

# Structural dynamics and ionic conductivity of amorphous type plasticized solid polymer electrolytes

Shobhna Choudhary & R J Sengwa\*

Dielectric Research Laboratory, Department of Physics, J N V University, Jodhpur 342 005, India

*Received 5 November 2015; revised 18 January 2016; accepted 10 February 2016*

Poly(ethylene oxide) and poly(methyl methacrylate) blend based solid polymer electrolytes consisting of lithium triflate as a dopant ionic salt with varying concentration of propylene carbonate as plasticizer have been prepared by classical solution cast and ultrasonic-microwave irradiated solution cast methods. The X-ray diffraction study confirms that these electrolyte films have predominantly amorphous morphology. Dielectric relaxation spectroscopy in the frequency range 20 Hz - 1 MHz reveals that the complex dielectric spectra of the electrolytes have dispersion at high frequencies corresponding to polymer chain segmental relaxation process in the solid ion-dipolar complexes, whereas the electrode polarization relaxation process dominates at low frequencies. Significant changes in the polymer chain dynamics and dielectric parameters of the electrolytes are observed with change of plasticizer concentration and the sample preparation methods. Relatively enhanced polymer chain segmental dynamics, ordered ion-dipolar cooperativity and favourable ion conductive paths increase three times the ionic conductivity of 15 wt% PC polymeric electrolyte film prepared by ultrasonic-microwave irradiated method as compared to that of the classical solution cast method. The ionic conductivity and dielectric relaxation time have the Arrhenius temperature dependence characteristics of their same values of activation energies. Results infer that the ions transportation in the solid complexes of these electrolytes is predominantly governed by polymer segmental dynamics.

**Keywords:** Polymers, Electrolytes, Dielectric properties, Electrical properties, X-ray diffraction

## 1 Introduction

In last one decade, the ion conducting solid polymer electrolytes (SPEs) have been an intense research topic of solid state materials science<sup>1-16</sup>. The SPE materials based on different polymers as host matrices with ion conducting lithium salts as dopant have proved their potential technological applications in fabrication of solid state rechargeable batteries and the ion conducting electrochromic devices<sup>1,2</sup>. Studies have revealed that the amount of amorphous phase and the dynamics of polymer chain segments in solid ion-dipolar complexes are the key factors in enhancement of ions transport mechanism in the SPE materials<sup>4-6,11,15-17</sup>. To explore the ions transport behaviour in depth regarding how the ions are coupled to the functional group of polymer matrix and their mechanism of transport coupled with the polymer chain dynamics in SPEs have been frequently investigated using dielectric relaxation spectroscopy (DRS). The DRS has established as the most suitable and powerful technique for characterization

of dielectric polarization and relaxation processes, and the structural dynamics in the SPE materials<sup>4-6,8-21</sup>.

In preparation of SPE materials, poly(ethylene oxide) (PEO) matrix is repetitively used due to its high solid state solvating power for alkali metal salts<sup>3-11</sup>. The PEO based SPE films have high flexibility and also the required mechanical stability at room temperature (RT) which attracted the researchers from the initial stage of work on the SPEs. But, crystalline morphology of PEO is its main drawback which hinders the required fast ion transportation for enhancement of ionic conductivity of PEO based SPE materials at RT. The intense work on plasticized and inorganic nanofillers added PEO based electrolytes confirmed their increased conductivity due to increase in amorphous phase which proved the suitability of such materials in all-solid-state ion conducting devices<sup>3,7,22-26</sup>. Besides the PEO matrix, amorphous-type poly(methyl methacrylate) (PMMA) matrix is also used in preparation of SPE materials<sup>14,27-32</sup>. But, high brittleness of PMMA film restricts its suitability in preparation of flexible type SPE materials to fulfill the recent technological demand in design of ion conducting devices of varying shapes and sizes.

\*Corresponding author (E-mail: rjsengwa@rediffmail.com)

Therefore, in search of new SPE materials of improved properties, intense research work is in progress on the PEO–PMMA blend based electrolyte films which have comprising ion conduction and flexible characteristics<sup>15,16,19-21,33-40</sup>.

Recently, the PEO–PMMA blend based electrolytes consisting of lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) salt with varying concentrations of montmorillonite (MMT) clay as nanofiller<sup>15</sup> and also with poly(ethylene glycol) (PEG) as plasticizer<sup>16</sup> using DRS measurements have been investigated. The results of these materials are found to be highly interesting because of their use as electrolytes in fabrication of lithium ion batteries. The electrolytes based on PEO–PMMA blend matrix with fixed concentration of  $\text{LiCF}_3\text{SO}_3$  salt and varying concentrations of propylene carbonate (PC) plasticizer, have been studied in the present paper. The aim of this study is to confirm the effects of plasticizer concentration and the sample preparation methods on the structural dynamics and ionic conductivity of these SPE materials by their dielectric characterization.

## 2 Experimental Procedure

The PEO ( $M_w = 6 \times 10^5 \text{ g mol}^{-1}$ ), PMMA ( $M_w = 3.5 \times 10^5 \text{ g mol}^{-1}$ ) and  $\text{LiCF}_3\text{SO}_3$  were obtained from Sigma–Aldrich, USA. The propylene carbonate (PC), anhydrous acetonitrile and tetrahydrofuran of spectroscopic grade were purchased from Loba Chemie, India. All the chemicals were vacuum dried before their use. For the preparation of PEO–PMMA blend based electrolyte films, equal weight amounts of PEO and PMMA were used. The required amounts of PEO (1 g), PMMA (1 g) and  $\text{LiCF}_3\text{SO}_3$  (0.4425 g) were taken for each sample. This composition has stoichiometric ratio  $[\text{EO} + (\text{C}=\text{O})]:\text{Li}^+=9:1$ , where  $\text{EO} + (\text{C}=\text{O})$  is the number of ethylene oxide units (EO) of PEO and the carbonyl groups ( $\text{C}=\text{O}$ ) of PMMA in the prepared polymer blend to the lithium cations ( $\text{Li}^+$ ) of the  $\text{LiCF}_3\text{SO}_3$ . To plasticize the compositions,  $x$  wt% amount of PC ( $x = 0, 5, 10$  and  $15$ ) to the 2 g weight of PEO–PMMA blend were used.

Initially, the PEO and PMMA amounts were dissolved in solvents acetonitrile and tetrahydrofuran, respectively, in separate glass bottles for preparation of each sample. After that, the  $\text{LiCF}_3\text{SO}_3$  and  $x$  wt% PC were added into the PEO solution, and mixed homogeneously by magnetic stirrer. Finally, the PMMA solution was mixed in this electrolyte solution and again rigorously stirred, which resulted into homogeneous (PEO–PMMA)– $\text{LiCF}_3\text{SO}_3$ – $x$  wt% PC

electrolyte solution. The half amount of this electrolyte solution was casted onto teflon petri dish. The slow evaporation of solvent at room temperature resulted in the free standing ‘classical’ solution cast (SC) prepared electrolyte film. For the preparation of ultrasonic–microwave (US–MW) irradiated electrolyte film, the remaining half amount of the electrolyte solution was firstly ultrasonicated (US) using sonicator (250 W power, 25 kHz frequency) for 10 m duration with 15 s ON-OFF step. In this processing technique, the stainless steel sonotrode was directly immersed into the electrolyte solution for strong dose of the ultrasound. After that the same solution was irradiated by microwave (MW) electromagnetic energy using commercial microwave oven (600 W power, 2.45 GHz frequency) for 2 m duration with irradiation step of 10 s. This US–MW irradiated solution was casted to achieve the US–MW prepared electrolyte film. The same steps were repeated for the preparation of varying PC concentration SPE films. The surfaces of these electrolyte films prepared by both methods were found to be uneven at micro scale level of smoothness, which were made smooth by melt–pressing technique using the polymer film making press unit as described elsewhere<sup>15</sup>.

The X–ray diffraction (XRD) patterns of the SPE films were recorded in reflection mode using a PANalytical X’pert Pro MPD diffractometer of  $\text{Cu K}\alpha$  radiation ( $1.5406 \text{ \AA}$ ) operated at 45 kV and 40 mA with a scanned step size of  $0.05^\circ \text{ s}^{-1}$ . The DRS measurements of the electrolyte films over the frequency range from 20 Hz to 1 MHz were carried out using Agilent technologies 4284A precision LCR meter along with 16451B solid dielectric test fixture having active electrode of 38 mm diameter. The dielectric test fixture loaded with electrolyte film was placed in a microprocessor-controlled heating chamber to record the measurements at constant temperature. Frequency dependent values of capacitance  $C_p$ , resistance  $R_p$  and dissipation factor  $D$  (loss tangent  $\tan\delta = \frac{''}{'}$ ) of each SPE film loaded in the dielectric fixture were measured in the parallel circuit operation mode. Prior to a sample measurement, the open circuit calibration of the dielectric test fixture was performed to eliminate the effect of stray capacitance of the connecting leads. The spectra of intensive quantities, namely, complex dielectric function  $\epsilon^*(\omega) = \epsilon' - j\epsilon''$ , alternating current (ac) electrical conductivity  $\sigma^*(\omega) = \sigma' + j\sigma''$  and electric modulus  $M^*(\omega) = M' + jM''$ , and the extensive

quantity i.e. complex impedance  $Z^*(\omega) = Z' - jZ''$  of the SPE films were determined using the expressions described in detail elsewhere<sup>5,14</sup>.

### 3 Results and Discussion

#### 3.1 Structural analysis

The XRD patterns of the SC and US–MW methods prepared (PEO–PMMA)–LiCF<sub>3</sub>SO<sub>3</sub>–*x* wt% PC electrolyte films over the  $2\theta$  range from 10 to 30° are shown in Fig. 1. The XRD patterns of SC method prepared electrolyte films of 0 and 5 wt% PC, and US–MW method prepared 5 wt% PC electrolyte film have tiny sharp peak around 19° and also a diffused peak around 23° on a broad hump, whereas such peaks were not observed for other electrolyte films. Further, the XRD patterns of same composition electrolyte films prepared by both the methods were found almost identical (except for  $x = 0$ ). At  $x = 0$ , film prepared by the SC method has tiny peak around 19° whereas it is absent in US–MW method prepared electrolyte film. The electrolyte films, which did not have any peak in the XRD patterns, reveal their complete amorphous structure whereas the presence of tiny peaks is an indication of some crystalline phase's presence in the predominated amorphous structures.

In order to understand the structural variation due to change in PC concentration and also with the preparation methods of the electrolyte films, it is

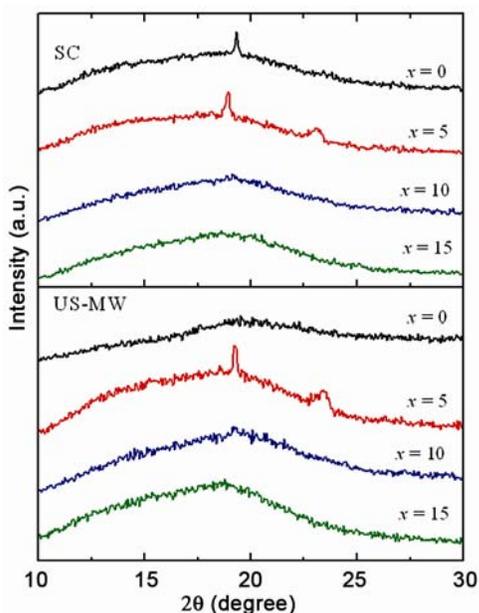


Fig. 1—XRD spectra of (PEO–PMMA)–LiCF<sub>3</sub>SO<sub>3</sub>–*x* wt% PC electrolyte films prepared by SC and US–MW methods

needed to firstly consider the structures of the constituents of these films. Earlier XRD studies confirmed that the pristine PEO has sharp and highly intense peaks at  $2\theta = 19.22^\circ$  and  $23.41^\circ$  corresponding to its crystal reflection planes 120 and concerted 112,032, respectively<sup>8</sup>. The amorphous PMMA has a broad and diffused peak<sup>14</sup> around  $16^\circ$ , and crystalline LiCF<sub>3</sub>SO<sub>3</sub> has various intense characteristic peaks<sup>15</sup> at  $16.62^\circ$ ,  $19.87^\circ$ ,  $20.53^\circ$ ,  $22.77^\circ$  and  $24.71^\circ$ . The absence of LiCF<sub>3</sub>SO<sub>3</sub> characteristic peaks in the XRD patterns of these electrolyte films confirms the complete dissolution of the ionic salt in the PEO–PMMA matrix. Further, the formation of ion-dipolar complexes and some miscible behaviour of PEO with PMMA result in suppressed PEO crystallinity in the prepared electrolyte films. The tiny peaks around  $19^\circ$  in the XRD patterns of some electrolyte samples indicate that there are few clusters of PEO spherulites but this amount is negligible in comparison to the total amorphous amount, and therefore, these electrolytes are predominately of amorphous morphology. Earlier, it was observed that the use of PEG plasticizer in the PEO–PMMA blend electrolyte increases the crystallinity of the material with increase of PEG concentration<sup>16</sup>, which was because of the same repeat unit (ethylene oxide) in the PEG and PEO chain. But the structural behaviour of PEO–PMMA blend based on these electrolytes is little affected by the added PC concentration up to 15 wt% which indicates higher suitability to use PC as plasticizer as compared to PEG in preparation of these polymer blend based electrolytes. The unplasticized electrolyte film ( $x = 0$ ) prepared by SC method has some PEO crystalline clusters which are completely suppressed by US–MW irradiation. The identical structures of SC and US–MW methods prepared plasticized films ( $x = 5, 10$  and  $15$ ) reveal that regarding to the structural morphology, the US–MW irradiation did not contribute much in the structural modification of these electrolytes.

#### 3.2 Plasticizer concentration dependent dielectric and electrical spectra

The room temperature complex permittivity (real part  $\epsilon'$  and dielectric loss  $\epsilon''$ ), *ac* electrical conductivity (real part  $\sigma'$  and loss  $\sigma''$ ) and loss tangent  $\tan\delta$  spectra of the (PEO–PMMA)–LiCF<sub>3</sub>SO<sub>3</sub>–*x* wt% PC electrolyte films prepared by SC and US–MW methods are shown in Fig. 2. It is observed that the  $\epsilon'$  and  $\epsilon''$  spectra [Fig. 2(a and b)] of SPE films vary

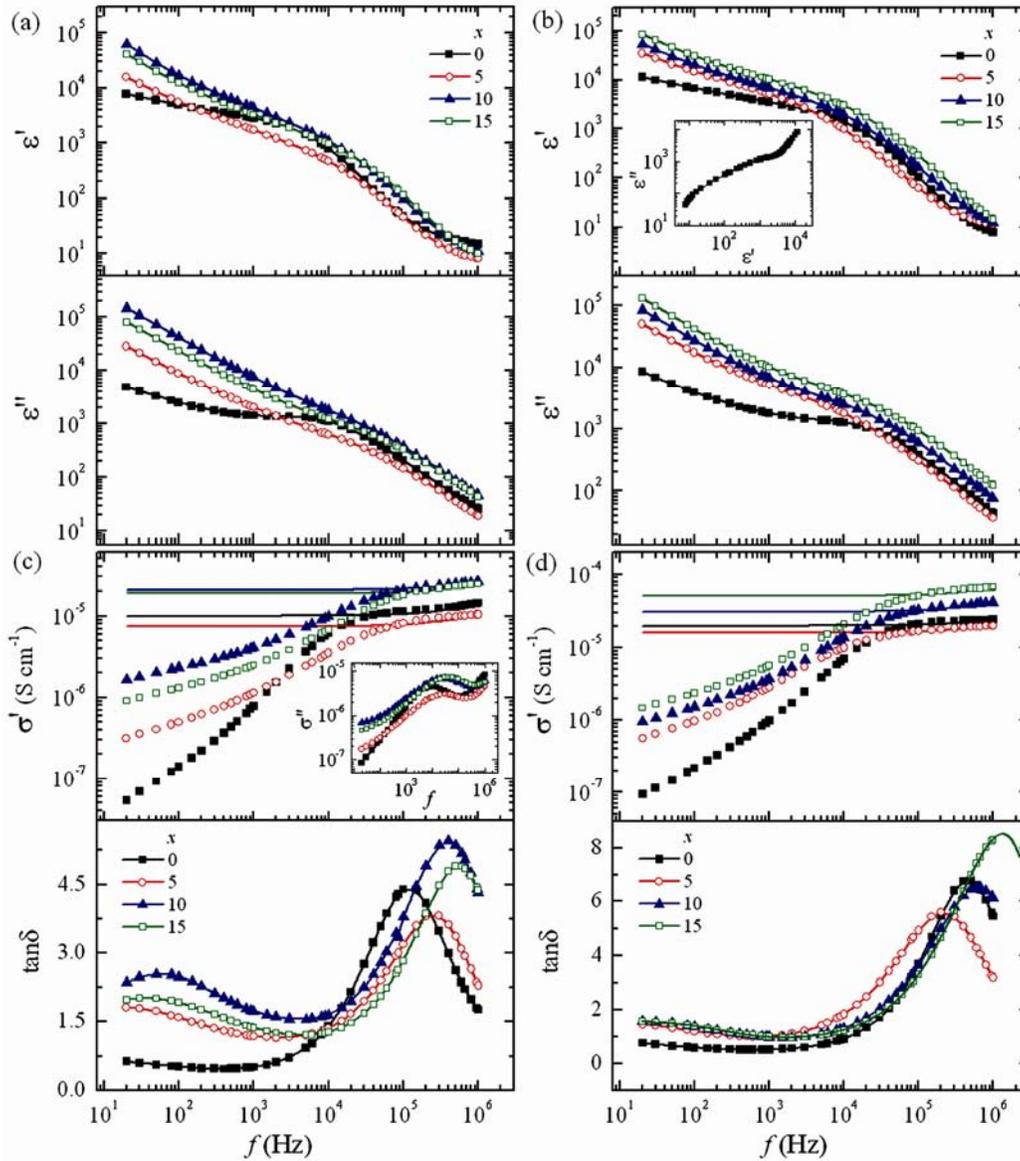


Fig. 2—Frequency dependent real part  $\epsilon'$  and loss  $\epsilon''$  of the complex dielectric function of (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3-x</sub> wt% PC films prepared by (a) SC and (b) US-MW methods, and real part of *ac* conductivity  $\sigma'$  and loss tangent ( $\tan\delta$ ) of these films prepared by (c) SC and (d) US-MW methods. The solid lines in  $\sigma'$  spectra represent the Jonscher power law fit of experimental data. Inset of (b) shows  $\epsilon''$  versus  $\epsilon'$  plot and inset of (c) shows  $\sigma''$  spectra

anomalously with PC concentration and also with the sample preparation methods, and have some interesting noticeable features. Firstly, there is a large increase of  $\epsilon'$  and  $\epsilon''$  values (~4 to 5 orders of magnitude) in low-frequency region which is owing to the dominance contribution of electrode polarization (EP) effect over the bulk material properties. This effect commonly occurs in the SPE materials due to accumulation of ions near the electrode surfaces resulting in formation of electric double layers (EDLs) when the applied alternating

electric field reversal duration is slow<sup>5,8,11,17</sup>. Secondly, the  $\epsilon'$  spectra have points of inflection around 1 kHz and approach steady state near 1 MHz, which represent that the 1 kHz - 1 MHz frequency region is corresponding to material bulk properties. Therefore, it is reasonable to assume the  $\epsilon'$  values of 1 kHz and 1 MHz corresponding to the estimated values of static permittivity  $\epsilon_s$  and the high frequency limiting permittivity  $\epsilon_\infty$ , respectively, for these electrolytes. In case of SPE materials, it is complicated to exactly separate the bulk property

frequency region and the EP affected frequency region in their complex permittivity spectra, owing to their very high values of  $\epsilon'$  and  $\epsilon''$ . For this reason, the point of inflection in  $\epsilon'$  spectra can be considered to identify the values of static permittivity of the SPE material.

The inset of Fig. 2(b) shows that the complex plane plot ( $\epsilon''$  versus  $\epsilon'$ ) for unplasticized ( $x = 0$ ) sample as a representative has semicircular arc in high frequency region and spike in low frequency region. These are corresponding to the polymer chain segmental relaxation process and the EDLs relaxation process, respectively. Such behaviour of  $\epsilon''$  versus  $\epsilon'$  plots is also reported for several SPE materials<sup>8,9,13</sup>. The values of  $\epsilon_s$ ,  $\epsilon_\infty$  and the dielectric strength  $\Delta\epsilon = \epsilon_s - \epsilon_\infty$  of the SC and US-MW methods prepared electrolyte films at different PC concentrations are presented in Table 1. It is found that the  $\Delta\epsilon$  values of all the US-MW prepared SPE films are significantly higher than the corresponding SPE films prepared by SC method (Table 1). This result infers that the US-MW processed solution cast electrolyte film possesses more ion-dipolar ordering as compared to that of the classical solution cast electrolyte film. Further, the trend of variation in  $\Delta\epsilon$  values with PC concentration is also found to be different for the films prepared by different methods.

Figure 2(c and d) shows the  $\sigma'$  and  $\tan\delta$  spectra of the SC and US-MW methods prepared electrolyte films, respectively. The  $\sigma'$  values of these SPE films increase non-linearly from  $\sim 10^{-7}$  to  $10^{-5}$  S cm<sup>-1</sup> with the increase of frequency from 20 Hz to 1 MHz. In order to evaluate the *dc* ionic conductivity  $\sigma_{dc}$  of these

electrolytes, their  $\sigma'$  values from the start of *dc* plateau region to the end of spectra were fitted to the Jonscher's power law<sup>41</sup>  $\sigma'(\omega) = \sigma_{dc} + A\omega^n$ , where  $A$  is the pre-exponential factor and  $n$  is the fractional exponent ranging between 0 and 1. The power law fits to the experimental data of the electrolytes, is shown by solid lines in the  $\sigma'$  spectra. It is found that the experimental  $\sigma'$  values start to deviate from the power law fit lines below 100 kHz. The deviation increases by a large magnitude with further decrease of frequency due to increase of EDLs thickness. The EDLs act as blocking electrode which reduces the conductivity of the electrolytes by several orders of magnitude at low frequencies. The PC concentration dependent values of  $\sigma_{dc}$  denoted as  $\sigma_{dc}(I)$  and  $n$  of these electrolyte films obtained from power law fits of their  $\sigma'$  spectra are given in Table 1. The observed room temperature  $\sigma_{dc}$  values are of the order of  $10^{-5}$  S cm<sup>-1</sup> which confirms satisfactory ion conduction performance in these electrolyte materials. The  $n$  values of the electrolytes are found less than unity (Table 1) suggesting the hopping-type ion transportation behaviour. The inset of Fig. 2(c) shows the  $\sigma''$  spectra of SC method prepared electrolytes. These spectra have peaks in high frequency region which are close to the peaks frequency positions observed in their  $\tan\delta$  spectra.

The  $\tan\delta$  spectra of the electrolyte films [Fig. 2(c and d)] have intense relaxation peaks in the high frequency region corresponding to the polymer chain segmental dynamics which occur in the transient-type ion-dipolar complexes. It is found that the magnitude and the frequency positions of these

Table 1—Room temperature (27 °C) values of static permittivity  $\epsilon_s$ , high frequency limiting permittivity  $\epsilon_\infty$ , dielectric strength  $\Delta\epsilon$ , polymer chain segmental relaxation time  $\tau_s$ , *dc* ionic conductivity  $\sigma_{dc}(I)$  and  $\sigma_{dc}(II)$ , and fractional exponent  $n$  of SC and US-MW prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3-x</sub> wt% PC electrolyte films

$x$ wt% PC	$\epsilon_s$	$\epsilon_\infty$	$\Delta\epsilon$	$\tau_s$ ( $\mu$ s)	$\sigma_{dc}(I) \times 10^5$ (S cm <sup>-1</sup> )	$\sigma_{dc}(II) \times 10^5$ (S cm <sup>-1</sup> )	$n$
SC prepared electrolyte films							
0	2820.9	14.8	2806.1	1.40	1.01	1.21	0.91
5	1720.4	8.2	1712.2	0.63	0.74	1.01	0.89
10	4297.2	10.8	4286.4	0.40	2.08	2.49	0.92
15	3280.6	10.0	3270.6	0.29	1.91	2.42	0.92
US-MW prepared electrolyte films							
0	3478.4	8.0	3470.4	0.34	2.02	2.42	0.92
5	5127.6	11.5	5116.1	0.77	1.62	1.87	0.91
10	6828.1	12.4	6815.7	0.26	3.12	3.88	0.96
15	10244.1	14.7	10229.4	0.12	5.18	6.26	0.97

peaks have anomalous variation with increase of PC concentration and also with the sample preparation methods. Using the values of  $\tan\delta$  peak frequency  $f_{p(\tan\delta)}$ , the values of relaxation time  $\tau_{\tan\delta}$  (also denoted by  $\tau_s$ ) of the polymer chain segmental motion is determined by the relation  $\tau_{\tan\delta} = 1/2\pi f_{p(\tan\delta)}$ . The  $\tau_s$  values of the electrolyte films are found of the order of microsecond duration and these are given in Table 1.

The complex impedance plane plots ( $Z''$  versus  $Z'$ ) of the electrolyte films prepared by SC and US–MW methods are shown in Fig. 3. The frequency value decreases on going from right to left on these plots. These plots are commonly used for the electrochemical characterization of the ion conducting materials<sup>3</sup>. The values of  $dc$  ionic conductivity of the electrolyte materials are frequently determined from these plots. The ion conducting SPE materials commonly exhibit a spike at low frequency region due to capacitive behaviour of EDLs and an arc at high frequencies corresponding to bulk property<sup>3,8,9,16</sup> in their  $Z''$  versus  $Z'$  plots. The investigated electrolyte

films also have same characteristics which can be seen in the enlarged view of their high frequency region plots as shown in the inset of Fig. 3. The common intercept of the arc and the spike on the real axis (as marked in the insets) is corresponding to the bulk resistance  $R_b$  value of the electrolyte film<sup>3</sup>. The  $\sigma_{dc}$  value of the ion conducting electrolyte film is determined using  $R_b$  value, with the relation  $\sigma_{dc} = t_s/R_b A$ , where  $t_s$  is the thickness and  $A$  is the surface area (equal to the surface area of active electrode of the dielectric test fixture) of the film. In the present study, the  $\sigma_{dc}$  values of these electrolyte films as determined from  $R_b$  values are denoted by  $\sigma_{dc}(\text{II})$  in order to distinguish from the  $\sigma_{dc}$  values obtained from power law fit ( $\sigma_{dc}(\text{I})$ ), and these values are given in Table 1. The  $\sigma_{dc}(\text{II})$  values are found to be slightly higher than those of the  $\sigma_{dc}(\text{I})$  values (Table 1) for all the electrolyte films, which reveal that the determined  $\sigma_{dc}$  values of the electrolyte material also depend on the procedure of their evaluation.

### 3.3 Temperature dependent dielectric and electrical spectra

In order to confirm the effect of temperature on the dielectric properties of the electrolyte films, the SC method prepared (PEO–PMMA)–LiCF<sub>3</sub>SO<sub>3</sub>–10 wt% PC electrolyte film has been studied as a representative sample. Figure 4 shows the spectra of  $\epsilon'$ ,  $\epsilon''$ ,  $\sigma'$ ,  $\tan\delta$ ,  $M'$  and  $M''$  and the impedance plots ( $Z''$  versus  $Z'$ ) at different temperatures of the electrolyte film. It is observed that there is a uniform enhance in  $\epsilon'$  and  $\epsilon''$  spectra of the electrolyte film with the increase of its temperature [Fig. 4(a)], which is common characteristic of thermally activated electrolyte materials. Due to increase of  $\epsilon''$ , the  $\sigma'$  values of the electrolyte film also increase with increasing temperature [Fig. 4(b)]. For ion conducting electrolyte, its ionic conductivity is given by the relation  $\sigma_{dc} = \sum q_i n_i \mu_i$ , where  $q_i$ ,  $n_i$  and  $\mu_i$  are the charge, concentration and mobility of the ions, respectively. The XRD spectra of the electrolyte film reveal that the total salt exists in dissociated form at RT, and hence it seems that the increase of temperature does not have any additional contribution in the ion concentration. Therefore, the increase of ions mobility with increase of temperature mainly contributed in the enhancement of  $\sigma_{dc}$  value which confirms the thermally activated conductivity behaviour of the studied electrolyte film. It means that the rise in temperature increases the free volume and favourable vacant sites for the

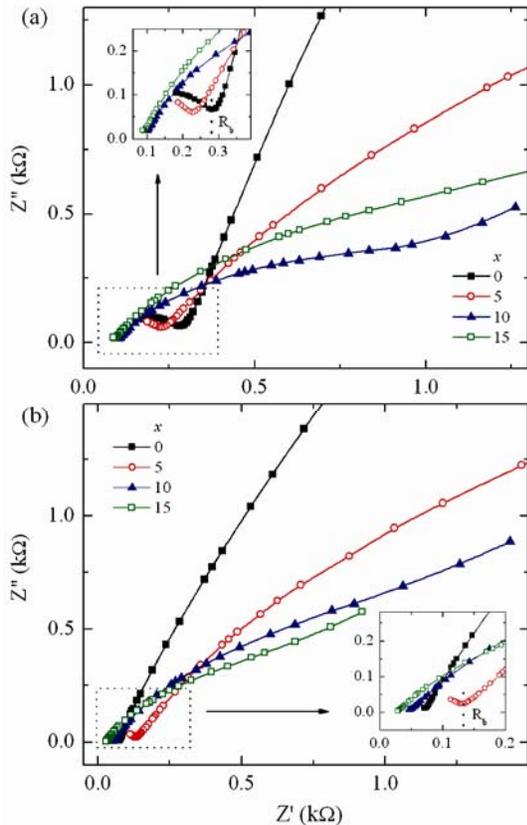


Fig. 3—Complex impedance plane plots ( $Z''$  versus  $Z'$ ) of (PEO–PMMA)–LiCF<sub>3</sub>SO<sub>3</sub>– $x$  wt% PC films prepared by (a) SC and (b) US–MW methods. Insets show the enlarged view of the plots at high frequencies

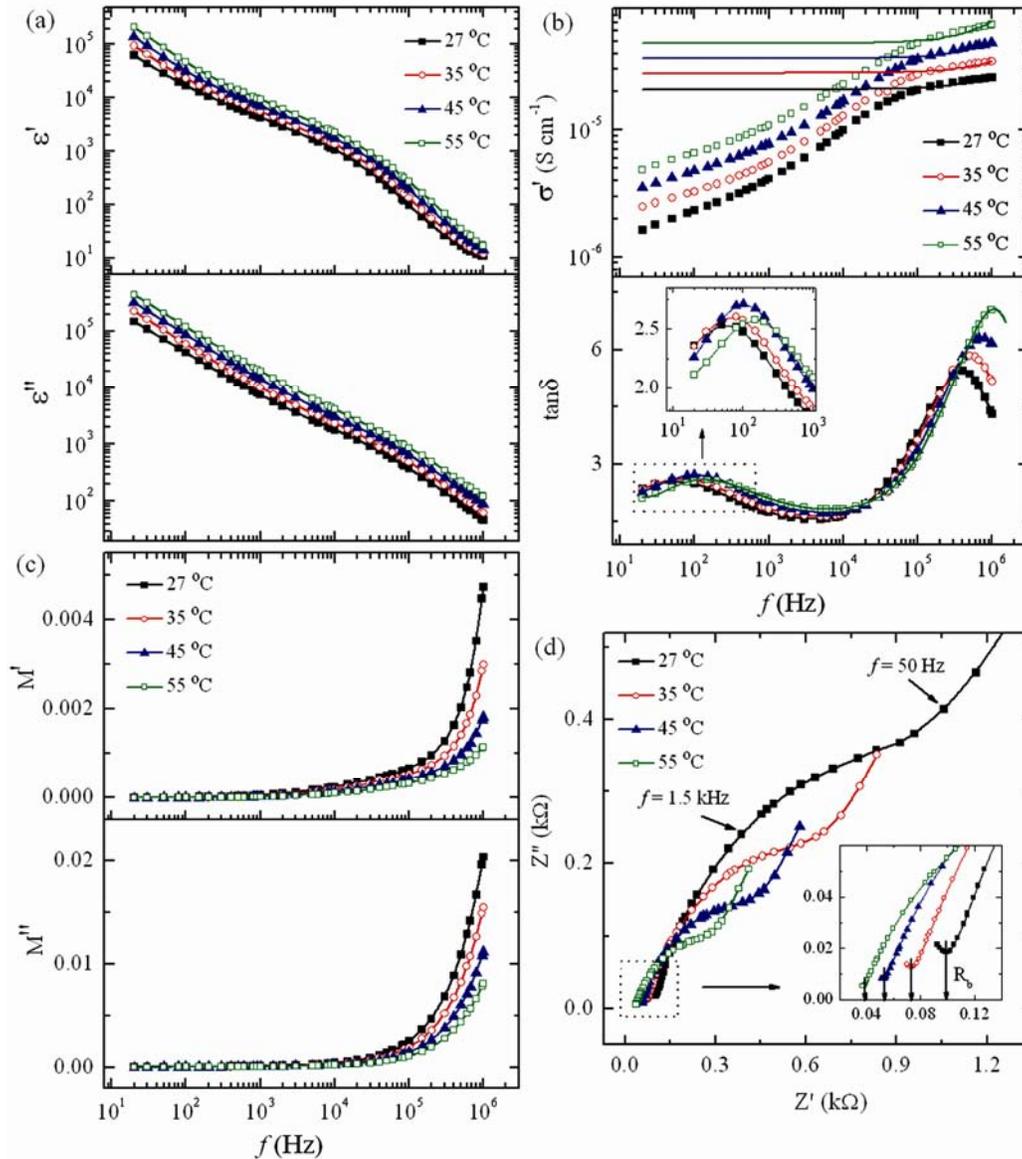


Fig. 4—Frequency dependent (a) real part  $\epsilon'$  and loss  $\epsilon''$  of the complex dielectric function, (b) real part of ac conductivity  $\sigma'$  and loss tangent ( $\tan\delta$ ) and (c) real part  $M'$  and loss  $M''$  of complex electric modulus, and (d) complex impedance plane plots ( $Z''$  versus  $Z'$ ) of SC prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC electrolyte film at different temperatures. The solid lines in  $\sigma'$  spectra represent the Jonscher power law fit of experimental data. Insets of (b) and (d) show the enlarged view

easy ions transportation in the electrolyte matrix, which in turn enhances the ion conductivity of such electrolyte materials<sup>9,10,13,16</sup>.

The temperature dependent  $\tan\delta$  plots [Fig. 4(b)] of the film have diffused peaks at low frequencies which represent the charging and discharging relaxation process of EDLs, whereas the intense peaks appeared in high frequency region are corresponding to polymer chain segmental motion. The high frequency peak intensity increases with the increase of temperature and also have gradual shift towards

higher frequency side confirming the enhancement in polymer chain segmental dynamics. The enlarged view of low frequency peak at different temperatures is shown in the inset of Fig. 4 (b), which clearly shows that the EDLs relaxation peaks also have shift towards higher frequency side with the increase of temperature. The EDLs relaxation time  $\tau_{EDL}$  is determined from these peak frequency values and reported in Table 2. The temperature dependent values of  $\sigma_s$ ,  $\sigma_\infty$ ,  $\Delta$ ,  $\sigma_{dc}$ ,  $\sigma_{dc}(I)$  and  $n$  (given in Table 2) of the electrolyte film were determined by following

Table 2—Temperature dependent values of static permittivity  $\epsilon_s$ , high frequency limiting permittivity  $\epsilon_\infty$ , dielectric strength  $\Delta$ , electric double layers relaxation time  $\tau_{EDL}$ , polymer chain segmental relaxation time  $\tau_s$ , dc ionic conductivity  $\sigma_{dc}(I)$  and  $\sigma_{dc}(II)$ , and fractional exponent  $n$  of SC prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC electrolyte film

Temperature (°C)	$\epsilon_s$	$\epsilon_\infty$	$\Delta\epsilon$	EDL (ms)	$\tau_s$ ( $\mu$ s)	$\sigma_{dc}(I) \times 10^5$ (S cm <sup>-1</sup> )	$\sigma_{dc}(II) \times 10^5$ (S cm <sup>-1</sup> )	$n$
27	4297.2	10.8	4286.4	2.49	0.40	2.08	2.49	0.92
35	5526.7	12.1	5514.7	2.12	0.31	2.80	3.34	0.93
45	7082.3	14.2	7068.2	1.53	0.22	3.65	4.66	0.95
55	9412.5	17.2	9395.3	1.02	0.15	4.80	6.33	0.96

the same procedure as discussed in previous section of the manuscript.

Figure 4(c) shows the temperature dependent electric modulus (real part  $M'$  and loss  $M''$ ) spectra of SC method prepared electrolyte film having 10 wt% PC concentration. The modulus spectra are mostly plotted and analyzed for the ion conducting materials, because these are independent of EP effect, the electrode material, the electrode/ dielectric specimen contact and the adsorbed impurities in the sample<sup>4,5,10,12,16,19,20</sup>. The  $M'$  and  $M''$  spectra of the studied electrolyte film have dispersion above 100 kHz, whereas in the EP effect dominated low frequency region their values are almost zero which is owing to inverse relation between  $M^*(\omega)$  and  $\epsilon^*(\omega)$  i.e.  $M^*(\omega) = 1/\epsilon^*(\omega)$ . Mostly, the  $M''$  spectra of the ion conducting electrolytes exhibit a peak in high frequency region corresponding to the ionic conductivity relaxation time<sup>4,5,15,16,18</sup>. But in the present case, the peak of  $M''$  spectra seems to appear above the upper limit of the experimental frequency range, which confirms the relatively fast dynamical behaviour of the ions in this PEO-PMMA blend based electrolyte film. Further, with increase of temperature, the  $M'$  and  $M''$  dispersions have shift towards higher frequency side which indicate that the ionic conductivity relaxation is also a thermally activated process.

Figure 4(d) shows the  $Z''$  versus  $Z'$  plots of the electrolyte film at different temperatures. The inset of figure shows that the size of high frequency arc reduces and has a shift towards low resistance side on the real axis with increasing temperature. The temperature dependent  $\sigma_{dc}(II)$  values of this SPE film are also determined from the  $R_b$  values and these are presented in Table 2.

### 3.4 Effect of PC concentration and preparation methods on the dielectric parameters

The PC plasticizer concentration dependent  $\Delta$ ,  $\tau_s$  and  $\sigma_{dc}$  values of (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>- $x$  wt% PC

electrolyte films prepared by SC and US-MW methods are plotted in Fig. 5(a). The  $\Delta$  and  $\sigma_{dc}$  values of the US-MW method prepared films are found to be significantly higher than that of the SC method prepared films. Further, the  $\Delta$  values of US-MW method prepared films increase with increase of PC concentration, whereas SC method prepared films have anomalous behaviour. The  $\Delta$  values of the SPE material are governed by its ion-dipolar ordering. Higher ion-dipolar ordering in the solid complexes results in increase of  $\Delta$  value of the SPE material. The changes in  $\Delta$  values with the samples preparation methods and the variation of PC concentration directly correlate with the behaviour of ion-dipolar ordering in the complexes of studied electrolytes. The  $\tau_s$  values of SC prepared films decrease with increasing PC concentration but anomalous variation in these values is observed for US-MW prepared film. The  $\sigma_{dc}$  value of 5 wt% PC electrolyte film has a small decrease as compared to without plasticizer electrolyte film prepared by both the SC and US-MW methods (Table 1). This variation in  $\sigma_{dc}$  is supported by their XRD patterns which indicate that the presence of few PEO crystalline clusters at 5 wt% PC reduces the  $\sigma_{dc}$  value. At 10 and 15 wt% PC concentrations, the US-MW method prepared films have progressive increase in their  $\sigma_{dc}$  values, but the SC method prepared film has an increase in  $\sigma_{dc}$  value at 10 wt% PC and shows a little variation with further increase of PC concentration (15 wt% PC). These results suggest that the ionic conductivity is not influenced by addition of 5 wt% PC, but at higher concentration it increases and is also influenced by the sample preparation methods. At 15 wt% PC concentration, the US-MW method prepared film has about 3 times increase of conductivity as compared to the SC method prepared film confirming the suitability of US-MW preparation method in enhancement of ionic conductivity of PC plasticizer added PEO-PMMA

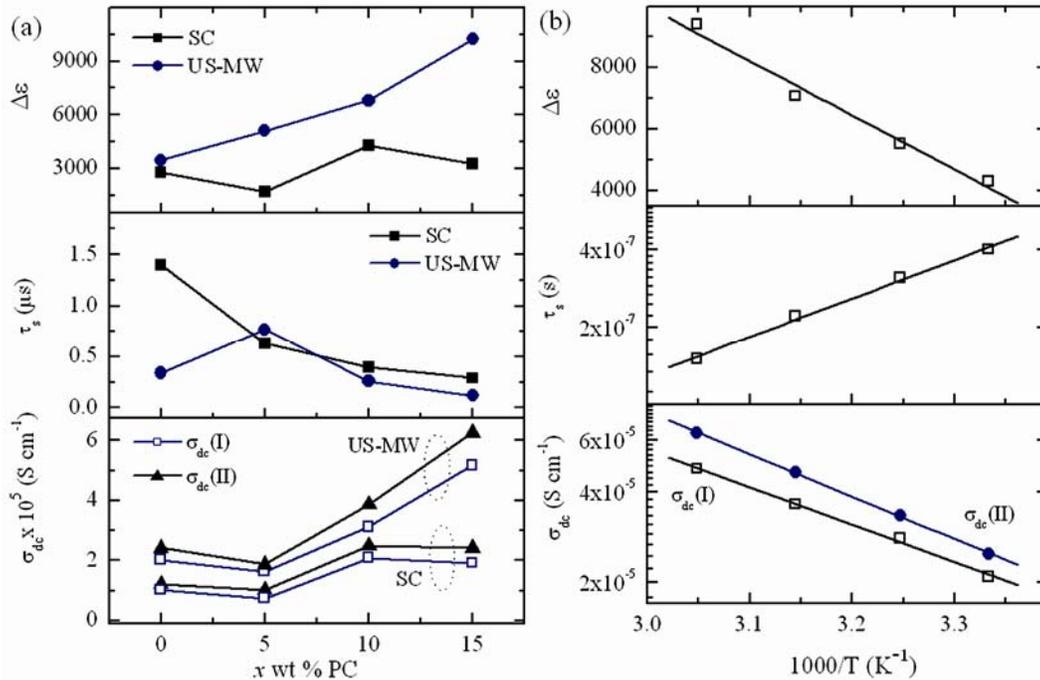


Fig. 5—(a) PC concentration dependent dielectric strength  $\Delta$ , loss tangent relaxation time  $\tau_s$  and dc ionic conductivity  $\sigma_{dc}$  of (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-x wt% PC electrolyte films prepared by SC and US-MW methods, and (b) reciprocal temperature dependence of  $\Delta$ ,  $\tau_s$  and  $\sigma_{dc}$  of (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC electrolyte film prepared by SC method

blend based electrolytes. The 15 wt% PC concentration SPE films prepared by both the methods are completely amorphous. Therefore, it seems that at 15 wt% PC concentration, the US-MW prepared film may have more favourable ion conductive paths which promote the ions mobility and hence increase the ionic conductivity. But the US-MW preparation method was not found suitable for the increase of ionic conductivity when PEG plasticizer was added in (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub> electrolyte, which is due to enhancement in crystallinity of the material with PEG concentration<sup>16</sup>. The comparative study on different types of plasticizers added electrolyte reveals that the suitability of the film preparation method depends on the constituents of the polymeric electrolyte.

The dependence of  $\sigma_{dc}$  on the  $\Delta$  and  $\tau_s$  values of the electrolytes has been studied. A close look on the plotted  $\Delta$ ,  $\tau_s$  and  $\sigma_{dc}$  values with PC concentration reveals that the increase of  $\Delta$  and the decrease of  $\tau_s$  enhance the  $\sigma_{dc}$  values of these electrolytes [Fig. 5(a)]. In case of US-MW prepared film of 5 wt% PC, its  $\sigma_{dc}$  did not increase due to the increase of both the  $\Delta$  and  $\tau_s$  values. Further, for 10 and 15 wt% PC concentrations electrolyte films prepared by US-MW method have low  $\tau_s$  value and there is significant increase of  $\Delta$  value due to which the value of  $\sigma_{dc}$

increases. This correlation suggests that increased ion-dipolar ordering, as revealed from increase in  $\Delta$ , also favours the formation of more favourable ion conductive paths in the SPE complexes. In case of SC prepared film of 5 wt% PC, the value of  $\tau_s$  decreases but its  $\Delta$  also decreases, and therefore, the  $\sigma_{dc}$  has a little change. At 10 wt% PC concentration, the increase of  $\Delta$  and decrease of  $\tau_s$  favour in increase of its  $\sigma_{dc}$  value. At 15 wt% PC,  $\tau_s$  has decrease but  $\Delta$  also decreases due to which  $\sigma_{dc}$  value has a little variation. From these interpretations, it can be concluded that the ionic conductivity of an electrolyte film is governed by the simultaneous changes in its  $\Delta$  and  $\tau_s$  values.

The conductivity values of PEO-LiCF<sub>3</sub>SO<sub>3</sub> and PMMA-LiCF<sub>3</sub>SO<sub>3</sub> with the PEO-PMMA blend based electrolyte have also been compared. The literature survey shows that the  $\sigma_{dc}$  values<sup>4,17,23,24,42</sup> of PEO-LiCF<sub>3</sub>SO<sub>3</sub> at RT are in the range  $\sim 10^{-7}$ - $10^{-9}$  S cm<sup>-1</sup>, which vary with the salt concentrations, the sample preparation methods and the conductivity evaluation procedure. These conductivity values also increase by one to two orders of magnitude with the addition of appropriate concentration plasticizers and the inorganic nanofillers<sup>23-26</sup>. The  $\sigma_{dc}$  value of PMMA-LiCF<sub>3</sub>SO<sub>3</sub> at RT is  $\sim 10^{-6}$  S cm<sup>-1</sup>, which have an

increase of one to two orders of magnitude with the plasticizers<sup>30-32</sup>. But the  $\sigma_{dc}$  values of the US-MW method prepared (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-15 wt% PC electrolyte at RT is  $> 5 \times 10^{-5} \text{ S cm}^{-1}$  (Table 1), which confirms a significant increase in  $\sigma_{dc}$  value of the PEO-PMMA blend based and plasticizer added electrolyte as compared to the conductivity values of PEO and PMMA based electrolytes.

### 3.5 Temperature dependent dielectric parameters

Figure 5(b) shows the temperature dependent  $\Delta \epsilon$ ,  $\epsilon''$  and  $\sigma_{dc}$  values of the (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>-10 wt% PC electrolyte film prepared by SC method. On logarithmic scale, these dielectric parameters have linear variation with reciprocal of temperature confirming their Arrhenius characteristics. The decrease of  $\epsilon''$  and the increase of  $\Delta \epsilon$  with the increase of temperature enhance the ionic conductivity of the electrolyte. The increase of temperature increases the flexibility and dynamics in the cations coordinated polymer chain segments and thereby increases Li<sup>+</sup> mobility which results in the increase of ionic conductivity of such electrolytes<sup>8-11,13,15-17</sup>. The conductivity activation energy  $E_{\sigma}$  and dielectric relaxation activation energy  $E$  values of the electrolyte film are determined by the Arrhenius relations  $\sigma_{dc} = \sigma_0 \exp(-E_{\sigma}/kT)$  and  $\epsilon'' = \epsilon_0 \exp(E/kT)$ , respectively, which are found to be  $\sim 0.3 \text{ eV}$ . These activation values are in consistent with the other SPE materials<sup>9,13,16</sup>. The low activation energy infers the transient-type coupling between the mobile cations and the dynamical polymer chain segments. Further, the equal values of  $E_{\sigma}$  and  $E$  also reveal that during the hopping mechanism of ion transportation, the ions have to overcome the same barrier while relaxing as well as while conducting in the solid ion-dipolar complexes which is reported for other SPE materials<sup>11,16</sup>.

### 4 Conclusions

The detailed dielectric and electrical properties of amorphous type (PEO-PMMA)-LiCF<sub>3</sub>SO<sub>3</sub>- $x$  wt% PC electrolyte films prepared by SC and US-MW methods were reported. The ionic conductivity of the electrolyte film is governed by the dielectric strength and the polymer chain segmental relaxation time. As compared to SC method, the US-MW sample preparation method is found to be effective for increasing ionic conductivity of 10 and 15 wt% PC electrolyte films which is due to formation of ordered ion-dipolar complexes and more favourable

ion conductive paths by US-MW irradiation. The temperature dependent ionic conductivity and relaxation time obey the Arrhenius characteristics. The equal values of ionic conductivity and dielectric relaxation activation energies of the electrolyte film confirm that the ions surmount the same potential barrier while relaxing as well as conducting in the solid ion-dipolar complexes. The ionic conductivity value at room temperature of 15 wt% PC electrolyte film prepared by US-MW method is about  $5 \times 10^{-5} \text{ S cm}^{-1}$  which confirms the suitability of this PEO-PMMA blend based electrolyte for rechargeable lithium ion batteries.

### Acknowledgement

Authors are grateful to the Department of Science and Technology (DST), New Delhi for providing the experimental facilities through research projects Nos. SR/S2/CMP-09/2002, SR/S2/CMP-0072/2010 and the DST-FIST program. One of the authors SC is thankful to the DST, New Delhi for the award of SERB Fast Track Young Scientist research project No. SR/FTP/PS-013/2012.

### References

- 1 Agrawal R C & Pandey G P, *J Phys D: Appl Phys*, 41 (2008) 223001.
- 2 Scrosati B & Garche J, *J Power Sources*, 195 (2010) 2419–2430.
- 3 Syzdek J, Armand M, Marcinek M, Zalewska A, Żukowska G & Wieczorek W, *Electrochim Acta*, 55 (2010) 1314–1322.
- 4 Karmakar A & Ghosh A, *J Appl Phys*, 107 (2010) 104113 (1–6).
- 5 Sengwa R J, Sankhla S & Choudhary S, *Ionics*, 16 (2010) 697–707.
- 6 Choudhary S & Sengwa R J, *Ionics*, 17 (2011) 811–819.
- 7 Kumar Y, Hashmi S A & Pandey G P, *Solid State Ionics*, 201 (2011) 73–80.
- 8 Choudhary S & Sengwa R J, *Mater Chem Phys*, 142 (2013) 172–181.
- 9 Sengwa R J & Choudhary S, *Indian J Phys*, 88 (2014) 461–470.
- 10 Nath A K & Kumar A, *Electrochim Acta*, 129 (2014) 177–186.
- 11 Karmakar A & Ghosh A, *Curr Appl Phys*, 12 (2012) 539–543.
- 12 Chilaka N & Ghosh S, *Electrochim Acta*, 134 (2014) 232–241.
- 13 Kumar M & Srivastava N, *J Non-Cryst Solids*, 389 (2014) 28–34.
- 14 Sengwa R J & Choudhary S, *J Phys Chem Solids*, 75 (2014) 765–774.
- 15 Sengwa R J, Choudhary S & Dhatarwal P, *Ionics*, 21 (2015) 95–109.
- 16 Sengwa R J, Dhatarwal P & Choudhary S, *Electrochim Acta*, 142 (2014) 359–370.

- 17 Karan N K, Pradhan D K, Thomas R, Natesan B & Katiyar R S, *Solid State Ionics*, 179 (2008) 689–696.
- 18 Pradhan D K, Choudhary R N P & Samantaray B K, *Mater Chem Phys*, 115 (2009) 557–561.
- 19 Sharma P & Kanchan D K, *Ionics*, 19 (2013) 1285–1290.
- 20 Sharma P, Kanchan D K, Gondaliya N, Pant M & Jayswal M S, *Ionics*, 19 (2013) 301–307.
- 21 Sengwa R J, Dhatarwal P & Choudhary S, *Curr Appl Phys*, 15 (2015) 135–143.
- 22 Deka M & Kumar A, *J Solid State Electrochem*, 17 (2013) 977–986.
- 23 Chen H W & Chang F C, *Polymer*, 42 (2001) 9763–9769.
- 24 Pitawala H M J C, Dissanayake M A K L, Seneviratne V A, Mellander B E & Albinson I, *J Solid State Electrochem*, 12 (2008) 783–789.
- 25 Johan M R, Shy O H, Ibrahim S, Yassin S M M & Hui T Y, *Solid State Ionics*, 196 (2011) 41–47.
- 26 Johan M R & Fen L B, *Ionics*, 16 (2010) 335–338.
- 27 Meneghetti P, Qutubuddin S & Webber A, *Electrochim Acta*, 49 (2004) 4923–4931.
- 28 Deka M & Kumar A, *Electrochim Acta*, 55 (2010) 1836–1842.
- 29 Ramesh S & Wong K C, *Ionics*, 15 (2009) 249–254.
- 30 Ahmad S, Saxena T K, Ahmad S & Agnihotry S A, *J Power Sources*, 159 (2006) 205–209.
- 31 Ali A M M, Yahya M Z A, Bahron H, Subban R H Y, Harun M K & Atan I, *Mater Lett*, 61 (2007) 2026–2029.
- 32 Ramesh S & Wen L C, *Ionics*, 16 (2010) 255–262.
- 33 Rajendran S, Kannan R & Mahendran O, *J Power Sources*, 96 (2001) 406–410.
- 34 Rajendran S, Mahendran O & Kannan R, *J Solid State Electrochem*, 6 (2002) 560–564.
- 35 Shanmukaraj D, Wang G X, Murugan R & Liu H K, *J Phys Chem Solids*, 69 (2008) 243–248.
- 36 Tan S M & Johan M R, *Ionics*, 17 (2011) 485–490.
- 37 Jeddi K, Qazvini N T, Jafari S H & Khonakdar H A, *J Polym Sci Part B: Polym Phys*, 48 (2010) 2065–2071.
- 38 Jeddi K, Qazvini N T, Jafari S H, Khonakdar H A, Seyfi J & Reuter U, *J Polym Sci Part B: Polym Phys*, 49 (2011) 318–326.
- 39 Ghelichi M, Qazvini N T, Jafari S A, Khonakdar H A, Farajollahi Y & Scheffler C, *J Appl Polym Sci*, 129 (2013) 1868–1874.
- 40 Choudhary S & Sengwa R J, *J Appl Polym Sci*, 132 (2015) 41311 (1–12).
- 41 Jonscher A K, *Dielectric relaxation in solids* (Chelsea Dielectric Press, London), 1983.
- 42 Appetecchi G B, Croce F, Hassoun J, Scrosati B, Saloman M & Cassel F, *J Power Sources*, 114 (2003) 105–112.