

# Synthesis, Characterization and Electrical Properties of [PEO-LiClO<sub>4</sub>] SPE System

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**Abstract** – The most promising materials are SPEs in the field of material science and engineering. SPEs are the most effective materials for the compact nature of the solid state electrochemical system. Among the polymer hosts, polyethylene oxide (PEO) based composites were intensively studied. The aim of the present study is to optimize LiClO<sub>4</sub> loading in to the PEO host with respect to film stability and conductivity. The structural and electrical properties of synthesized SPE films are also elaborated here. In this current work, Lithium ion conducting SPEs are prepared. PEO is used as a polymer host with lithium perchlorate (LiClO<sub>4</sub>) as added metal salt and various fillers distributed in the [85%PEO+15%LiClO<sub>4</sub>] SPE method.

**Key Words** – Solid Polymer Electrolytes, Polyethylene Oxide, Lithium Perchlorate

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## I. INTRODUCTION

Solid Polymer electrolytes (SPE) are the best suitable electrolytes for applications of Li-ion batteries when compared with their counterpart of liquid and gel electrolytes. The main advantages of SPE are flexibility, light-weight and ease of fabrication, no leakage, and electrode- electrolyte interfacial stability. Generally more research work has been focussed on polymer hosts like polypropylene oxide (PPO) and polyethylene oxide (PEO) complexed with inorganic metallic salt like LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiBF<sub>4</sub> and LiTFS etc are used in Li-ion batteries [1]. PEO still remains the most promising polymer host for the SPE due to its capacity to dissolve wide varieties of salts, light weight and easy processability compared to other polymer hosts. Movement of Polymer segments associated with cations of the salt plays an important role in enhancing ionic conductivities of SPE system [2]. The major limitations of SPE are lower ionic conductivity at ambient temperatures, development of highly resistive layers at electrode-electrolyte interface and limited lithium ion transference number [3]. The high conductivity of PEO is generally observed in amorphous state i.e. when the temperature is exceeding melting temperature of 65°C. This limits the application of Li/PEO electrolytes for practical applications.

The objective of the current work is described below:

Polymer Electrolyte system-I: In this system, SPE films are prepared according to: [(1-x)% PEO+(x)% LiClO<sub>4</sub>, where x=0, 5, 7.5, 10, 12.5 and 15].

## II. REIEW OF LITERATURE

Yu Jiang et. al.[4] reported that Solid polymer electrolytes (SPEs) have attracted tremendous interest due to the accelerated growth of the need for more protection and efficient lithium ion batteries. The prime specifications of solid polymer electrolytes are high ion conductivity, low glass transition temperature, excellent solubility to the conductive lithium salt, and strong interface stability against Li anode, which makes PEO and its derivatives possible candidate polymer matrixes. This analysis mainly encompasses on the synthetic production of PEO-based SPEs (PSPEs), and the possible application of the resulting PSPEs for high efficiency, all-solid-state lithium ion batteries.

Choudhury et. al.[5] discussed as potentially revolutionary technological systems for electrical energy storage, electrochemical cells based on alkali metal anodes are of intensive scientific importance.. Inequal metal electrodeposition and low anode reversibility are produced by chemical, morphological, mechanical and hydrodynamic instability at the metal anode, which are among the many recognised challenges that constrain development. Here, we report that in cells based

on lithium metal anodes, solid-state electrolytes based on crosslinked polymer networks will overcome all of these challenges. Via transport and electrochemical research, we show that by controlling thermodynamic interactions between covalently anchored polymer segments in the network and "free" segments belonging to an oligomeric electrolyte hosted in the network pores, hybrid electrolytes that exhibit liquid-like barriers to ion transport and solid-like resistance to morphology can easily be produced.

Zhao et. al. [6] examined that four types of Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP) with different particle sizes are selected as active fillers incorporated into polyethylene oxide (PEO) matrix to fabricate PEO/LAGP hybrid electrolytes at drying room. The results show that LAGP particles have a positive effect on ionic conductivity, the number of transfers of lithium ions, electrochemical stability and mechanical characteristics. The PEO-20 percent LAGP-I hybrid electrolyte displays a maximal ionic conductivity of  $6.76 \times 10^{-4}$  S cm<sup>-1</sup> and an electrochemical window of 0-5.3 V at 60 °C among the PEO/LAGP hybrid electrolytes. The possible reasons for improving conductivity are discussed through the characterization of electrolyte phase transition behaviours. All-solid-state battery LiFePO<sub>4</sub>/Li is fabricated and presents fascinating electrochemical performance with high capacity retention (close to 90% after 50 cycles at 60 °C) and attractive capacities of 166, 155, 143 and 108 mAh g<sup>-1</sup> at current rates of 0.1, 0.2, 0.5 and 1 C, respectively. This particular work gives a promising PEO/LAGP hybrid electrolyte which is simply prepared by a method which can be easily manufactured in industry scale.

Sun et. al. [7] reported the synthesis and application of high-molecular-weight poly (trimethylene carbonate) (PTMC) as a new host material for solid polymer electrolyte-based Li-ion batteries. PTMC was synthesised by bulk ring-opening polymerization of the cyclic monomer to yield a high-molecular-weight polymer to act as a base material for the electrolytes. The thermal properties and ionic conductivity of polymer electrolytes with different salt ratios were calculated by TGA/DSC and electrochemical impedance spectroscopy, respectively. The most conductive structures were located at [Li<sup>+</sup>]:[carbonate] ratios of 1:13 and 1:8, which displayed electrochemical stability up to 5.0 V vs. Li/Li<sup>+</sup> and an ionic conductivity on the order of  $10^{-7}$  S cm<sup>-1</sup> at 60 °C. LiFePO<sub>4</sub> half-cells using the electrolytes showed a plateau in the specific discharge capacity around 153 mAhg<sup>-1</sup> after long-term cycling. The versatility of the electrolytes for three-dimensional micro batteries was also verified.

Sheng et. al. [8], investigated that High ionic conductivity, adequate mechanical properties and large electrochemical windows are main factors for solid-state lithium-ion battery composite electrolytes (SSLIBs). Based on these considerations, we

fabricate Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> nanowire enabled poly(ethylene oxide) (PEO)-based solid-state electrolytes (SSEs). These SSEs notably have increased ionic conductivity and a large electrochemical window. The increased ionic conductivity is due to the enhanced movement of PEO chains and the increased migratory pathway of Li on the interface between Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> and PEO-LiTFSI. Moreover, the interaction between Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> and -SO<sub>2</sub>- in TFSI- anions could also benefit the improvement of conductivity. In addition, the SSEs which contains Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> nanowires exhibit better mechanical properties and flame-retardant performance, which are all superior to the pristine PEO-LiTFSI electrolyte. When these multifunctional SSEs are combined with LiFePO<sub>4</sub> cathodes and lithium metal anodes, the SSLIBs display better rate efficiency and higher cyclic potential of 150, 106, and 50 mAh g<sup>-1</sup> under 0.2 C at 50, 40, and 30°C. This technique of employing Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> nanowires provides the design guidance of assembling multifunctional SSLIBs with high ionic conductivity, excellent mechanical properties, and flame-retardant efficiency at the same time.

Lin et. al.[9] investigated that High ionic conductivity solid polymer electrolyte (SPE) and High energy and secure rechargeable lithium batteries have long been needed for the next generation. Among all the SPEs, owing to the improvement of ionic conductivity, composite polymer electrolyte (CPE) with ceramic fillers has gathered considerable interest. The high degree of polymer crystallinity, ceramic filler agglomeration, and poor polymer-ceramic interaction, however, restrict the further enhancement of ionic conductivity. Unlike the latest methods of mixing preformed ceramic particles with polymers, an in situ synthesis of ceramic filler particles in polymer electrolyte is applied here.. Much stronger chemical/mechanical interactions were developed by in situ hydrolysis between monodispersed 12 nm diameter SiO<sub>2</sub> nano-spheres and poly (ethylene oxide) (PEO) chains, which greatly suppresses PEO crystallization and thus facilitates polymer segmental motion for ionic conduction. Moreover, it is also possible to obtain an increased degree of LiClO<sub>4</sub> dissociation All of these ( $1.2 \times 10^{-3}$  S cm<sup>-1</sup> at 60°C,  $4.4 \times 10^{-5}$  S cm<sup>-1</sup> at 30°C) contribute to strong ionic conductivity. At the same time, it is possible to find a largely expanded electrochemical stability window of up to 5.5 V. We also showed all-solid-state lithium batteries with outstanding rate capability and excellent cycling efficiency.

### III. MATERIALS AND METHODS

#### ► Polyethylene oxide (PEO)

Polyethylene oxide contains a regular ordered repeating units of -(CH<sub>2</sub>-CH<sub>2</sub>-O)-. PEO is nontoxic, odorless white powder. Its T<sub>g</sub> and T<sub>m</sub> are 65°C and -60°C respectively. It is semi crystalline in

nature with about 70-85% crystallinity and amorphous elastomeric phase at ambient temperature [10, 11]. Because of its semicrystalline behaviour in the structure, the problem arises at macroscopic and microscopic levels. Microscopic level represents arrangement of atoms present in the PEO, whereas macroscopic level represents the semi/crystalline and amorphous stage in the pure polymer and polymer-salt complex. PEO polymer behaves like a Lewis base, these oxygen atoms present in the PEO host mutual interaction with cations/anions present in the complex inorganic salts.

► **Lithium perchlorate (LiClO<sub>4</sub>)**

High purity of LiClO<sub>4</sub> (molar mass =106.39 g/mol) salt was procured from Sigma Aldrich U.S.A. The structure of LiClO<sub>4</sub> is shown in Fig. 3.2, LiClO<sub>4</sub> is an inorganic salt and highly soluble in many organic liquids. Its melting and boiling point are 236°C and 430°C respectively. Due to its higher electrochemical stability and conductivity properties, it is used as electrolyte material in the Li-batteries.

► **Cobalt oxide (CoO)**

Cobalt oxide (CoO) is procured from Alfa Aesar (95% purity). In industries, CoO is widely used as an inorganic metal oxide.

► **Methanol**

Methanol is a simple polar liquid. Generally it is considered as the common solvent for synthesis of polymer electrolytes. Methanol is also called as methyl alcohol. Its molecular mass is 32.04 g/mol, boiling point is 64.7°C and melting point is -97.6°C

**SYNTHESIS OF PE SYSTEM**

This PE system is employed to know the best optimized ratio of PEO to LiClO<sub>4</sub> (in terms of ionic conductivity). Solid polymer electrolyte systems [(100-x)% PEO+ (x)% LiClO<sub>4</sub>, where x=0, 5, 7.5, 10, 12.5 and 15] are prepared. The required amounts of PEO and LiClO<sub>4</sub> are dissolved in the methanol solvent and obtained solutions are magnetically stirred for 30-35h at room temperature. The homogeneous mixture solution obtained from above reaction is transferred into petri-plates. Which are dried under normal atmospheric conditions for 3 days and thin films are takeout carefully from the plates and preserved in desiccators. The prepared various SPE films are presented in the Table 3.1. Conductivity studies of above prepared SPE samples reveal that, [85%PEO+15% LiClO<sub>4</sub>] SPE sample is identified as the best optimized sample. This SPE sample is further used for addition of fillers and plasticizers.

**Table 3.1 Polymer electrolyte system-I**

S. No.	Composite name	PEO (wt%)	LiClO <sub>4</sub> (wt%)
1	PO (pure PEO)	100	0
2	PL-4	95	5
3	PL-3	92.5	7.5
4	PL-2	90	10
5	PL-1	87.5	12.5
6	PL	85	15

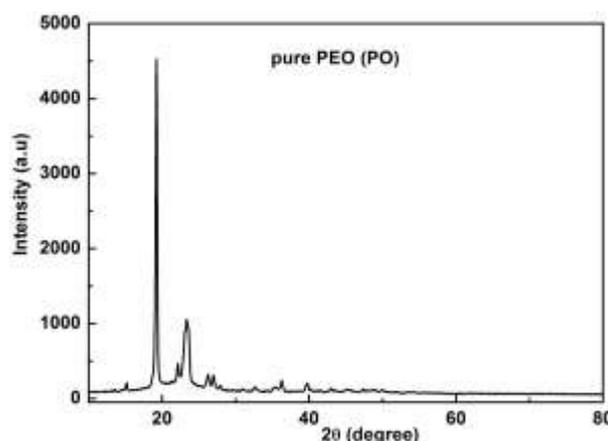
**IV. CHARACTERIZATION TECHNIQUES**

Characterization technique	Instrument	Description
XRD	SHIMDZU XRD 7000	X-ray diffractometer in 2θ range of 10-60° using CuKα radiation
SEM	Hitachi S-4700	The surface identifications of the SPE films were studied by SEM
DSC	DSC7 (Perkin Elmer)	Over a temperature range of 193K to 373K at a heating rate of 10° C min <sup>-1</sup> .
Complex impedance spectroscopy	(HIOKI- 3532-50) LCR HiTESTER	Frequency range of 100Hz to 5MHz in the temperature range in between 303K to 353K.

**V. RESULTS AND DISCUSSION**

**5.1 X-ray diffraction (XRD) analysis**

XRD technique is widely used tool to know the quantitative/qualitative information about the materials. It gives the information about structure, degree of crystallinity, crystallite size and micro strain of the crystalline compounds. XRD spectra of polymer materials consist of both spiky (sharp) and defused peaks, in which spiky peaks correspond to semicrystalline regions and defused peaks represents amorphous regions.



**Fig. 5.1 XRD spectrum of pure PEO (PO) film**

The XRD spectra of prepared host PEO and [PEO+LiClO<sub>4</sub>] (PL-4, PL-3, PL-2, PL-1 and PL) SPE films are recorded and compared the structure of polymer complexes. The X-ray diffraction peaks of pure PEO are represented in Fig 5.1. From Fig

4.1 it is observed that characteristic diffraction peaks are present in the range of 15- 30° and two high intense diffraction peaks are observed at 2θ equal to 19.2° and 23.3° which indicates semi crystalline nature of PEO [12]. This crystalline nature of PEO is due to ordered arrangement of poly ether side chains.

The [(1-x) PEO+xLiClO<sub>4</sub> where x=5, 7.5, 10, 12.5 and 15] SPE films are represented in Fig 5.2. The diffraction peak intensities decreases and peak widths are broaden on loading of LiClO<sub>4</sub> content in the PEO. This is attributed to co-ordination interactions of Li<sup>+</sup> ions and ether oxygen side chains, which results in an increase of amorphous phase in the SPE films.

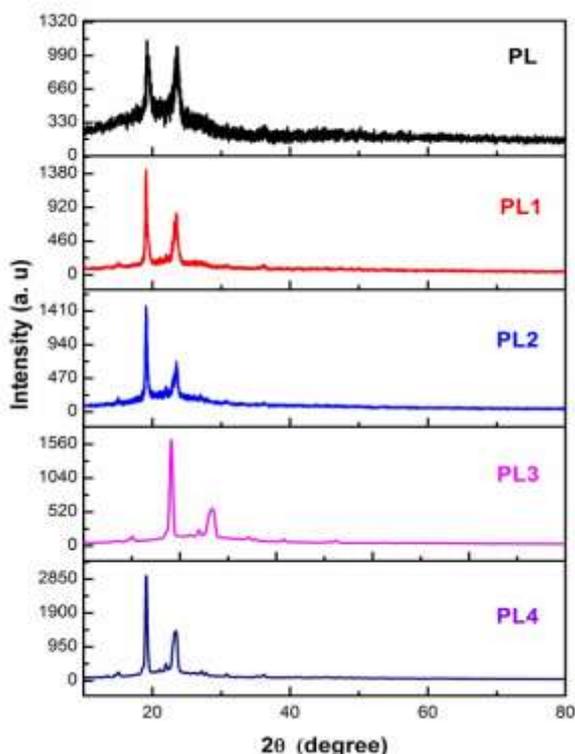


Fig.5.2 XRD spectra of PEO/LiClO<sub>4</sub> films

## 5.2 Scanning Electron Microscopy (SEM) analysis

The surface morphology of SPE films are show in Fig. 5.3 Micrograph of pure PEO (Fig.5.3.a) showed a rough surface contains many crystalline domains. On the addition of LiClO<sub>4</sub>, the SPE adopted spherulitic structure, diameter of the spherulites and its encroachment to adjacent spherulites increases with increase in LiClO<sub>4</sub> concentration. This may be due to LiClO<sub>4</sub> acting as a nucleating centre during film formation.

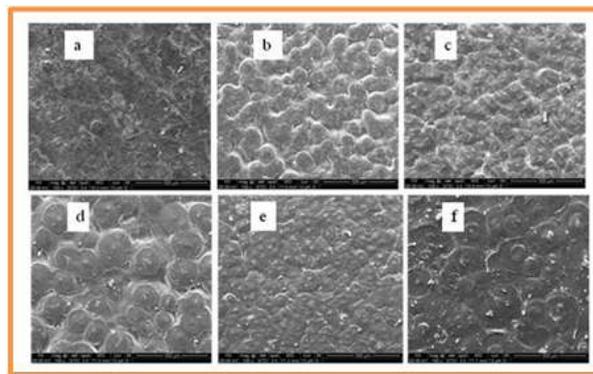


Fig.5.3 (a – f) SEM images of pure PEO (PO), PL-4, PL-3, PL-2, PL-1 and PL SPE films

## 5.3 Differential Scanning Calorimetry (DSC) Analysis

Thermal measurements such as a melting enthalpy, percentage of degree of crystallinity, glass transition temperature (T<sub>g</sub>) and melting temperature are studied by using DSC characterization analysis.

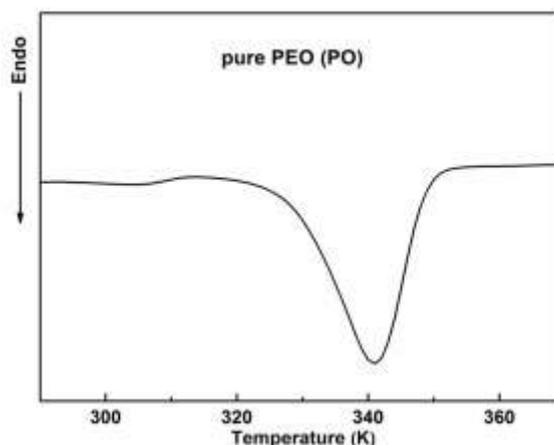


Fig.5.4 DSC curve of pure PEO polymer

The DSC plot of pure PEO (PO) is shown in Fig. 4.4. The DSC curve of host PEO shows an endothermic peak at around 341K, which represents a melting temperature of crystalline phase of Pure PEO. Fig. 4.5 shows typical DSC curves of PEO/LiClO<sub>4</sub> SPE systems. It is evident that the endothermic peak of PEO is broadened and peak height is decreased by adding LiClO<sub>4</sub> into polymer host. The observed endothermic peaks ascribed to conversion of crystalline state to amorphous state. In SPE system the melting temperature (T<sub>m</sub>) and melting enthalpy (ΔH<sub>m</sub>) gradually decreases with increase in LiClO<sub>4</sub> content. The observed lower melting enthalpy in [85%PEO+15%LiClO<sub>4</sub>] (PL) SPE system, may be due to co-ordination between Li ions and oxygen units present in the PEO chains, which can strongly resist restructuring of PEO side chains and results to formation of amorphous phase.

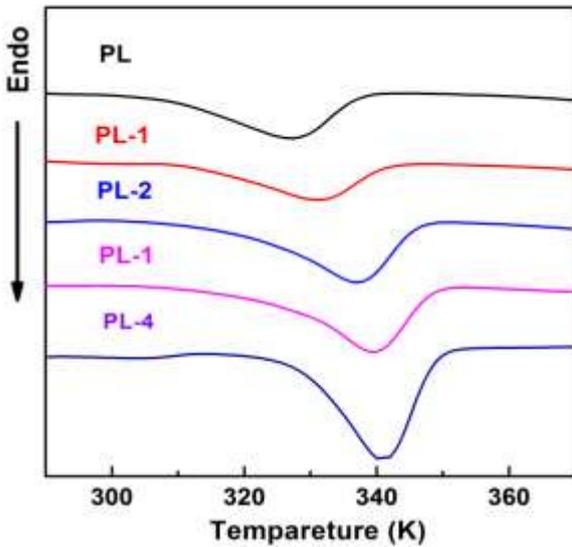


Fig.5.5 DSC curves of PEO/LiClO<sub>4</sub> SPE films

Percentage of degree of crystallinity ( $\chi_c$ ) is calculated on the basis of minimum quantity of heat energy needed to melt the given substance.

The percentage of degree of crystallinity ( $\chi_c$ ) is defined as the ratio of melting enthalpy of PEO+LiClO<sub>4</sub> complex to the melting enthalpy of pure PEO.

$\chi_c$  can be calculated by given equation

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_p} \dots\dots\dots(5.1)$$

Where,  $\Delta H_p = 203$  J/g (melting enthalpy of pure PEO of 100% crystallinity),  $\Delta H_m =$  melting enthalpy of composite.

The calculated values of  $\chi_c$ ,  $T_m$  and  $\Delta H_m$  are summarized in Table 5.1. From Table 5.1, it is observed that melting temperature of polymer host is found to be decreasing from 341- 327 K due to loading of LiClO<sub>4</sub>. The percentage degree of crystallinity of PEO decreases from 75 to 27% on loading of LiClO<sub>4</sub> salt content and also melting enthalpy changes from 153 to 55 J/g.

Table 5.1 Comparison of thermal parameters of PEO/LiClO<sub>4</sub> system

Sample SPE system	$\chi_c$ (%)	$T_m$ (K)	$\Delta H_m$ (J/g)
PO (pure PEO)	75.70	341.00	153.70
PL-4	68.30	340.05	138.60
PL-3	50.60	339.50	118.40
PL-2	58.30	337.10	102.70
PL-1	31.90	331.10	64.84
PL	27.00	327.10	54.95

### 5.4 Impedance and Ionic conductivity studies

Impedance spectra of [PEO-LiClO<sub>4</sub>] SPE films at various temperatures are represented in fig.4.6. It is observed from the fig.4.6 that, all the samples exhibits similar type of behaviour i.e., inclined straight lines at lower frequencies shows electrode polarization effect (EP) and small arcs at higher frequencies represents the bulk properties of the samples [166-D9-ref12]. The bulk resistance ( $R_b$ ) of SPE film is directly calculated from the graphs, the points of intersections of the arcs and inclined straight lines coincides at the X-axis ( $Z'$ ) are known as bulk resistance of the given sample. While on increasing the temperature, the point of intersection on the X-axis shifted towards higher frequency region. This indicates that  $R_b$  of SPE films decreases with increase of temperature. The ionic conductivity of the SPE films are estimated from the given formula

$$\sigma_{dc} = \frac{d}{A R_b} \dots\dots\dots(5.2)$$

Where  $A =$  area of cross-section of SPE film,  $d =$  thickness,  $R_b =$  bulk resistances, which is determined from the cole-cole plots. The dc ionic conductivity increases with temperature. The ionic conductivity at different temperature with variation of wt% content of LiClO<sub>4</sub> is represented in Fig.4.7 and conductivity data is summarized in Table 5.2. LiClO<sub>4</sub> plays a crucial role in improving of dc ionic conduction. Loading of LiClO<sub>4</sub> in to the PEO matrix increases the ionic conductivity. This behaviour may be due to the charge transportation in PEO/LiClO<sub>4</sub> complexes involving dissociation of Li<sup>+</sup> ions from its counterparts of oxygen atoms present in PEO. In the SPE samples, the transportation of ions behaves like liquid type behaviour. By which the movement of ions through polymer matrix is associated with large amplitudes of the segmental motion. Maximum conductivity is obtained for 15 wt% of LiClO<sub>4</sub> (PL). Generally, conductivity depends on percentage of degree of crystallinity. The increase in conductivity of SPE with salt concentration is due to a decrease in degree of crystallinity, which is proved by DSC analysis.

### 5.5 Temperature dependent of conductivity

The inverse temperature verses conductivity graphs of PEO-LiClO<sub>4</sub> SPE films are represented in the Fig.4.8. The conductivity is found to be increasing with temperature in all the SPE films. From Fig.4.8 it is observed that the graphs obey Arrhenius equation of conductivity. The Arrhenius equation is given by following formula.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{K_B T}\right) \dots\dots\dots(5.3)$$

Where

$KB$  = Boltzmann constant,

$T$  = absolute temperature,

$\sigma_0$  = pre-exponential factor,

$E_a$  = activation energy.

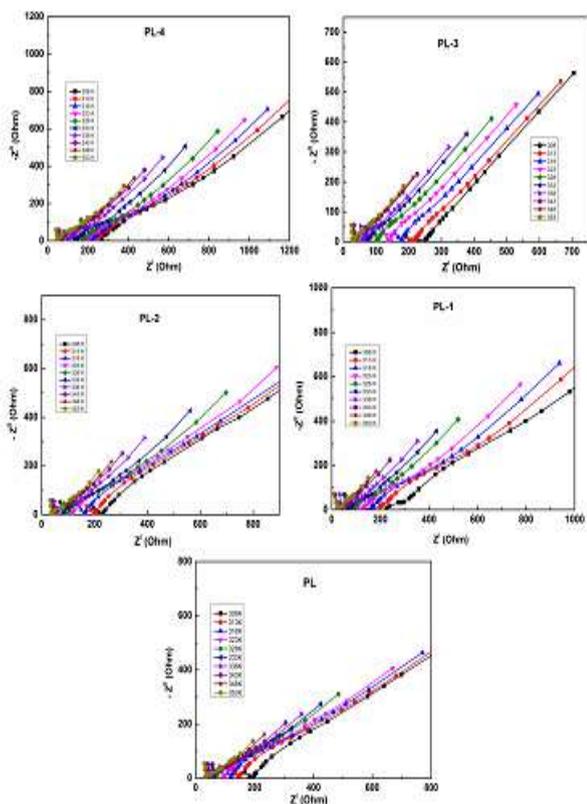


Fig 5.6 Impedance spectra of PL-4, PL-3, PL-2, PL-1 and PL at different temperatures

The conductivities increase slowly up to their melting points and above that the conductivity increases rapidly and after that PEO/LiClO<sub>4</sub> SPE films begin to soften. Activation energy ( $E_a$ ) values of different SPE films are calculated using linear fit program in origin software and listed in Table 4.3. Inspection of Table 4.3 shows that,  $E_a$  values of SPE films are found to be decreased from 0.67 to 0.15 eV with an increase of LiClO<sub>4</sub> concentration. The lower  $E_a$  values of Li<sup>+</sup> ion transport are due to the amorphous nature of polymer electrolytes which facilitates the fast Li<sup>+</sup> motion in polymer matrix. The amorphous nature also provides a more free volume in the polymer electrolyte system with increase in the temperature. It can be observed that 85%PEO+15% LiClO<sub>4</sub> (PL) film having maximum ionic conductivity with lesser  $E_a$  when compared with the other SPE.

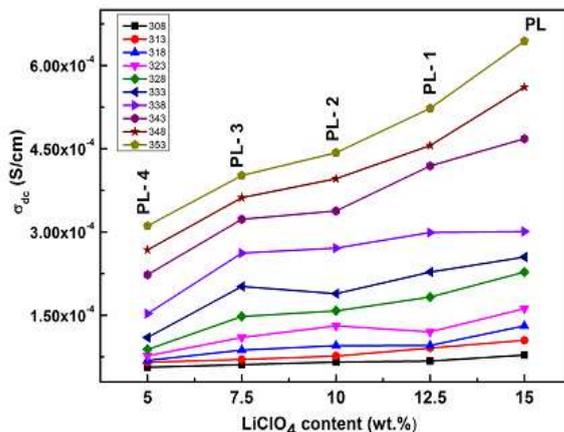


Fig 5.7 Variation of ionic conductivity with LiClO<sub>4</sub> wt% contents at different temperatures

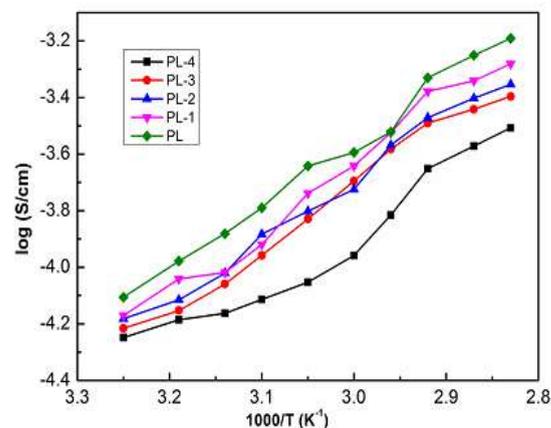


Fig.5.8 Arrhenius plots of PEO/LiClO<sub>4</sub> SPE films.

Table.5.2 Bulk resistance and conductivity of [PEO-LiClO<sub>4</sub>] SPE films at different temperatures

Temperature (K)	Bulk resistance ( $R_b$ ) ( $\Omega$ )					Ionic conductivity ( $\sigma_{dc}$ ) (S/cm)				
	PL-4	PL-3	PL-2	PL-1	PL	PL-4	PL-3	PL-2	PL-1	PL
300	270.40	250.90	232.10	226.00	195.00	5.65E-05	6.09E-05	6.58E-05	6.76E-05	7.84E-05
313	234.00	217.40	199.29	168.00	145.30	6.53E-05	7.03E-05	7.67E-05	9.10E-05	1.05E-04
318	222.06	175.10	160.21	159.48	116.20	6.88E-05	8.73E-05	9.54E-05	9.58E-05	1.31E-04
323	198.45	138.64	116.63	126.90	94.10	7.70E-05	1.10E-04	1.31E-04	1.20E-04	1.62E-04
328	172.41	103.09	96.70	83.63	67.00	8.86E-05	1.48E-04	1.58E-04	1.83E-04	2.28E-04
333	138.51	75.63	81.00	67.04	60.00	1.10E-04	2.02E-04	1.89E-04	2.28E-04	2.55E-04
338	100.01	58.40	56.46	51.10	50.80	1.53E-04	2.62E-04	2.71E-04	2.99E-04	3.01E-04
343	68.50	47.28	45.20	36.50	32.68	2.23E-04	3.23E-04	3.38E-04	4.19E-04	4.68E-04
348	56.99	42.24	38.60	33.53	27.23	2.68E-04	3.62E-04	3.96E-04	4.56E-04	5.61E-04
353	49.20	38.03	34.50	29.20	23.71	3.11E-04	4.02E-04	4.43E-04	5.23E-04	6.44E-04

5.6 Dielectric studies

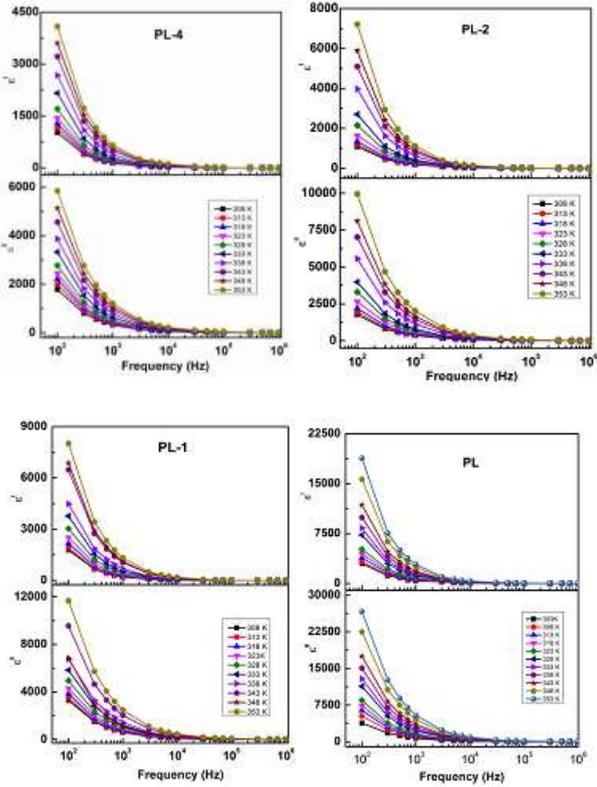


Fig.5.9 Dielectric spectra of PEO/LiClO<sub>4</sub> SPE films

The complex dielectric spectra of SPE films are given by

$$\epsilon^*(\omega) = \epsilon' - j \epsilon'' \quad (5.4)$$

where

$$\epsilon' = \frac{d C_p}{A \epsilon_0} \quad (5.5)$$

$$\epsilon'' = \epsilon' \tan \delta \quad (5.6)$$

where d = thickness of the SPE films, A = area of cross-section of SPE film and  $\epsilon_0 = 8.854 \times 10^{-12}$  F/m (permittivity of free space). The dielectric spectra of SPE films (PL-4, PL-2, PL-1 and PL) are shown in the Fig.5.9. It is observed that the large values of dielectric permittivity ( $\epsilon'$ ) and imaginary part dielectric constant ( $\epsilon''$ ) are observed at the lower frequency region, The charge accumulation takes place at electrode-electrolyte interface and forms electric-double layer causes the electrode polarization effect (EP). At higher frequency region, the ions are not followed by applied field direction and stop responding hence minimum values of ( $\epsilon'$ ) and ( $\epsilon''$ ) are observed.

5.7 AC conductivity analysis

The AC conductivity ( $\sigma_{ac}$ ) of CPE film was calculated by using the formula,

$$\sigma_{ac} = \frac{G d}{A} \quad (5.7)$$

where G = conductance, A = area of cross-section of SPE film, d = thickness of sample. Frequency dependent of  $\sigma_{ac}$  plots of PEO-LiClO<sub>4</sub> at room temperature (308K) is shown in Fig.5.10. It is observed that  $\sigma_{ac}$  is increasing with increase in frequency. It is also identified as two separate regions namely region I (lower frequency) and region II (higher frequency) basing on their slope values. The frequency dependence of  $\sigma_{ac}$  obeys Jonscher's power law expressed using the following relation.

$$\sigma_{ac}(\omega) = \sigma_{dc} + A \omega^{n_1} + B \omega^{n_2} \quad (5.8)$$

Where  $\sigma_{dc}$  is the dc conductivity,  $\omega = 2\pi f$  is the angular frequency, A, B are pre-exponential functions and  $n_1$  and  $n_2$  are the fractional exponents which varies between 0 and 1.

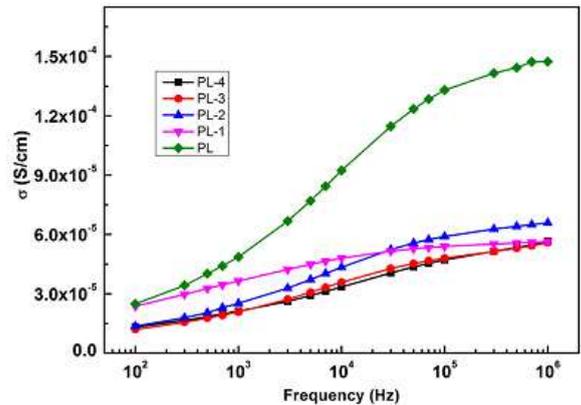


Fig.5.10 Frequency dependence of ac-conductivity plots of PEO-LiClO<sub>4</sub>

If the fractional exponent is less than one, the site relaxation time is faster than backward hopping, which is a consequence of the translational motion of Li<sup>+</sup> ion. If the fractional exponent is more than one, the site relaxation time is slower than backward hopping rate. The activation energy ( $\Delta E$ ) in the two regions is calculated using following equation.

$$\Delta E = (4.9)$$

Where

T = absolute temperature,

$K_B$  = Boltzmann constant

$n$  = exponent factor.

These values are tabulated in Table 5.3 Activation energy represents the inter site hopping energy required by an ion in the polymer matrix.

**Table 5.3**  $E_a$ ,  $n_1$ ,  $n_2$  and  $A$ ,  $B$  and  $\Delta E$  values of PEO-LiClO<sub>4</sub>

Sample	Region-I			Region-II			$E_a$ (eV) From dc conductivity
	$A \times 10^{-5}$	$n_1$	$E_1$ (eV)	$B \times 10^{-5}$	$n_2$	$E_2$ (eV)	
PL-4	0.53	0.29	0.22	1.66	0.08	0.17	0.19
PL-3	0.40	0.24	0.21	2.09	0.07	0.17	0.18
PL-2	0.44	0.24	0.21	2.88	0.06	0.17	0.19
PL-1	1.28	0.24	0.20	3.75	0.03	0.16	0.18
PL	2.99	0.37	0.24	0.10	0.07	0.16	0.15

## VI. CONCLUSION

[PEO-LiClO<sub>4</sub>] SPE films are synthesized by solution cast method. Structural identification, thermal behaviour and morphological studies are carried out by XRD, DSC and SEM characterization techniques. From dc ionic conductivity studies reveals that, PL-SPE film showed highest ionic conductivity than other SPE films. Temperature dependent of ionic conductivity curves obeys the Arrhenius type of behaviour. The frequency dependence of dielectric spectra of SPE films follows electrode polarization effect (EP) at lower frequency region.

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