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Electrical Properties of PEO-Based Electrolytes

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ABSTRACT: Polyethylene oxide (PEO) based electrolytes are used as electrolyte materials for Li-ion batteries. [PEO+LiClO₄] solid polymer electrolyte films were prepared by solution casting method using methanol as a solvent. The structural and thermal properties were studied by XRD and DSC techniques. XRD and DSC results reveals that degree of crystallinity is decreases on loading of salt content into the polymer host. Temperature dependence of conductivity plots of SPE films follows Arrhenius equation. Impedance spectroscopic studies were carried out as a function of frequency and temperature using Hioki LCR Hitester. The dielectric properties were studied using the complex dielectric permittivity spectra of the SPE films. It is observed that magnitude of dielectric permittivity is high in the lower frequency region due to electrode polarization (EP) effect. The dielectric permittivity and loss were increased with increase of temperature.

KEYWORDS: PEO, LiClO₄, ionic conductivity, impedance, dielectric.

I. INTRODUCTION

Polymer electrolytes have gained technological importance as electrolyte materials for the solid state electrochemical devices such as batteries, smart windows and photo-electrochemical cells [1]. The advantages of using solid polymer electrolyte (SPE) over their counterpart of liquid electrolytes are flexibility, no leakage, ease of processing as thin films of large surface area, electrochemical stability and volumetric stability over repeated charge-discharge cycles in a given device. A large number of Li⁺, Na⁺ and H⁺ conducting polymer electrolytes, formed by the dissolution of alkali metal salts in various polymer hosts have been reported in literature [2]. In order to achieve a good complexed polymer-metal-salt system, the choice of polymer host and the metal salt plays a key role. The choice of polymer host depends mainly on factors such as atoms or group of atoms with sufficient electron donor capacity to form coordination bond with cations, low barrier to bond rotations, so that segmental motion of the polymer chain can take place easily, suitable distance between coordinating centers, to facilitate the formation of multiple intrapolymer ion bonds. In this context, a variety of polymers such as poly (ethylene oxide) (PEO), poly (ethylenimine), poly (propylene oxide), poly (ethylene succinate), have been examined as polymer hosts [3]. The high molecular weight polyethylene oxide (PEO) has widely been investigated because of its ability to dissolve high concentrations of a wide variety of a metal salts. Such electrolytes have mainly been confined to alkali metal salt systems, with particular attention being focused on lithium. However, this polymer showed low ionic conductivity in the range of 10⁻⁸ ohm⁻¹ cm⁻¹ to 10⁻⁷ ohm⁻¹ cm⁻¹ which restricted the mobility of ions [4]. Attempts have been made to increase the ionic conductivity of PEO by adding metallic salts. Certain Li⁺ conducting electrolyte systems have been explored in order to understand the structure, conduction mechanism and its application in solid state lithium batteries. The conductivities of PEO with Lithium trifluoromethanesulfonate (LiCF₃SO₃) LiTf bis(trifluoromethanesulfonylimide) (Li(CF₃SO₂)₂N)

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(LiTFSI), Lithium perchlorate (LiClO_4) and Lithium bis(oxalato)borate ($\text{LiB}(\text{C}_2\text{O}_4)_2$) (LiBOB) salts are reviewed in the literature; the highest conductivity was recorded for LiTFSI and the lowest for LiBETI.[5].

The conduction mechanism in polymer electrolytes can be understood by knowing the dielectric relaxation phenomena. The study of the dielectric relaxation phenomenon in SPE materials is an efficient tool to understand the characteristics of ionic and molecular interactions. The dielectric constant plays an important role, by identifying the ability of a polymer host material to dissolve salts [6]. The ac conductivity frequency relaxation spectroscopy gives valuable information regarding ion dynamics and segmental relaxation process.

The present manuscript reports the work carried out on SPE films of pure PEO and various compositions of complexed PEO with LiClO_4 salt of wt% ratios (95:5), (90:10), were synthesized and characterized by means of X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The complex impedance spectroscopy studies were carried out using Hioki LCR Hitester. The systematic studies of the impedance spectroscopy and dielectric properties of solid polymer electrolyte using complex impedance spectroscopy have been presented.

II. EXPERIMENTAL

Materials: Pure reagent materials of Poly (ethylene oxide) PEO (with average molecular weight of 8×10^6 , Sigma Aldrich, USA), LiClO_4 (ACS reagent, $\geq 95.0\%$, Sigma Aldrich, Japan), methanol (HPLC grade, SDfine) were used as starting materials to prepare solid polymer electrolytes.

2.1 Preparation of solid polymer electrolyte

The SPE films of $[\text{PEO} + x\% \text{LiClO}_4 \text{ where } x = 0, 5, 10 \text{ wt\% of PEO}]$ were prepared in the by solution cast technique using methanol as a solvent. The required amount of PEO and salt were dissolved in the methanol solvent and solutions were magnetically stirred for 35 h at room temperature to get viscous solution with high homogeneity. The viscous solution was poured into petri dish and left to dry at room temperature for 3 days to allow the slow solvent evaporation. The prepared SPE films with different salt concentrations were then kept in desiccators. Bubble free regions of the films were employed for the characterization techniques.

2.2 Characterization techniques

The X-ray diffraction spectra of these SPE films were carried out using (SHIMDZU XRD 7000) X-ray diffractometer in 2θ range $10-80^\circ$ using $\text{CuK}\alpha$ radiation. Differential Scanning Calorimetry (DSC) studies were performed using *NETZSCH DSC204* over a temperature range of -100 to $+100^\circ \text{C}$ and at a heating rate of $10^\circ \text{C min}^{-1}$. The samples of about 10–15mg were sealed in an aluminum pans and all experiments were carried out under nitrogen gas atmosphere. The complex impedance measurements were performed using computer controlled (HIOKI-3532-50) LCR HiTESTER in the frequency range 100Hz to 1MHz and in the temperature range 308K- 353K.

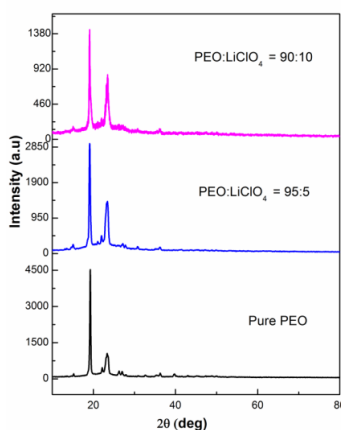


Fig.1 XRD plots of PEO: LiClO_4

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III.RESULTS AND DISCUSSION

3.1 X-ray diffraction

Generally polymer electrolytes are composed of amorphous phase and crystalline phase. XRD technique is widely used to study the phase compositions of polymer electrolytes. Inherent relations between the crystal structure and the diffraction pattern can be solved by analysing the diffraction peak characteristics. The XRD patterns of SPE films of [PEO: LiClO₄] ratios of (100:0), (95:5) and (90:10), are shown in Fig 1. The XRD pattern reveals that there is decline in characteristic crystalline diffraction peaks of SPE with increase of LiClO₄ concentration. As to pure PEO, there are two high intensity characteristic peaks appearing at $2\theta=19.19^\circ$ and 23.33° . XRD pattern indicates that the pure PEO polymer electrolyte has strong ability of crystallization. The high degree of crystallinity is not suitable for ion transfer as it mainly happens in the amorphous regions. Addition of LiClO₄ has considerably decreased the crystallinity of the polymer electrolyte and XRD pattern of complexes showed broadening and reduction of PEO peak intensity. This can be attributed to distribution of the ordered arrangement of polymer side chain and homogeneous dispersion of LiClO₄ in the PEO host.

3.2 Thermal analysis

DSC traces of [PEO: LiClO₄] wt % ratios of (100:0), (95:5) and (90:10) are shown in Fig. 2. The DSC curve of pure PEO showed a melting temperature around 341 K. In SPE films the melting temperature (T_m) and melting enthalpy (ΔH_m) gradually decreased with increase in LiClO₄ loading. The observed low melting enthalpy in SPE film of wt% ratio (90:10) as compared to PEO indicates that the presence of Li⁺ ions reduces the crystallinity considerably.

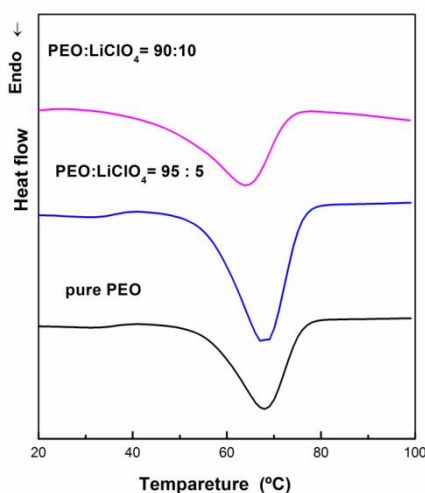


Fig.2 DSC plots of PEO: LiClO₄

DSC provides a rapid method for determining degree of crystallinity based on the amount of heat required to melt the crystalline sample. In other words, the melting enthalpy is proportional to the crystallinity of sample [7]. The melting enthalpy (ΔH_m) of the crystalline phase of SPE films can be evaluated by considering the area under the melting peak. The degree of crystallinity (χ_c) has been calculated by taking into account pure PEO as 100% crystallinity [8] and using equation

$$\chi_c = \frac{\Delta H_c}{\Delta H_p} \quad (1)$$

Where, ΔH_p equals to 203 J/g which is melting enthalpy of pure PEO of 100% crystallinity and ΔH_c is melting enthalpy of composites. The calculated relative crystallinity (χ_c), melting temperature (T_m), change in melting enthalpy (ΔH_m) of crystalline phase of polymer evaluated during the heating process from -100°C to $+100^\circ\text{C}$ are summarized in Table 1.

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From Table 1, it is observed that the endothermic peak of PEO is broadened and peak height is decreased by doping of LiClO_4 into polymer host. The melting temperature of polymer host is found to be decreasing from ~ 341 K to ~ 337 K due to the addition of LiClO_4 salt.

Table. 1 Comparison of thermal parameters of PEO: LiClO_4 system

Sample PEO: LiClO_4	χ_c (%)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)
100 : 0	75.7	68.0	153.7
95 : 05	68.3	67.05	138.6
90 : 10	58.3	64.1	102.7

3.3 Impedance spectroscopy

Impedance spectra of different compositions of [PEO: LiClO_4] solid polymer electrolyte film at various temperatures are shown in Fig. 3(a, b). The electrochemical characterization of ion conducting polymer electrolytes can be studied from these plots. From the impedance plots we can determine, bulk resistance (R_b), ionic conductivity, electrode-electrolyte contact behaviour and type of charge carriers (ions or electrons) of polymer electrolytes [9,10].

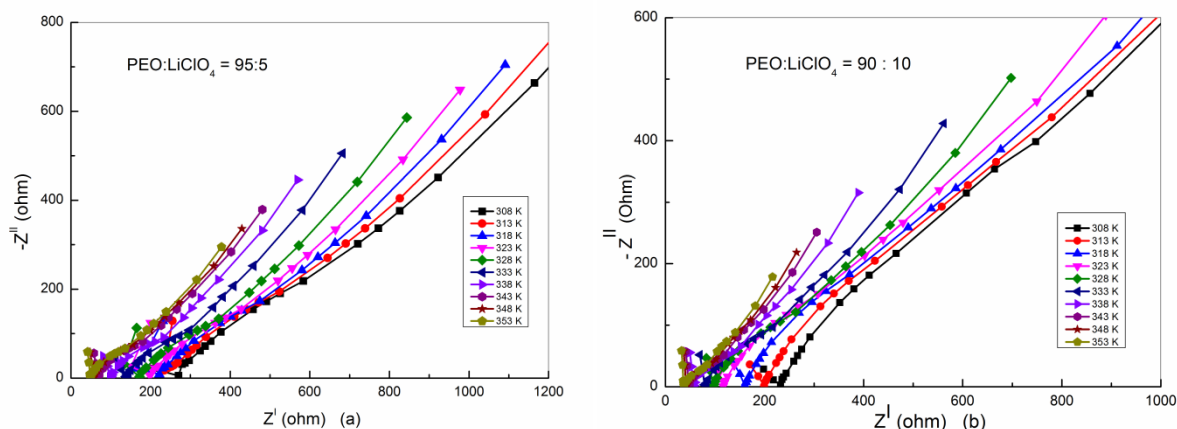


Fig. 3 (a, b) Impedance plots of PEO: LiClO_4

In impedance plots a compressed semicircular arc represents the bulk properties of the electrolyte film at the high frequency region. An inclined straight line in the low frequency region is due to the dominance of EP effect. The complete semi-circle is not observed in the high frequency region. This indicates that the applied frequency and temperature are insufficient for the complete circular arc. The bulk resistance intercept on X-axis is shifting towards the lower Z' region with increasing of temperatures. However it is known that the region below the intercept represents the impedance due to EP effect while above the intercept gives the impedance due to bulk of the SPE [11]. The bulk resistance R_b of the polymer electrolyte at different temperatures was obtained directly from the common intercept of the arc and the inclined straight line with the Z' -axis. The ionic conductivity of the SPE is calculated using the relation [12],

$$\sigma_{dc} = \frac{t}{A R_b} \quad (2)$$

where t is the thickness of the SPE film, A is the area of electrode contacting with SPE film. The R_b values of [PEO- LiClO_4] SPE film decrease with increasing of temperature. The R_b values and the ionic conductivity of the PEO- LiClO_4 SPE system at different temperatures are presented in Table. 2. The highest ionic conductivity of 6.58×10^{-5} S/cm at 308 K has achieved at (90:10) electrolyte system.

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Table. 2 Bulk resistance (R_b) and ionic conductivity (σ_{dc}) values of PEO: LiClO₄ system at different temperatures.

Temperature (K)	R_b (ohm) [PEO:LiClO ₄] (95:5)	R_b (ohm) [PEO:LiClO ₄] (90:10)	σ_{dc} (s/cm) [PEO:LiClO ₄] (95:5)	σ_{dc} (s/cm) [PEO:LiClO ₄] (90:10)
308	270.4	232.1	5.65×10^{-5}	6.58×10^{-5}
313	234.0	199.3	6.53×10^{-5}	7.67×10^{-5}
318	222.0	160.2	6.88×10^{-5}	9.54×10^{-5}
323	198.45	116.63	7.70×10^{-5}	1.31×10^{-4}
328	172.4	96.7	8.86×10^{-5}	1.58×10^{-4}
333	138.51	81.0	1.10×10^{-4}	1.89×10^{-4}
338	100.0	56.4	1.53×10^{-4}	2.71×10^{-4}
343	68.5	47.28	2.23×10^{-4}	3.23×10^{-4}
348	56.99	42.24	2.68×10^{-4}	3.62×10^{-4}
353	49.2	38.0	3.11×10^{-4}	4.02×10^{-4}

3.4 Temperature dependence of conductivity

The temperature dependence of ionic conductivity of different compositions of [PEO+LiClO₄] polymer electrolytes at different temperatures is shown in Fig 4. It is observed that, the conductivity is found to increase of temperature in all electrolyte systems. It is also observed that the plots follow Arrhenius type behaviour with two regions and two activation energies [13]. The temperature dependent conductivity can be expressed by Arrhenius equation.

$$\sigma_{dc} = \sigma_0 \exp \left(\frac{-E_a}{KT} \right) \quad (3)$$

where σ_0 is the pre-exponential factor, E_a the activation energy, K Boltzmann constant and T is the absolute temperature.

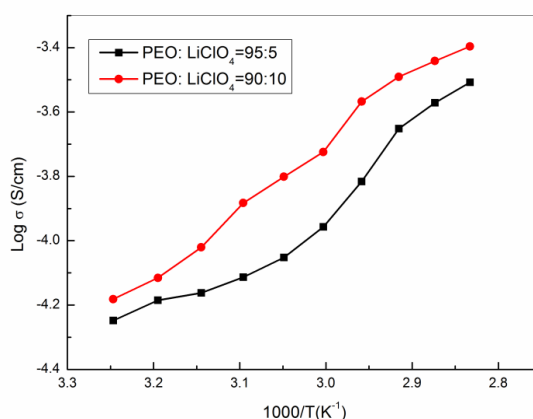


Fig. 4 Temperature dependence of conductivity of [PEO: LiClO₄]

The increase in the conductivity versus temperature plots may be attributed to the transitions from semi-crystalline phase to amorphous phase. The increasing of conductivity with temperature is interpreted as a hopping mechanism between co-ordination sites, local structural relaxation and segmental motion of polymer [14]. The polymer chain acquires faster internal modes in which bond rotations produce segmental motion. The activation energies are presented in Table.3.

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Table. 3 activation energy (E_a) and n values of [PEO: LiClO₄]

Sample [PEO:LiClO ₄]	Region I E_a	Region II E_a	Region I n_1	Region II n_2
95:05	0.07	0.22	0.19	0.08
90:10	0.16	0.15	0.25	0.06

3.5 Dielectric analysis

The complex dielectric permittivity is defined as $\epsilon^*(\omega) = \epsilon' - j\epsilon''$, where ϵ' is the real part of the dielectric permittivity (dielectric constant) and ϵ'' is the imaginary part of the dielectric permittivity (dielectric loss). The dielectric constant was evaluated from capacitance (C_p) using the relation,

$$\epsilon' = \frac{t C_p}{A \epsilon_0} \quad (4)$$

where t is the thickness of the SPE film, A is the area of electrode contacting with SPE film and ϵ_0 is the permittivity of free space $8.854 \times 10^{-12} \text{ Fm}^{-1}$.

$$\text{Loss factor } \epsilon'' = \epsilon' \tan \delta \quad (5)$$

Fig. 5(a, b), shows the complex permittivity spectra of the PEO-LiClO₄ solid polymer electrolyte at different temperatures.

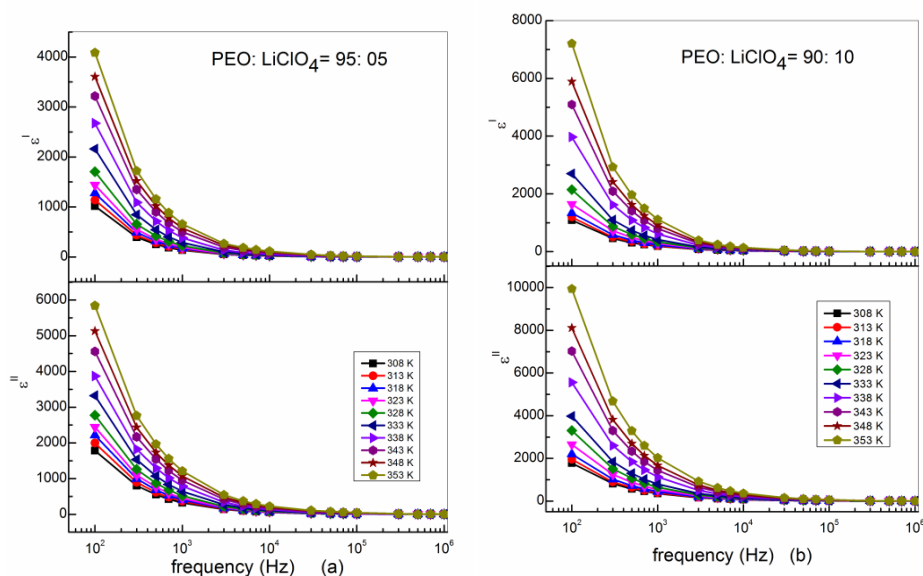


Fig.5 (a, b) Dielectric spectra of [PEO: LiClO₄]

From this it is evident that a large ϵ' and ϵ'' values are observed at low frequencies. At these low frequencies, dipoles follows the field direction and the values of ϵ' and ϵ'' are found to be very high due to the electrode-polarization phenomenon [11].

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At moderate frequencies, dipoles begin to lag behind the field so the values of ϵ' and ϵ'' start to decrease. However, in the high frequency range dipoles cannot orient themselves in the applied electric field direction and hence the values of ϵ' and ϵ'' are constant and reach its minimum values [15]. It is also observed from Fig. 6 (a, b), that the values ϵ' and ϵ'' are gradually increase with temperature, which is attributed to migration and interfacial polarization of lithium ions. This type of trend is observed in the polar dielectrics in which orientation of dipoles facilitated with increasing temperature and thereby the values of ϵ' and ϵ'' are increased. In addition, the ϵ'' has shifted to a higher frequency region with increase of temperature, which confirms the thermally activated dynamical behaviour of the PEO-LiClO₄ electrolyte system. The conductivity in PEO-LiClO₄ solid polymer electrolyte is due to the migration of Li⁺ ions.

3.4. AC conductivity analysis

AC ionic conductivity (σ_{ac}) of PEO-LiClO₄ SPE film at different temperature is shown in Fig. 6. The σ_{ac} values indicate a progressive rise in ac conductivity with increase in frequency up to a certain frequency and then it remains almost steady. In the high frequency region the PEO-LiClO₄ electrolytes follows the Jonscher's universal power law [16].

$$\sigma_{ac}(\omega) = \sigma_{dc} + A \omega^{n_1} + B \omega^{n_2} \quad (8)$$

where A is pre-exponential function and n is the fractional exponent which varies between 0 and 1. In the present study it is noticed that there are two linear regions with frequency.

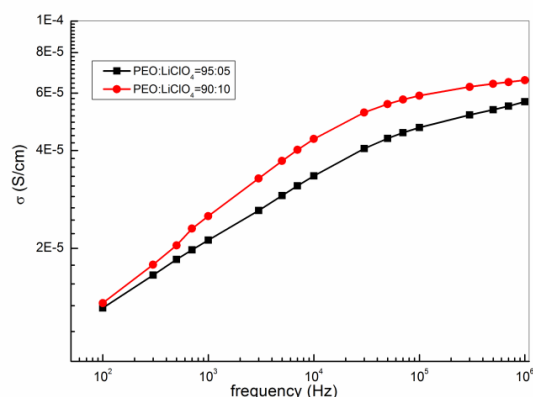


Fig.6 Ac-conductivity spectra of PEO:LiClO₄

The low frequency region (Region I) up to 30 KHz with the exponent values represented by n_1 . While the high frequency region is denoted as Region II represented by the second exponent n_2 . The two slopes indicate that the conduction takes place due to two different hopping frequencies. The n value physically represents the strength of ion-ion and ion-dipolar interactions [17]. The calculated exponents n_1 and n_2 in low and higher frequency regions are tabulated in Table.3. At high frequency region the n values of electrolyte film increases with temperature. This weakens ion-ion and ion-dipolar interactions and increases polymer segmental motion of SPE films. The n values of the electrolytes are observed to be less than one suggesting the ion transportation is happening through hopping mechanism [18].

IV.CONCLUSIONS

SPE films were prepared by solution casting method. The broadening and reduction in intensity of the Bragg peaks confirms the dissolution of LiClO₄ salt in the polymer host. The DSC results have further confirmed a reduction in the crystallinity. The temperature dependence of conductivity plots follow the Arrhenius behaviour throughout with two activation energy ranging between 308 and 353K. The ionic conductivity increases and activation energy decreases with the increase in salt concentration. The decrease in dielectric permittivity with frequency is described to polar nature of the sample. Large magnitudes of ϵ' and ϵ'' values are observed in the low frequency region is due to EP effect.

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The ac conductivity follows Jonscher's universal power law in the higher frequency region with a small deviation in the EP dominated low frequency region.

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