

Effect of mechanical and electromagnetic irradiation on dielectric properties of solid polymer electrolytes

Shobhna Choudhary*

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

*E-mail: shobhnachoudhary@rediffmail.com

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Poly(ethylene oxide) and lithium perchlorate based electrolyte films were prepared through classical solution casting, high intensity ultrasonic (mechanical wave) assisted, microwave (electromagnetic) irradiated and ultrasonication followed by microwave irradiated solution casting methods and direct melt press technique. The complexations of these electrolytes are confirmed by X-ray diffraction measurements. The dielectric behaviour of intermediate salt concentration (EO:Li⁺=12:1) electrolyte films has been investigated by dielectric relaxation spectroscopy at ambient temperature, which is considerably affected by mechanical and electromagnetic irradiation. The ionic conductivity of melt pressed electrolyte (18.3×10^{-7} S/cm) is found to be 2.4 times higher than that of the classical solution cast electrolyte (7.7×10^{-7} S/cm). The conductivity and relaxation times of ultrasonic followed by microwave assisted electrolyte film obey the Arrhenius behaviour and have the activation energy 0.4 eV. The *dc* conductivity has nearly 4 times increase from 11.8×10^{-7} to 44.7×10^{-7} S/cm with rise in temperature from 27 to 55°C.

Keywords: Polymer electrolyte, Dielectric property, Ionic conductivity

1 Introduction

Investigations on solid polymeric electrolytes (SPEs) have been an intense area of advances in materials science and engineering, because of their direct applications in fabrication of electrochromic and energy storage devices¹⁻¹⁶. The advantages of these materials over the other solid state electrolytes are their light weight, leak proof, flexible in nature, compact in size, longer life span and these SPEs can be easily fabricated by solution casting (classical method) technique. For the enhancement of ambient temperature ionic conductivity of the SPEs, the plasticizers^{4,8-10,17} and inorganic nanofillers^{3-7,12-15,18-22} are widely used in order to increase their amorphous phase, which is needed for fast ions transportation in such types of electrolyte materials. Survey of literature reveals that effects of various synthesization techniques on the ionic conduction and amorphous phase of the SPEs were merely attempted. Most of the investigations are focused on the preparation of electrolytes by 'classical' solution cast method.

The recent study on polymeric electrolytes confirms that the use of high intensity ultrasonication (mechanical wave energy) and microwave (electromagnetic energy) irradiation during the processing of electrolyte solutions produces significant changes in the structural properties and the

conductivity behaviour of such solution cast electrolyte films^{23,24}. Although ultrasonic treatments were widely used during the synthesis of polymeric nanocomposite electrolytes for homogenous dispersion of inorganic nanofillers^{10,25-27}, but its effect on dielectric properties have not been confirmed, separately. In the present paper, the SPEs comprising poly(ethylene oxide) (PEO) and lithium perchlorate (LiClO₄) have been synthesized through ultrasonication and microwave irradiation processed electrolyte solutions. The effect of these irradiations on the dielectric properties and structural behaviour of the SPEs is explored by dielectric relaxation spectroscopy (DRS) and X-ray diffraction (XRD) measurements, respectively. These electrolytes were also prepared by 'classical' solution cast and melt compounded hot press techniques for the comparison of their dielectric behaviour. Due to promising solvent behaviour of PEO in solid state for alkali metal salts (LiClO₄, LiBF₄, LiCF₃SO₃ etc.) and its good film forming ability, the consideration of PEO and LiClO₄ is reasonable in the present study for the preparation of the electrolyte films by different methods.

2 Experimental Details

The PEO of molecular weight 600,000 g/mol and LiClO₄ (battery grade, dry, 99.9% metal basis) was

obtained from Sigma-Aldrich, USA. Acetonitrile of spectroscopy grade was purchased from Loba Chemie, India.

The films of PEO₁₂-LiClO₄ electrolyte (EO:Li⁺ = 12:1, where the composition ratio EO:Li⁺ represents the number of ethylene oxide units (EO) to the number of lithium cations (Li⁺)) were prepared by taking vacuum dried PEO (0.832 g) and LiClO₄ (0.168 g) separately for each film through the following five different techniques:

(i) *Dry blended melt pressed (MP) technique*: The SPE film was prepared using hot polymer press film making unit (Technosearch, Mumbai). Initially, the required amounts of PEO and LiClO₄ were mechanically mixed in dry form by agate mortar and pestle. The homogenous dry mixture was melted at 80°C for 10 min duration in circular film making die of 60 mm diameter with suitable spacer and immediately pressed at 2 tons of pressure per unit area. After that by slow cooling up to room temperature, the free-standing MP film of PEO₁₂-LiClO₄ electrolyte was obtained.

(ii) *Solution casting (SC) technique*: In this technique, the electrolyte film was prepared by dissolving the required amounts of PEO and LiClO₄ in acetonitrile solvent. The vigorous magnetic stirred viscous solution was cast onto a teflon petri dish and the solvent was allowed to evaporate slowly at room temperature. The free-standing SC film of PEO₁₂-LiClO₄ was vacuum dried at 40°C for 24 h in vacuum oven (Bio-Technics, India) to remove the solvent traces present, if any.

(iii) *Ultrasonic (US) assisted technique*: Initially required amounts of PEO and LiClO₄ were dissolved in acetonitrile and the viscous electrolyte solution was sonicated using a high intensity ultrasonicator (Trans-O-Sonic, Mumbai; 250 W power, 25 kHz frequency) for 10 min duration with 15 s ON-OFF step. In this processing, the stainless steel sonotrode was directly immersed into the electrolyte solution for strong dose of the ultrasound (mechanical wave) energy and its transmission in the solution through caviations, which resulted significant rise in temperature of the electrolyte solution. After that the US assisted electrolyte film was obtained by solution casting technique.

(iv) *Microwave (MW) irradiated technique*: In this technique, initially the required amounts of PEO and LiClO₄ were dissolved in acetonitrile and subsequently irradiated under microwave

(electromagnetic wave) energy in a domestic microwave oven (Samsung, India; 600 W power, 2.45 GHz frequency) for 2 min duration with 10 s irradiation step and intermediate cooling. After that the MW irradiated electrolyte film was obtained by solution casting method using the MW irradiated electrolyte solution.

(v) *Ultrasonication followed by microwave (US & MW) irradiated technique*: In this process, the electrolyte solution consisted of PEO and LiClO₄ in acetonitrile solvent was initially sonicated and subsequently irradiated by microwave energy. After that following the solution casting method, the US and MW irradiated film of the PEO₁₂-LiClO₄ electrolyte was obtained.

The X-ray diffraction (XRD) patterns of these electrolyte films were recorded using PAN analytical X'pert Pro MPD diffractometer of Cu K α radiation (wavelength $\lambda = 1.5406 \text{ \AA}$) operated at 45 kV and 40 mA with a scanned step size of 0.05° and 1 s duration. The pure PEO and electrolyte films were placed on the top of the sample holder for their XRD measurement in the angular range (2θ) from 10-30° at room temperature, whereas LiClO₄ powder was tightly filled in the sample holder for its XRD characterization.

Agilent 4284A precision LCR meter and 16451B solid dielectric test fixture of 38 mm diameter active electrode were used for the characterization of dielectric relaxation spectroscopy (DRS) of the SPEs films in the linear frequency f range 20 Hz-1 MHz at ambient temperature (27°C) and also with temperature variation (27-55°C for the US and MW electrolyte film). Frequency dependent values of parallel capacitance C_p , parallel resistance R_p and loss tangent ($\tan\delta = \epsilon''/\epsilon'$) of the SPE films were measured for the determination of their dielectric/electrical spectra. Prior the samples measurement, the open circuit calibration of the cell was performed to eliminate the effect of stray capacitance of the cell 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 PEO₁₂-LiClO₄ films prepared by different methods were determined by the expressions described in Refs (12,28). These complex functions are mutually related

according to the scheme $1/\varepsilon^*(\omega) = j\omega C_0 Z^*(\omega) = M^*(\omega) = j\omega \varepsilon_0 / \sigma^*(\omega)$, where $\omega = 2\pi f$ is an angular frequency of the electric field wave and ε_0 is the permittivity in vacuum.

3 Results and Discussion

The XRD patterns of PEO₁₂-LiClO₄ electrolyte films along with PEO film and LiClO₄ powder are shown in Fig. 1. The major diffraction peaks observed at $2\theta = 19.03^\circ$ and 23.22° are corresponding to 120 and concerted 112, 032 crystal reflections of the pure

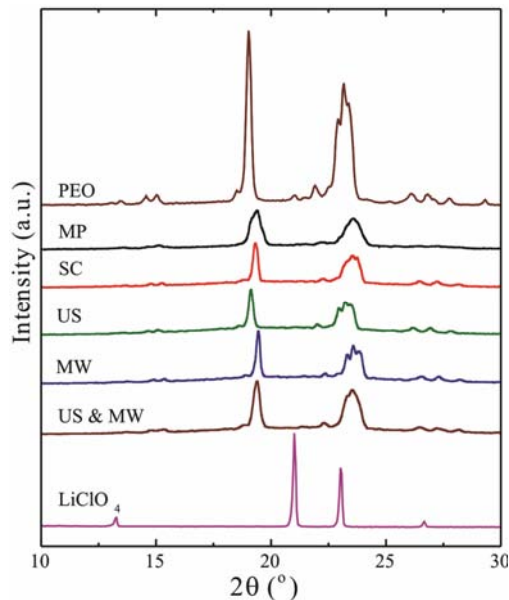


Fig. 1 — XRD patterns of LiClO₄ powder, pure PEO film and PEO₁₂-LiClO₄ electrolyte films synthesized by various techniques

PEO crystalline phases, which are found to in agreement with the earlier reported values^{3,18,29}. The LiClO₄ has the major crystalline peaks at $2\theta = 21.02^\circ$ and 23.04° over the angular range $10\text{--}30^\circ$. Comparative XRD traces reveal significant changes in the intensity profile of PEO peaks of the electrolyte films with their preparation methods. The values of Bragg's angle 2θ of main crystalline peaks, basal spacing d , full width at half maximum (FWHM) β (the broadening of peak at half-height expressed in radians of 2θ i.e. width measured in 2θ degrees and then multiplied by $\pi/180$), mean crystallite length L (crystalline lamellar thickness) and peak intensity I (counts) of the PEO₁₂-LiClO₄ electrolyte films were determined and recorded in Table 1. The value of d -spacing between diffractive lattice planes of the PEO was determined by Bragg's relation $\lambda = 2d\sin\theta$, whereas the mean crystallite length L in the direction perpendicular to hkl plane was evaluated by Scherrer's equation $L = 0.94\lambda/\beta\cos\theta$. PANalytical X'Pert Pro® software was used to determine the precise values of various parameters related to the crystalline structures of these electrolytes.

The significant decrease in relative intensity values of PEO main crystalline peaks (Table 1), and no signature of LiClO₄ peaks in the XRD traces of the electrolyte films confirm the complexations of PEO with LiClO₄ (ion-dipolar interactions between ether oxygen atoms and cations i.e. $O\cdots Li^+$), which resulted an increase of amorphous phase of the electrolytes. The variation in intensity values of the PEO crystalline peaks with synthesis route of the electrolyte films also confirms the changes in their

Table 1 — Values of Bragg's angle 2θ , basal spacing d , full width at half maximum FWHM, crystallite size L and crystalline peak intensity I of pure PEO and PEO₁₂-LiClO₄ films synthesized by various techniques

Synthesis techniques	2θ (°)	d (nm)	FWHM $\times 10^3$ (rad)	L (nm)	I (counts)
120 reflection peak parameters of PEO					
PEO film	19.03	0.466	4.38	33.52	15296
PEO ₁₂ -LiClO ₄ films					
MP	19.37	0.458	9.86	14.89	3221
SC	19.34	0.459	4.39	33.40	3679
MW	19.45	0.456	3.49	42.09	4330
US	19.13	0.464	3.96	37.07	3854
US & MW	19.39	0.457	5.81	25.28	4466
112,032 reflection peak parameters of PEO					
PEO film	23.22	0.383	13.23	11.18	9515
PEO ₁₂ -LiClO ₄ films					
MP	23.60	0.377	13.23	11.18	2275
SC	23.59	0.377	14.15	10.45	2313
MW	23.59	0.377	13.16	11.24	2821
US	23.26	0.382	13.47	10.97	2471
US & MW	23.53	0.378	13.37	11.06	3260

complex structures. Table 1 presents that the d -spacing values of the PEO main crystalline peaks of all these electrolytes were found slightly lower than that of pure PEO. Further, the crystallite length corresponding to 120 reflection of these electrolytes is greatly influenced by the preparation methods, and in case of MP electrolyte film it is comparatively very low. It is also observed that the L values of concerted 112, 032 crystalline reflection of PEO are almost independent of the electrolytes preparation.

Figure 2 shows the frequency dependence of real part (permittivity) ϵ' and dielectric loss ϵ'' of the complex dielectric function of PEO₁₂-LiClO₄ electrolyte films prepared by various methods at room temperature. The comparative variations in ϵ' and ϵ'' values of the electrolytes infer that their dielectric

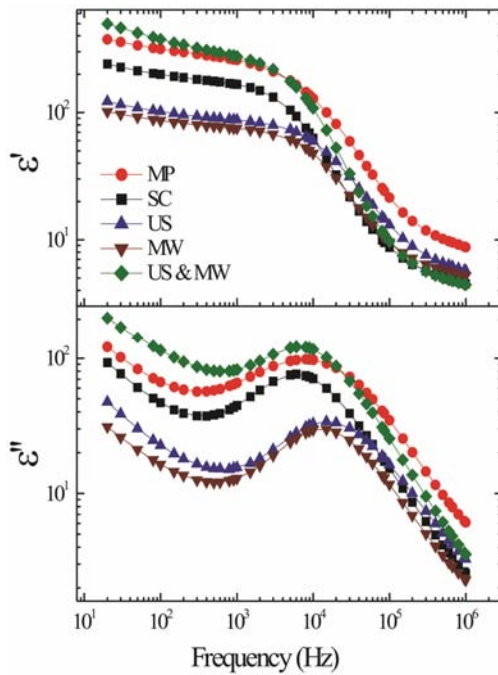


Fig. 2 — Frequency dependent real part ϵ' and loss ϵ'' of the complex dielectric function of the PEO₁₂-LiClO₄ electrolyte films synthesized by various techniques

polarizations are strongly influenced by the sample preparation methods. Near low frequency end of the ϵ' spectra, the ϵ' values are almost steady which are corresponding to low frequency limiting permittivity (static permittivity ϵ_s) values, but there is dispersion that starts around 1 kHz and again approaches the steady state (high frequency limiting permittivity ϵ_∞) near 1 MHz. The values of dielectric relaxation strength $\Delta\epsilon$ of these electrolytes are estimated by the relation $\Delta\epsilon \approx \epsilon'(1 \text{ kHz}) - \epsilon'(1 \text{ MHz}) = \epsilon_s - \epsilon_\infty$ which is mainly a measure of ionic polarization, and these values are listed in Table 2. The $\Delta\epsilon$ values of PEO₁₂-LiClO₄ films synthesized by various processes have the order $\Delta\epsilon(\text{US and MW}) > \Delta\epsilon(\text{MP}) > \Delta\epsilon(\text{SC}) > \Delta\epsilon(\text{US}) > \Delta\epsilon(\text{MW})$, which confirm the large enhancement in ionic polarization due to US and MW irradiation. Further, the high $\Delta\epsilon$ value of MP synthesized PEO₁₂-LiClO₄ film suggests that the direct melt pressing increases ionic polarization density of the electrolyte material due to the smoothing of film surfaces, which is in agreement with the earlier findings⁹.

The dielectric loss ϵ'' spectra of PEO₁₂-LiClO₄ electrolytes have single dielectric relaxation peak in the frequency range ~ 5 -30 kHz (Fig. 2). This peak represents the Li⁺ coordinated PEO chain segmental dynamics^{1,13-16,27}. Assuming the Debye-type dispersion of ϵ'' spectra, the dielectric relaxation time τ_ϵ of these electrolytes was determined using the relation $\tau_\epsilon = 1/2\pi f_p(\epsilon'')$, where $f_p(\epsilon'')$ is the value of dielectric loss peak frequency¹². The evaluated τ_ϵ values of the electrolytes at ambient temperature are recorded in Table 2.

Figure 3 shows the spectra of real part $\sigma' = \omega\epsilon_0\epsilon''$ of complex ac conductivity and loss tangent $\tan\delta$ of PEO₁₂-LiClO₄ films synthesized by various processes. Initially, the σ' values have an increase with the increase of frequency due to electrode polarization effect, and after that approach the dc plateau in high frequency region. The dc ionic conductivity σ_{dc} of

Table 2 — Values of dielectric strength $\Delta\epsilon = \epsilon'(1 \text{ kHz}) - \epsilon'(1 \text{ MHz})$, dielectric relaxation time τ_ϵ , loss tangent relaxation time $\tau_{\tan\delta}$, electric modulus relaxation time τ_M , dc ionic conductivity σ_{dc} , pre-exponential factor A and fractional exponent n of the PEO₁₂-LiClO₄ electrolyte films synthesized by various techniques

Film preparation techniques	$\Delta\epsilon$	τ_ϵ (μs)	$\tau_{\tan\delta}$ (μs)	τ_M (μs)	$\sigma_{dc} \times 10^7$ (S/cm)	$A \times 10^{12}$	n
MP	250.2	19.62	1.74	0.15	18.3	3.07	0.838
SC	161.9	27.16	3.02	0.23	7.7	2.97	0.783
US	82.0	10.23	1.73	0.20	8.3	3.14	0.810
MW	69.9	12.78	2.56	0.30	5.5	3.02	0.790
US & MW	270.9	26.18	1.96	0.15	11.8	3.27	0.799

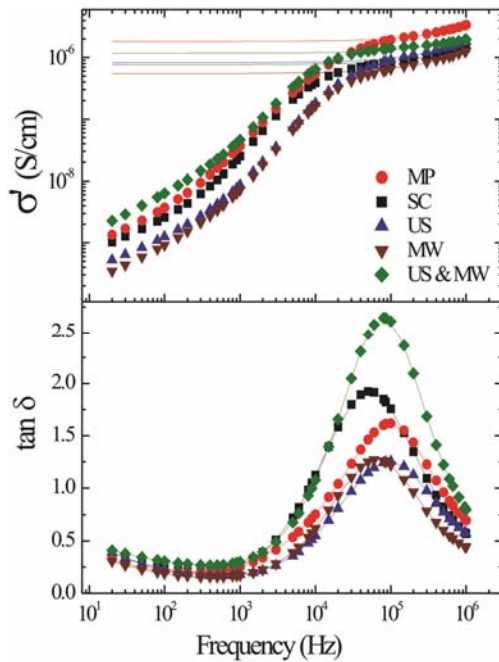


Fig. 3 — Frequency dependent real part of ac conductivity σ' and loss tangent ($\tan\delta$) of the $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte films synthesized by various techniques. The continuous solid lines in σ' spectra represent the fit of experimental data to the Jonscher power law $\sigma'(\omega) = \sigma_{dc} + A\omega^n$

these electrolytes was determined by fitting the high frequency experimental values of σ' to the Jonscher power law³⁰ $\sigma'(\omega) = \sigma_{dc} + A\omega^n$, where A is the pre-exponential factor and n is the fractional exponent ranging between 0 and 1. The solid lines in the σ' spectra represent the power law fit data, which were obtained by Origin® non-linear curve fitting software. The evaluated σ_{dc} values along with A and n values of the $\text{PEO}_{12}\text{-LiClO}_4$ electrolytes prepared by different methods are given in Table 2. The $\tan\delta$ spectra of these electrolytes also have relaxation peak at frequency $f_{p(\tan\delta)}$ from which the values of loss tangent relaxation time $\tau_{\tan\delta}$ are determined by the relation $\tau_{\tan\delta} = 1/2\pi f_{p(\tan\delta)}$ and these values are recorded in Table 2.

The electric modulus (real part M' and loss M'') spectra of the $\text{PEO}_{12}\text{-LiClO}_4$ films synthesized by various processes are shown in Fig. 4. The M' and M'' values are almost zero in the electrode polarization affected frequency region, whereas the dispersion in M'' spectra approaches close to modulus relaxation peak near the high frequency end. The M'' peak frequency $f_{p(M'')}$ values of these electrolytes were

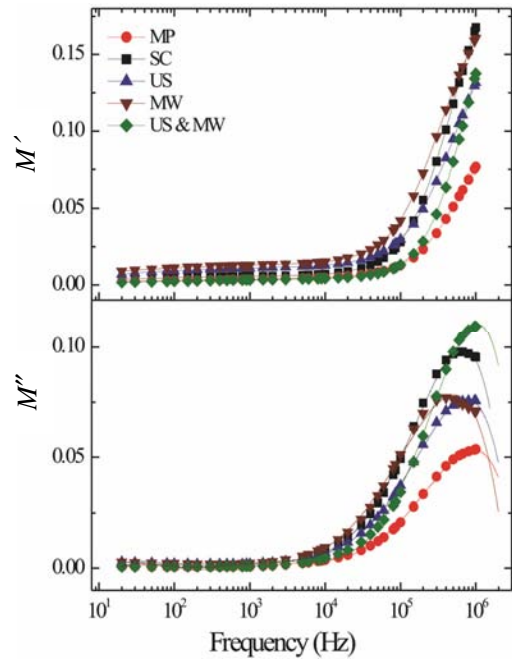


Fig. 4 — Frequency dependent real part M' and loss M'' of complex electric modulus of the $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte films synthesized by various techniques. In M'' spectra, the solid lines show the polynomial fit of the experimental data

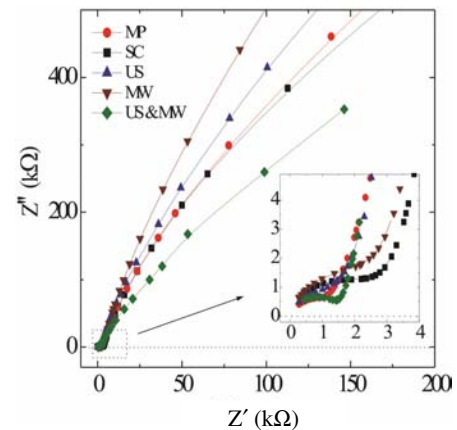


Fig. 5 — Complex impedance plane plots (Z'' vs Z') of the $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte films synthesized by various techniques. Inset shows the high frequency arcs corresponding to bulk material properties

determined by extrapolation method and used for evaluation of modulus relaxation time by the relation $\tau_M = 1/2\pi f_{p(M'')}$. The evaluated τ_M values of the electrolytes were recorded in Table 2. The complex impedance plane plots (Z'' versus Z') of the $\text{PEO}_{12}\text{-LiClO}_4$ films are shown in Fig. 5. Inset shows that these electrolytes have semi-circular arc in high

frequency region corresponding to the bulk material properties and spikes at low frequencies referred to the electric double layers capacitive effect. Such a behaviour of impedance plots is common for the SPE materials^{3,11-14,23,31,32}.

The ambient temperature σ_{dc} value of PEO₁₂-LiClO₄ electrolyte is found to be comparatively low for MW irradiated film (5.5×10^{-7} S/cm), and about 2 times high for US & MW processed film (11.8×10^{-7} S/cm) (Table 2). The σ_{dc} value of MP electrolyte film is found significantly high as compared to the solution cast films prepared through various routes. It is expected because the hot pressing results the smooth surfaces of electrolyte film, and also forms new transient ion conductive paths favourable for ions transportations⁹. Beside these facts, the high amorphous phase as revealed from low intensity of crystalline peaks of the MP electrolyte (Table 1) is also responsible for its relatively high ionic conductivity, because in amorphous phase the presence of free volumes helps in ion transportation process.

The comparative variation of τ_ϵ , $\tau_{\tan\delta}$, τ_M and $\Delta\epsilon$ values of the PEO₁₂-LiClO₄ electrolyte films prepared through various methods also shows the correlation with their ionic conductivity. Table 2 presents that the electrolyte films of high $\Delta\epsilon$ and low relaxation times values have relatively high ionic conductivity. It has been established that the long range ions diffusion leading to ionic conductivity of solid polymeric electrolytes occurs in cations coupled local segmental motions of the polymer host^{1,2,15,16,27}. The low values of relaxation times represent the fast dynamics of Li⁺ coordinated PEO local chain motion due to which there is increase of ions mobility and simultaneously the ionic conductivity of the electrolyte increases^{1,2,12-16,33}. The n values of these electrolyte films are nearly 0.8 (Table 2), which suggest that the transport of ions in these systems are occurred through hopping mechanism^{1,12,13}.

The PEO₁₂-LiClO₄ electrolyte film synthesized through US & MW route has been selected as representative material for the temperature dependent dielectric study. Figure 6 shows the temperature dependent ϵ' and ϵ'' spectra of the US & MW synthesized PEO₁₂-LiClO₄ electrolyte film. It is observed that ϵ' and ϵ'' values of this electrolyte film increase with increase of temperature. The real part σ' of ac conductivity and peak values of loss tangent $\tan\delta$ of the electrolyte film also increase with increase

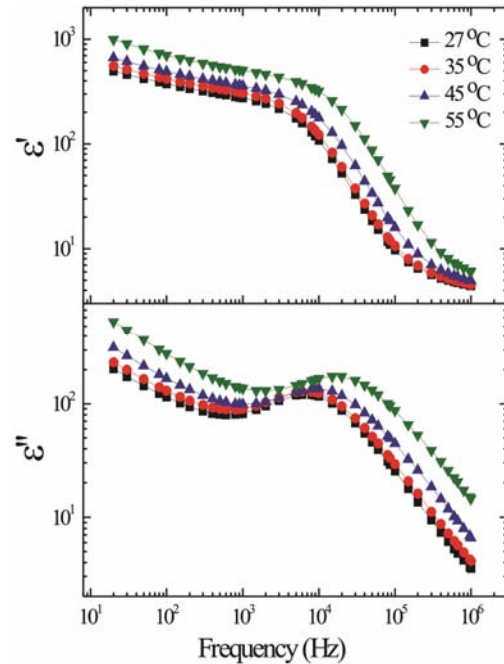


Fig. 6 — Frequency dependent real part ϵ' and loss ϵ'' of the complex dielectric function of US & MW synthesized PEO₁₂-LiClO₄ electrolyte film at different temperatures

of temperature (Fig. 7). It is found that the relaxation peaks of both the ϵ'' and $\tan\delta$ spectra have shift towards higher frequency side with increase of temperature. The temperature dependent electric modulus spectra of the electrolyte film are shown in Fig. 8. The M'' spectra indicate that the relaxation peak at higher temperatures is above the upper limit of experimental frequency range. Figure 9 shows the complex impedance plots (Z'' versus Z') of the electrolyte film at various temperatures. All these plots have semicircular arcs at high frequencies corresponding to bulk properties and their sizes shrink gradually with increase of temperature. Further, these plots have shift towards low resistance region which confirms the increase of their conductance as temperature increases. The temperature dependent values of $\Delta\epsilon$, τ_ϵ , $\tau_{\tan\delta}$ and σ_{dc} of the US & MW irradiated electrolyte film are determined using the various relations and these values are recorded in Table 3. It is found that the σ_{dc} , n and $\Delta\epsilon$ values of the electrolyte increase with increase of temperature whereas the relaxation times decrease. The increase of σ_{dc} and $\Delta\epsilon$ with increase of temperature confirms that the electrical conduction is due to ions transportation in the electrolyte film. Table 3 presents that the σ_{dc} value increases four times with increase of

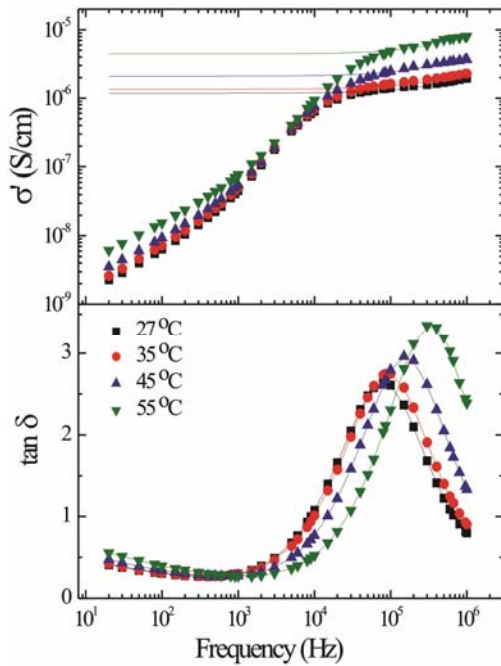


Fig. 7 — Frequency dependent real part of ac conductivity σ' and loss tangent ($\tan\delta$) of US & MW synthesized $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte film at different temperatures. The continuous solid lines in σ' spectra represent the fit of experimental data to the Jonscher power law $\sigma'(\omega)=\sigma_{dc}+A\omega^n$

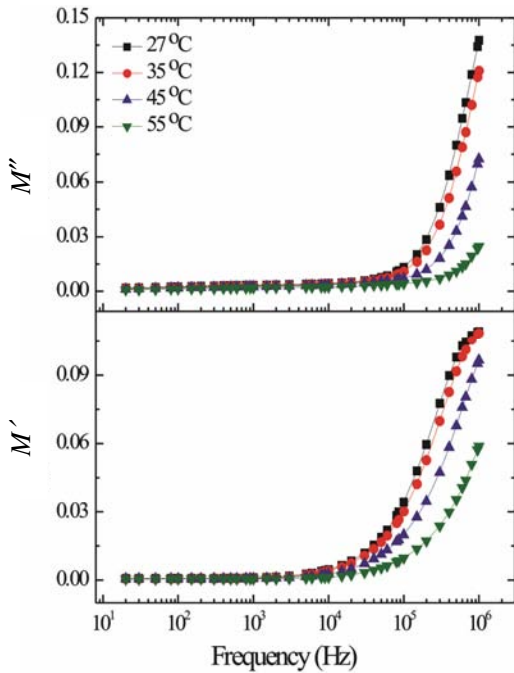


Fig. 8 — Frequency dependent real part M' and loss M'' of complex electric modulus of US & MW synthesized $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte film at different temperatures

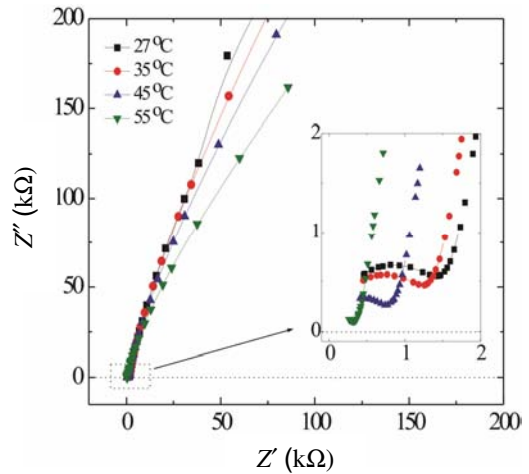


Fig. 9 — Complex impedance plane plots (Z'' versus Z') of US & MW synthesized $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte film at different temperatures. Inset shows the high frequency arcs corresponding to bulk material properties

Table 3 — Values of dielectric strength $\Delta\epsilon = \epsilon'(1 \text{ kHz}) - \epsilon'(1 \text{ MHz})$, dielectric relaxation time τ_ϵ , loss tangent relaxation time $\tau_{\tan\delta}$, dc ionic conductivity σ_{dc} , pre-exponential factor A and fractional exponent n of US & MW irradiated $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte film at different temperatures

Temperature (°C)	$\Delta\epsilon$	τ_ϵ (μs)	$\tau_{\tan\delta}$ (μs)	$\sigma_{dc} \times 10^7$ (S/cm)	$A \times 10^{12}$	n
27	270.9	26.18	1.96	11.8	3.27	0.799
35	301.9	22.82	1.61	13.5	3.34	0.819
45	354.5	13.38	0.96	21.0	3.40	0.857
55	497.9	7.24	0.52	44.7	3.71	0.884

temperature from 27° to 55°C, whereas a significant increase of n value (from 0.799 to 0.884) also reveals the enhancement of ions hopping transportation mechanism with rise in temperature. Further, the dielectric relaxation strength $\Delta\epsilon$ at 55°C becomes twice of its value at 27°C, which suggests the large enhancement in ionic polarization of the solid electrolyte polymer with increase of temperature.

Figure 10 shows the reciprocal temperature dependence behaviour of $\Delta\epsilon$, $\tau_{\tan\delta}$, τ_ϵ and σ_{dc} values of the US & MW synthesized $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte film. From this plot, it can be seen that the $\Delta\epsilon$ values increase non-linearly with increase of temperature, whereas the logarithmic of relaxation times ($\tau_{\tan\delta}$ and τ_ϵ) and σ_{dc} values exhibit an activated behaviour obeying the Arrhenius relations $\tau = \tau_0 \exp[E_\tau/k_B T]$ and $\sigma_{dc} = \sigma_0 \exp[-E_\sigma/k_B T]$, respectively. The values of activation energies E_τ and E_σ for the conductivity

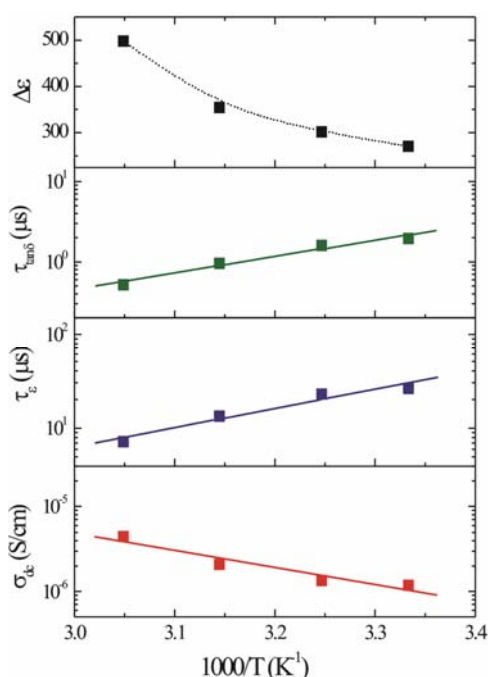


Fig. 10 — Reciprocal temperature dependence of $\Delta\epsilon$, τ_{amb} , τ_c and σ_{dc} for the US & MW synthesized $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte film. The solid lines are the least square straight-line fits to the experimental data

relaxation times and dc conductivity, respectively, were obtained from the least square linear fit. The E_σ value for the $\text{PEO}_{12}\text{-LiClO}_4$ film is found to be 0.402 eV, whereas the value of $E_\tau(\epsilon) = 0.398$ eV and $E_\tau(\tan\delta) = 0.407$ eV.

As compared to E_τ and E_σ values of $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte determined from their relaxation and conductivity study below room temperature^{1,2}, the energy values obtained in the present study above the ambient temperature were found very low. This suggests that there is slow hopping process at low temperature arising from the strong coupling between the mobile cations and the polymer backbone structure¹, whereas the present study infers that the strength of this transient coupling becomes weak above the ambient temperature. The observed E_σ value is also found to be in agreement with the earlier reported values of other polymeric electrolytes investigated above ambient temperature^{34,35}. Further, the equal values of both the activation energies (conductivity and relaxation) reveal that the transport of the ions in $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte above the room temperature occurs by hopping mechanism and the ions have to overcome the same barrier while relaxing as well as conducting, which is according to

the results observed for the electrolytes at low temperatures².

4 Conclusions

The dielectric properties of $\text{PEO}_{12}\text{-LiClO}_4$ electrolyte films prepared through five different methods were investigated by dielectric relaxation spectroscopy. This study revealed that the dielectric/electric behaviour of these electrolytes noticeably affected by the mechanical and electromagnetic irradiation employed during the samples preparation. The high intensity ultrasonication along with microwave irradiation increases the ionic conductivity 1.5 times as compared to the ambient temperature conductivity of classical solution cast electrolyte film having the same concentration of the salt. The ionic conductivity increases 2.4 times when the electrolyte film of same composition is prepared by direct melt pressing technique. The ion transport in these electrolyte materials is governed by hopping mechanism, and the cations coupled PEO segmental motion controls their ionic conductivity. Beside the polymer dynamics, the percentage of amorphous phase of the electrolyte material is also important for enhancing the ionic conductivity. The relaxation times and dc ionic conductivity of the ultrasonic along with microwave irradiated prepared electrolyte film obey the Arrhenius relation, and have the same values of activation energies for dc conductivity and relaxation processes. The moderate ionic conductivity ($\sim 10^{-6}$ S/cm) value at ambient temperature of these intermediate salt concentration electrolytes ($\text{PEO}_{12}\text{-LiClO}_4$) confirms their suitability in fabrication of electrochromic devices and also the lithium ion batteries to operate the low current rating electronic devices.

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