Nyquist plot. In fact, a spike inclined at an angle of less than  $90^\circ$  is found instead of a vertical spike. This is known to be due to the roughness of the film/electrode interface. The maximum ionic conductivity value is obtained for the sample A1 (order of  $1.34 \times 10^{-3} \text{ S cm}^{-1}$  at 301 K). It is higher than the values  $\sim 10^{-6}$  and  $1.8 \times 10^{-4} \text{ S cm}^{-1}$  for PVdF-HFP/ $\text{LiClO}_4$ /EC+PC and PVdF/ $\text{LiClO}_4$  (5 wt %) wetted by EC/PC mixture of 0.1M  $\text{LiClO}_4$  polymer electrolyte systems reported by Stephan et al.<sup>14</sup> and Shen et al.<sup>15</sup> Conductivities of the order of  $10^{-4}\text{--}10^{-3} \text{ S cm}^{-1}$  have been obtained for the prepared electrolytes. Sample A1 showed maximum ionic conductivity value, which is due to greater dissociative power and larger size of anion of  $\text{LiClO}_4$  than the other salts overrides its high viscosity drawback and plays a crucial role in contributing towards the conductivity and towards the electrochemical oxidation stability of the electrolyte.<sup>16</sup> Tobishima and



**Figure 2** Complex impedance spectra of PVdF-PEMA-LiX ( $X = \text{ClO}_4$ ,  $\text{BF}_4$ ,  $\text{CF}_3\text{SO}_3$ )-EC+PC based electrolytes at 301 K.



**Figure 3** Temperature dependence of PVdF-PEMA-LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>)-EC+PC based electrolytes in the temperature range 301–373 K.

Yamaji<sup>17</sup> obtained this difference in incremental conductivity for LiClO<sub>4</sub> and LiAsF<sub>6</sub> and correlated them in a similar way. Hence, the ionic conductivity is affected by the diffusion rate of ions, which depends on the size of the ion. Also the lower degree of dissociation of LiCF<sub>3</sub>SO<sub>3</sub> salt may be the cause for its lower conductivity when compared to the other electrolytes. Ion pairing also plays an important role in the conduction mechanism. The lower ion pairing nature of LiClO<sub>4</sub> and LiBF<sub>4</sub> produces higher conductivity values compared with the complex containing LiCF<sub>3</sub>SO<sub>3</sub>.

The temperature dependent ionic conductivity measurements were carried out in the temperature range 301–373 K and the plot (Fig. 3) gives the variation of ln of ionic conductivity with respect to temperature. Figure 3 suggests that the temperature dependent ionic conductivity plots seem to obey Arrhenius relation as given below and have been fitted to obtain the parameters.

$$\sigma = \sigma_0 \exp(-E_a/KT)$$

where  $\sigma$  is the conductivity,  $E_a$ , the activation energy associated with conduction,  $K$ , the Boltzmann constant and  $\sigma_0$ , the pre-exponential term. From the Figure 3, the activation energy values ( $E_a$ ) have been calculated from the slopes and are listed in the Table I. The lower activation energy and lower crystallinity (obtained from XRD pattern) of A1 support the higher conductivity value of the sample. The nonlinearity of the plots suggests that ion transport in polymer electrolytes is associated with polymer segmental motion.<sup>18</sup>

The XRD patterns of the samples are given in Figure 4 and the spectra pulls out to a conclusion that there are no specific peaks pertaining to the pure lithium salts. It dictates the complete dissociation of lithium salts in polymer(s)/plasticizer matrix. The peak appearing at  $2\theta = 20.05^\circ$  in all the samples attributes to pure

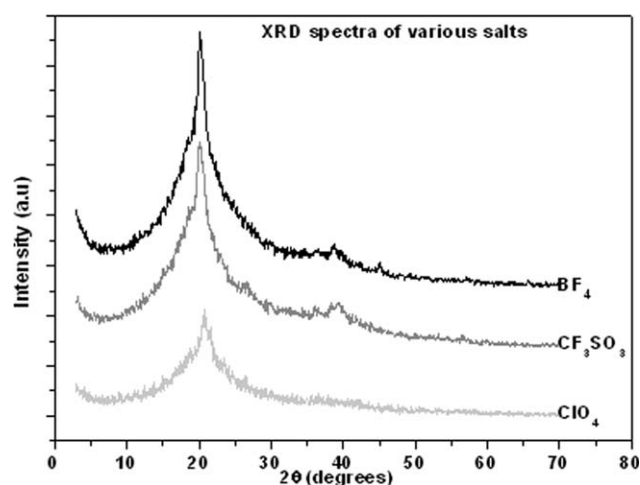
PVdF. The XRD spectra also support the conductivity values in the aspect of crystalline nature of the samples. The XRD studies confirmed the fact that there exists a definite complex coordination between polymer and lithium salts in plasticizer rich phase. The microstructures of the electrolytes have also been studied using the scanning electron microscopic images with 1000 magnification and are given in Figure 5. The SEM image of LiClO<sub>4</sub> based system (A1) depicts that the good network arrangement and there is no aggregation of anions as in LiBF<sub>4</sub> and LiCF<sub>3</sub>SO<sub>3</sub>. More crystalline nature hinders the mobility of charge carriers and thereby reduction of conductivity. It also strengthened the results of ionic conductivity measurements that the LiClO<sub>4</sub> has better dissociation than LiBF<sub>4</sub> and LiCF<sub>3</sub>SO<sub>3</sub>, which is clearly evidenced from the images.

### LSV

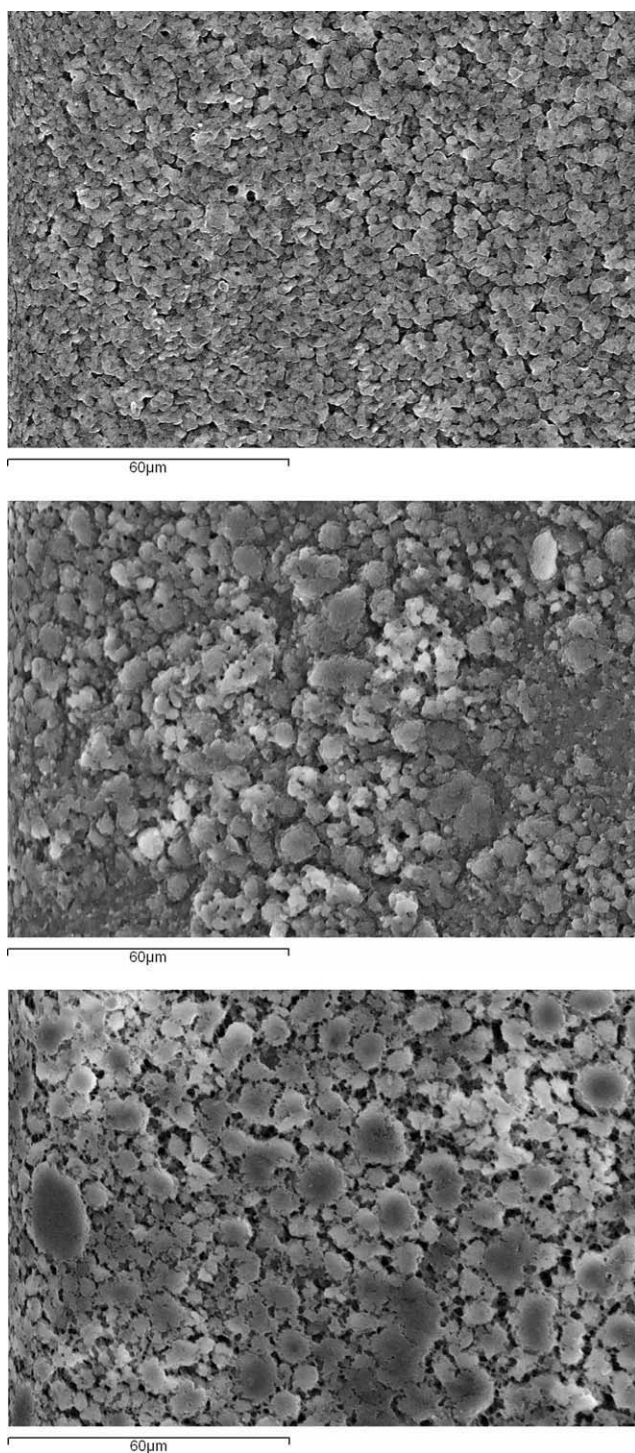
The electrochemical window was determined by running a sweep voltammetry on a Li/GPE/SS cell assembly, where SS electrode was the working and lithium served as the reference and counter electrode. The anodic decomposition voltage limits were assumed to be those at which current began to flow through the cell. The anionic part of the lithium salt plays an important role in contributing towards the conductivity and stability of the resultant electrolyte. Figure 6 suggests that the electrolytes containing different lithium salts have an anodic stability higher than 4.5 V versus Li and are thus compatible with the electrodes. Comparatively LiClO<sub>4</sub> based electrolyte system exhibits good electrochemical stability than other salts. The triflate salt exhibits very sharp decomposition current at 5V.

### Ionic transference number measurements

Total ionic transference number was measured by Wagner's polarization technique,<sup>19</sup> which is used to

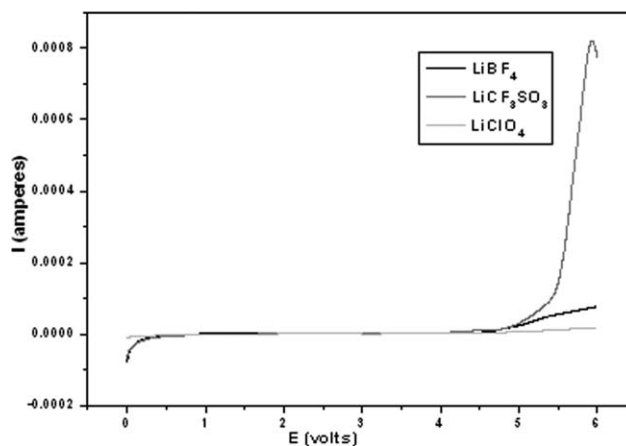


**Figure 4** XRD patterns of PVdF-PEMA-LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>)-EC+PC based electrolytes.



**Figure 5** SEM images of PVdF-PEMA-LiX ( $X = \text{ClO}_4$ ,  $\text{BF}_4$ ,  $\text{CF}_3\text{SO}_3$ )-EC+PC based electrolytes with the magnification of 1000.

determine the contribution of the total charge transport by measuring the residual electronic current passing through the electrolytes. On the basis of this, transference number for the prepared electrolytes were evaluated and listed in the Table I. The high values of the ionic transport number suggest that the charge transport in these polymer electrolytes is

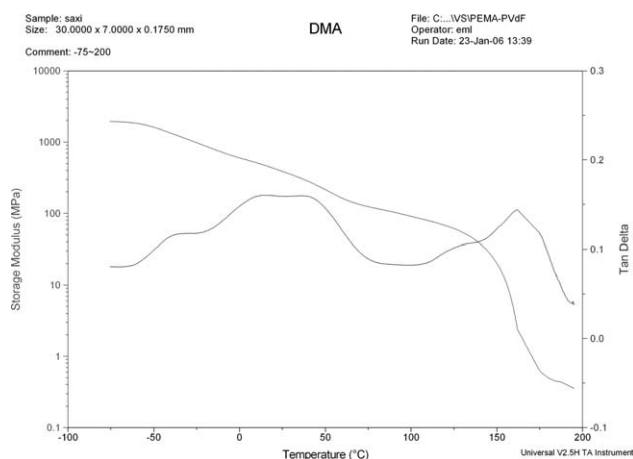


**Figure 6** Linear sweep voltammograms of PVdF-PEMA-LiX ( $X = \text{ClO}_4$ ,  $\text{BF}_4$ ,  $\text{CF}_3\text{SO}_3$ )-EC+PC based electrolytes.

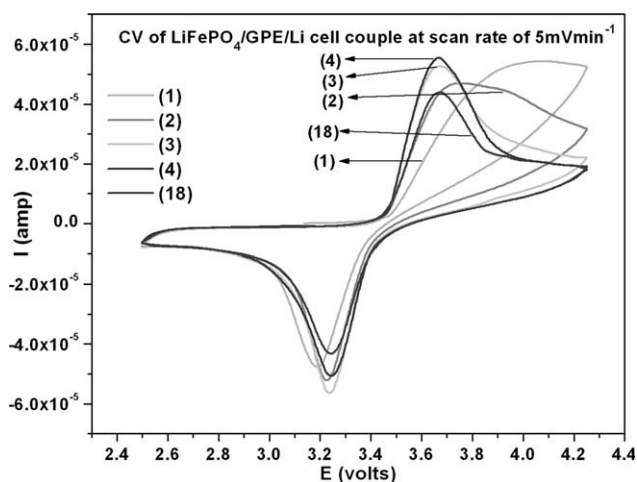
predominantly ionic accompanied by mass transport and electronic contribution to the total current is negligible, i.e., the lithium ions become more mobile than the anions. Among the system studied,  $\text{LiBF}_4$  based sample exhibits the maximum  $t_+$  of about 0.87, which may be due to the low lattice energy of  $\text{LiBF}_4$  salt and high viscous nature of  $\text{ClO}_4^-$ , etc. This value is quite obvious to use in the lithium battery application in accordance with Heitner.<sup>20</sup>

## DMA

The viscoelastic behavior of the sample possessing maximum conductivity (A1) has been studied using dynamic mechanical analysis and the storage modulus and  $\text{Tan}\delta$  versus temperature curves are given in Figure 7. The storage modulus ( $E'$ ) is about  $\sim 2000$  MPa PEMA has good interaction with the semi crystalline polymer, PVdF, and the excess side chain of PEMA gets interacted with PVdF, which results in more small crystalline domains in the matrix. The  $\beta$ -



**Figure 7** Dynamic mechanical analysis curve of PVdF-PEMA-LiClO<sub>4</sub>-EC+PC based electrolyte.



**Figure 8** Cyclic voltammogram of PVdF-PEMA-LiClO<sub>4</sub>-EC+PC based electrolyte at a scan rate of 5 mV min<sup>-1</sup>.

relaxation of A1 is decreased to 55 and 45°C, respectively, where as the glass transition temperature of pure PEMA is 65°C. The Tanδ curve gives the transition details in the electrolyte corresponding to the storage modulus at the temperatures -40, 12, 39, and 138°C, respectively. The PVdF based film exhibits a melting transition above 145°C, which is attributed to melting of pure PVdF. From the DMA analysis, one can conclude that the sample A1 has better thermal stability, which is fairly required for the fabrication of lithium batteries.

### Cyclic voltammetry

The cyclic voltammetric analysis has been performed for the sample possessing maximum ionic conductivity with the cell couple LiFePO<sub>4</sub>/GPE/Li at the scan rate of 5 mV min<sup>-1</sup>. The redox nature of LiFePO<sub>4</sub> has been observed about 3.5 Volts (Fig. 8) for the GPE comprising PVdF-PEMA-LiClO<sub>4</sub>-EC+PC system. The cyclic voltammogram shows that the system has excellent reversibility up to 17 cycles. An initial incompleteness of oxidation peak during first cycle is observed, which may be because of the intercalation of lithium, which has not been completed and it was completely eliminated in the subsequent cycles. The current during the redox reaction of lithium is decreased very slowly until 17 cycles, after that it starts to reduce rapidly. However, the sample has good reversibility; the current in the system is lower than LiFePO<sub>4</sub> with liquid electrolyte LiPF<sub>6</sub>/EC/DMC reported by Wang et al.<sup>21</sup> The CV analysis concludes that the sample A1 shows excellent reversibility with LiFePO<sub>4</sub> electrodes. The intense investigation is in progress on PVdF/PEMA system's charge-discharge analysis.

### CONCLUSIONS

The anionic effects of various lithium salts containing PEMA-PVdF-LiX (X = ClO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>)-EC+PC electrolytes were studied by characterizing using Impedance, microstructure, electrochemical impedance, ionic transference analyses, etc. The ClO<sub>4</sub><sup>-</sup> exhibits better performance among the other anions based systems studied. The maximum conductivity (1.3 × 10<sup>-3</sup> S cm<sup>-1</sup> at 301 K), reasonable ionic transference number (0.76), and ec window more than 4.5 V claims the betterment of ClO<sub>4</sub><sup>-</sup> anions, which results in studying the electrolytes for CV and DMA analyses. The ClO<sub>4</sub><sup>-</sup> anion based system has good cyclability and reversibility up to 18 cycles and has thermal stability above 140°C. Hence, the PVdF-PEMA-LiClO<sub>4</sub>-EC+PC electrolytes can be used as a potential candidate in the lithium battery fabrications.

M. Sivakumar acknowledges the postdoctor fellowship (NSC 94-2811-E-002-050).

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