

Optical, DC Conductivity and Electrochemical Parameter of Polymer Electrolyte Complexes*

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Abstract: Here reporting the results of optical, dc electrical conductivity and electrochemical properties of lithium sulphate (Li_2SO_4) doped polyethylene oxide (PEO) films have been studied. The pure and doped PEO films were prepared using solution casting technique at different weight percentages. The films are characterized through Fourier Transform Infra-red (FTIR) and Ultraviolet-visible (UV-Vis.) Spectroscopy techniques. The dc electrical conductivity measurement was made by using two-probe technique at different temperatures. The fabrication of electrochemical cell in the configuration anode/polymer electrolyte/cathode and cell parameters was carried out using the Wagner polarization technique. The FTIR results noticed that there is a significant change in the intensities as well as frequencies of spectra and the appearance of new peaks confirm the better complexation of dopant with PEO. The UV-Vis. spectra reveal that the absorption bands positioned at different absorption intensities with addition of dopant. The optical band gaps was evaluated using Tauc's expression and band gap found decreases from 5.42 to 2.41eV (direct) and 4.79 to 4.20eV indirect. The changes in the dipole strength, transition dipole moment, oscillator strength, and Urbach energy have been investigated with dopant concentration. This may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host polymer matrix and established the complexation. The electrical conductivity was found increases with increasing of dopant concentration and estimated the electrochemical cell parameters OCV is 1.62V and SSC is 273 μA . These obtained results suggest that these polymer systems are potential suitable candidates for solid state battery, optoelectronics display and electro chromic devices etc.

Keyword: Optical band gap, optical constants, FTIR, dc conductivity, activation energy, electrochemical parameter.

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1. Introduction

Today, there is a wide consumer demand for electric sources, optical displays, electro chromic devices¹ to power portable devices (laptop computer, cellular phone, etc.) which have created an ever increasing for lightweight and compact batteries². Polymers electrolytes represent a particularly attractive class of electrochromic materials since they are easily deposited as thin films³. At present, the lithium ion battery technology seems to have the potential to satisfy all requirements of high energy or/and high power applications, and to meet the low cost demands compared to other rechargeable battery systems⁴. Lithium-ion batteries of PEO-based polymer electrolytes offer a good mechanical, thermal properties and interfacial stability with lithium metal and wider range of operational temperatures⁵ to enhance conductivity⁶, potential capability⁷ of PEO-LiX (X=ClO₄-BF₄, PF₆, CF₃SO₃, N(CF₃SO₂)₂ etc.). Polymer electrolyte is use of lithium salts (Li-X) here Li₂ SO₄ has used, it contains very large anions which may interfere with and impede crystallization region of the polymer to yield primarily improving of volume of amorphous region within the polymer matrix, this may support to get still increasing conductivity, it is material significance interest to replace the lithium halide, Li-X by lithium sulfate, Li₂SO₄⁸. In solid electrolyte Li₂SO₄ the mobility of Li⁺ ions increases in temp range from 303-338K yielding higher electrical conductivity⁹. This is one of the important requirements for useful alternative materials include a large discharge capacity at potentials not far from that of elemental Li⁺, the ability to sustain high currents, and good reversibility for an attractive rechargeable cycle life mainly in solid state battery¹⁰⁻¹¹. In electrochemical cell the polymer electrolyte is sandwiched between the cathode and anode in the configuration anode/polymer electrolyte/cathode¹². During charging (oxidation), the lithium cations are removed from the oxide layers and introduced into the space of the graphite layers via an electrolyte containing lithium salts. The reverse reaction occurs during discharging (reduction). Thus, lithium-ion cells show good electrochemical abilities for rechargeable battery materials. Lithium metal has a high oxidation potential (3.0 V) and high energy density, making it ideal for this application¹³. In all these views, we report results on the dc conductivity, optical and electrochemical properties of Li₂SO₄ doped PEO. These polymer electrolytes are potential candidature for solid state batteries, electro chromic devices, and optical displays.

2. Experimental

The pure PEO & doped PEO + Li_2SO_4 in 5, 10, 20, 30, 40, and 50 wt % were prepared using the solution–cast technique. The polyethylene oxide (PEO) ($M_w=5 \times 10^6$), white powder had been procured from M/s. Shanghai Research Institute, Shanghai, China. $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Loba chemical M.W.127.96) and methanol (AR, M.W.32) were used. The PEO and Li_2SO_4 were dissolved in methanol (CH_3OH). The mixture is stirred well at room temperature for 12 hours. The stirred solution was cast on polypropylene dishes and allowed to evaporation slowly at room temperature. The films were then dried in a vacuum to eliminate all traces of the solvent and moisture. The UV-visible absorbance measurement was carried out using a UV-VIS (UV 1800 ENG 240V) Shimadzu spectrophotometer in the wavelength range 190-800nm at room temperature. FTIR measurement was carried out by using Shimadzu spectrophotometer [Model 8000] in the range $4000\text{--}400\text{cm}^{-1}$. The dc conductivity measurement was carried out using a Precision Impedance Analyzer (Wayne Kerr 6500B) with PID controlled unit in the temperature range of $30\text{--}64^\circ\text{C}$.

3. Results and Discussion

3.1. Infrared Spectra

The FTIR spectra of PEO and doped PEO are shown in figure 1. FTIR results it is seen that arise of new peaks due to interaction of Li_2SO_4 with PEO. Thus, the FTIR ($1500\text{--}500\text{ cm}^{-1}$) region of the PEO based polymer electrolytes provides a “fingerprint” for different possible PEO chain conformations. The spectra of these materials show characteristic bands at 950 and 850cm^{-1} due to CH_2 rocking vibration modes of the $\text{O-CH}_2\text{-CH}_2\text{-O}$ group. The strong band at 1099 cm^{-1} in doped PEO which is due to combination of symmetric and asymmetric C-O-C stretching modes is known to shift to lower frequencies on complexation with alkali metal cation. In the intercalated compounds, the lowest frequency is observed for Li^{2+} 1468 cm^{-1} is observed due to the interaction of Li^+ with PEO¹⁴. The splitting of the 2890 cm^{-1} band in doped PEO into components has been interpreted as being due to the interaction of the polymer with the dopant.

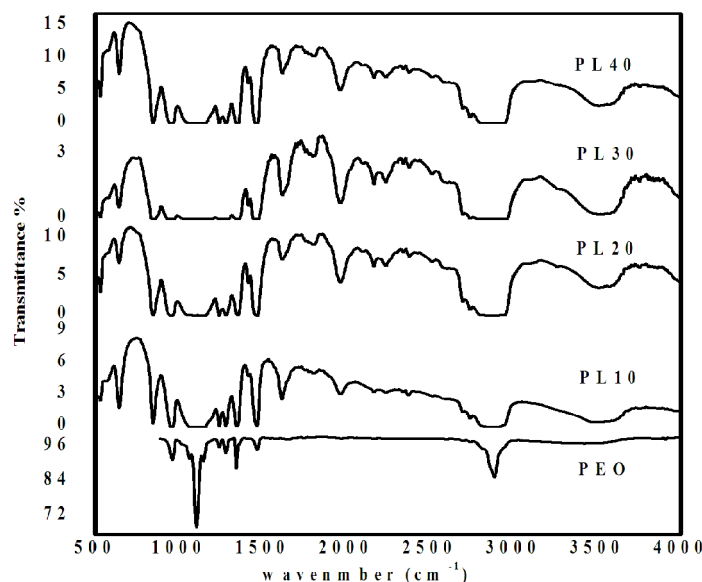


Figure 1 FTIR spectra of Li_2SO_4 doped PEO of PEO (100%), PL10(PEO: Li_2SO_4 = 90:10), PL20(PEO: Li_2SO_4 = 80:20), PL30(PEO: Li_2SO_4 = 70:30), PL40(PEO: Li_2SO_4 = 60:40)wt %.

The band observed at 1620cm^{-1} is assigned to C=C stretching. The vibration bands at 1394 , 1360 , and 1103cm^{-1} corresponds to the asymmetric S=O stretching frequency indicating the presence of two kinds of sulfated species ^[15]. More bands and mode of vibration is listed in the table.

3.2. Optical Properties

3.2.1. Absorption Spectra

The UV-Vis. study can provide the qualitative indications of size distribution, the sharp excitonic peaks in absorption are indeed indicative of the dopant distribution in the samples. *The idea behind being able to predict absorption maxima based on structure is the hope that the absorption will tell us about the structure of molecule. From absorption study it is found increases with increasing of dopant concentration in the UV-vis. region and the absorbance maximum shifts towards lower energy in the visible region i.e., the red shift.*

The red shift is caused by two effects, in the investigated range of 370-405nm wavelength are associated with $n \rightarrow \pi^$ electronic transitions. One is due to unsaturated centre of the molecules, i.e. in compounds containing double or triple bonds of, C=O and/or C=C mainly in the polymer and other is due to the increase in the concentration of Li_2SO_4 ¹⁶, in which the*

excitation of π electrons requires only low energy, and hence, transitions of this type occur at longer wavelengths¹⁷.

In general, $\pi \rightarrow \pi^*$ transitions absorb approximately 10 times more strongly than $n \rightarrow \pi^*$ transitions¹⁸. O/Li^{2+} exhibits a strong tendency for the formation of metal to ligand charge transfer. In the region from 380-650nm, a large broad absorption tail is observed for the doped PEO indicating an extended degree of conjugation in the polymer system. The similar observations have been made in the absorbance curve¹⁹⁻²⁰.

Optical absorption spectra of Li_2SO_4 doped PEO films were employed to determine the optical constants such as direct and indirect optical energy band gap (E_g). The absorption coefficient was determined using the formula

$$(1) \quad a = \frac{A}{d} \times 2.303,$$

where A is absorbance and d is film thickness.

When the direct gap exists, the absorption coefficient has the following dependence on the energy of the incident photon, given by Mott and Davis Model²¹,

$$(2) \quad \alpha h\nu = C (h\nu - E_g)^{1/2},$$

where E_g is the band gap, C ($C = 4\pi\sigma_0/nc\Delta E$) is a constant dependent on spectrum structure, ν is the frequency of the incident light and h is a plank's constant. Thus, a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), as shown in figure 2, should be linear.

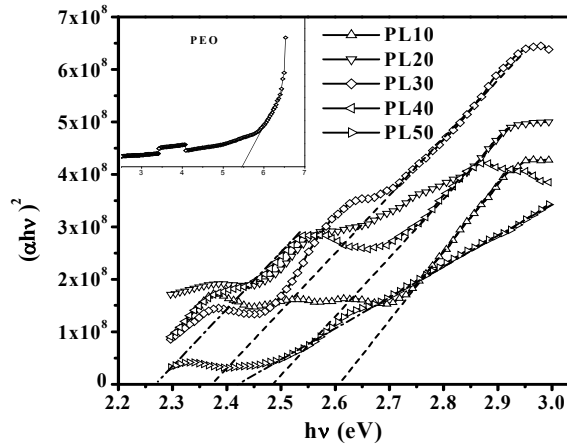


Figure 2. Plot of $(\alpha h\nu)^2$ versus photon energy for Li_2SO_4 doped PEO of PEO (100%), PL10(PEO: Li_2SO_4 = 90:10), PL20(PEO: Li_2SO_4 = 80:20), PL30(PEO: Li_2SO_4 = 70:30), PL40(PEO: Li_2SO_4 = 60:40), PL50(PEO: Li_2SO_4 = 50:50)wt %.

The intercept on the energy on extrapolating the linear portion of the curves to zero absorption value may be interpreted as the value of the direct band gap or the experimental absorption threshold corresponding to the direct band gap of samples. For pure PEO film the direct band gap found at 5.42 eV, while for doped polymer films values decreased to 2.6 eV are listed in the table 1.

Table 1. Absorption maximum, Optical energy band gap, Urbach energy, Conductivity of Li_2SO_4 doped polymer Samples (P=PEO & L= Li_2SO_4).

Sample	Absorption $\lambda_{\text{max}}(\text{nm})$	Assignment	Direct	Indirect band Gap(eV)	Urbach energy	Conductivity (S cm^{-1})
P (100:00)	198.0	$\pi \rightarrow \pi^*$	5.42	4.79	4.56	6.25×10^{-8}
PL (95:05)	-	-	-	-	-	1.95×10^{-4}
PL (90:10)	419.3	$n \rightarrow \pi^*$	2.60	4.90	0.95	-
PL (80:20)	382.8	$n \rightarrow \pi^*$	2.48	4.31	0.65	6.27×10^{-4}
PL (70:30)	419.3	$n \rightarrow \pi^*$	2.39	5.35	0.24	7.31×10^{-4}
PL (60:40)	433.3	$n \rightarrow \pi^*$	2.28	4.76	0.26	-
PL (50:50)	385.3	$n \rightarrow \pi^*$	2.41	4.20	1.16	-

These implications can be explained in the following sense. The direct band gap evidences the presence of another type of induced states depending on the mode of Li_2SO_4 chliation to the PEO matrix. These states are characterized by the allowed transition (also confirmed by f value). These transitions refer to the movement of O/Li^+ electrons between various allowed positions in atoms or molecules in the visible region²². For indirect transitions, which require photon assistance, the absorption coefficient has the following dependence on the photon energy²³,

$$(3) \quad \alpha h\nu = A[h\nu - E_g + E_p] + B[h\nu - E_g + E_p]^2.$$

where E_p is the energy of the photon associated with the transition, A and B are constants depending on the band structure.

The indirect band gaps were obtained from the plots of $(\alpha h\nu)^{1/2}$ vs. photon energy, as shown in figure 3. The intercept on the energy on extrapolating the linear portion of the curves to zero absorption value may be interpreted as the value of the indirect band gap. For pure film it was found the 4.79 eV, while for doped polymer films values sited between 4.2- 5.35eV are listed in the table 1. The decreasing of indirect band gap as a function of increasing concentration indicates the generating of sub energy levels within energy band^[24] and correspondingly it is also happen the creation of carbon-

enriched clusters because of the partial evolution of hydrogen molecules and/or to the formation of defects giving rise to levels in the band gap. Generally, it is state that a decrease in the energy gap indicates an increase in the conductivity of doped polymer electrolytes²⁵ and the same trend is observed here. The results of direct, indirect optical band gaps and activation energies for doped polymer films were well agreed with reported results²⁶.

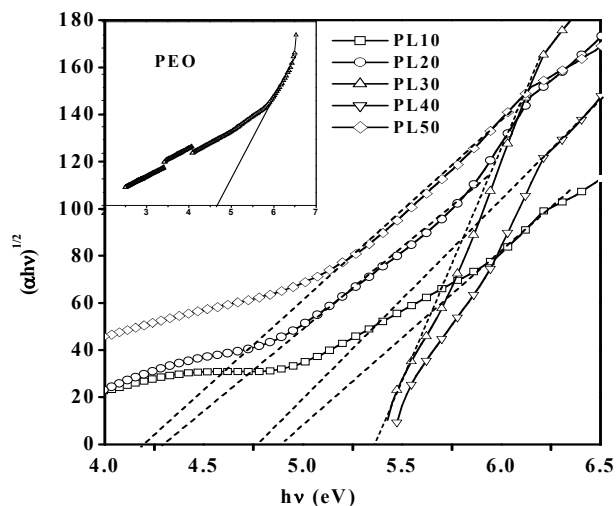


Figure 3. Plot of $(\alpha h\nu)^{1/2}$ versus photon energy for Li_2SO_4 doped PEO of PEO (100%), PL10(PEO: Li_2SO_4 = 90:10), PL20(PEO: Li_2SO_4 = 80:20), PL30(PEO: Li_2SO_4 = 70:30), PL40(PEO: Li_2SO_4 = 60:40), PL50(PEO: Li_2SO_4 = 50:50)wt %

The optical activation energy can be determined using the Urbach relation as

$$(4) \quad \alpha = B \exp(h\nu / Ea),$$

where B is a constant and Ea is the Urbach energy, i.e. the inverses slope of the exponential edge. The latter is interpreted as the width of the tail of localized states extending into the forbidden band gap from either the valence or conduction band. The values of the Urbach energy “Ea” were determined by taking the reciprocals of the slopes of the linear portions of these plots. The results show that decreasing nature up to 40% of dopant and 50% it observed slightly increases. Cluster grouping may suggest the increase in defect structure; these defects might lead to the formation of lower energy states resulting in an increasing in the charge carriers with in the conduction band. These defects may also cause a variation in the molecular mobility and hence the decreases activation energy of with

increasing of dopant concentration. It is reported that E_a of Li_2SO_4 1.3eV ²⁷, obtained results are shown in table 1.

Plotting the absorption spectrum of known concentration of sample allows obtaining the values of molar extinction coefficient (ϵ) at different wavelengths. Knowing the values of ϵ at different wavelengths is important for energy transfer studies. Molar extinction coefficient values are listed in the table 2. From the table, the excitation peaks corresponding to the electronic transitions corresponding to the $n \rightarrow \pi^$ transitions at about 23849.27cm^{-1} . It is observed from the table 2 that the molar extinction coefficient decreases with dopant concentration. The spectra features are the characteristic of the free carrier absorption of expected for Li^+ metal^[28].*

3.2.2. The Transition Dipole Moment

An oscillating electric or magnetic moment can be induced in an atom or molecular entity by an electromagnetic wave. Its interaction with the electromagnetic field is resonant if the frequency of the latter corresponds to the energy difference between the initial and final states of a transition ($\Delta E = h\nu$). The amplitude of this moment is referred to as the transition moment. The interaction of electromagnetic radiation with matter leads to absorption only if a dipole moment is created as a result of such interaction. It can be calculated from an integral taken over the product of the wave functions of the initial (1) and final (2) states of a spectral transition and the appropriate dipole moment operator (μ_e) of the electromagnetic radiation. And its square determines the strength of the transition (M). The SI unit of the transition dipole moment is Cm.

The common unit is Debye (D). *It can be calculated from the following equation*²⁹.

$$\mu_e = M^{1/2},$$

$$(5) \quad M = 9.18 \times 10^{-3} \int_{\nu_1}^{\nu_2} \frac{\epsilon}{\nu} d\nu,$$

where ϵ is the value of molar extinction coefficient at certain wavelength and ν is the reciprocal of wavelength in cm^{-1} the integration extends from ν_1 to ν_2 , which are the limits of the band associated with electronic transition (top of the valence band and bottom of the conduction band).

The intensity of the transition state from state 1 to state 2 is proportional to the dipole strength. The bottom of the conduction band is a measure of the response from the doping. The calculated values of dipole strength and dipole moment are tabulated.

Table2. Reciprocal of maximum absorption wavelength (ν), molar extinction co-efficient (ϵ), dipole strength (M), dipole moment (μ_e), oscillator strength (f), *The length of the transition dipole* (r), *The rate constant* (k_e), *Inherent emission life time* (τ) for different weight percentage samples in the UV-vis. regions.

Sample	$\nu (cm^{-1})$	$\epsilon_{max} (M^{-1}cm^{-1})$	M (D^2)	$\mu_e(D)$	f	r $\text{\AA}^o$	$k_e \times 10^8$	$\tau(ns)$
PL10	23849.27	1.29E+04	63.5	7.967952	0.668	1.61	2.64	03.79
PL20	26123.31	7.43E+03	37.7	6.140431	0.397	1.18	1.88	05.31
PL30	23849.27	5.30E+03	27.2	5.212794	0.284	1.05	1.12	08.91
PL40	23073.37	3.26E+03	16.4	4.044816	0.172	0.83	0.63	15.70
PL50	25953.82	2.85E+03	14.4	3.797352	0.152	0.74	0.71	14.10

It provides an intensity of the transition and it expresses the relative strength of the electronic transitions which can be calculated as follows³⁰,

$$(6) \quad f = 4.315 \times 10^{-9} \int_{\nu_1}^{\nu_2} \epsilon \, d\nu,$$

The calculated molar extinction coefficient, the dipole strength, the transition dipole moment and the oscillator strength for the lithium sulfate doped films is shown in the table 2. Figure 4 shows both dipole moment and oscillator strength decreases with weight percentage of dopant (Li_2SO_4). The formation of these of molecular dipoles could be a result of point defects created within the band gap region. The point defects are mainly resulted from the buildup of the molar functional groups due to the doping. *The existence of defects and corresponding variations are further verified using Urbach energy relation or optical activation energies of doped films. The oscillator strength is weakly size dependent, weakly cluster size dependent and found to be in the order of 0.6.*

The oscillator strength varies weakly with frequency in agreement with behavior of Lithium species in the polymer unit³¹. Similar results are obtained in other polar solvents³² and agree with the values obtained for Li^{+33} .

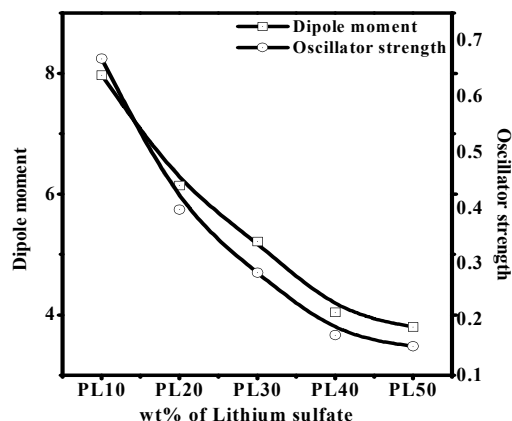


Figure 4. Plot of Dipole moment & Oscillator strength as a function of Li_2SO_4 weight percentage for PL10(PEO: Li_2SO_4 =90:10), PL20(PEO: Li_2SO_4 =80:20), PL30(PEO: Li_2SO_4 =70:30), PL40(PEO: Li_2SO_4 = 60:40), PL50(PEO: Li_2SO_4 = 50:50)

The length of the transition dipole(r) is approximately given by³⁴,

$$(7) \quad r^2 = \epsilon_v \Delta\nu / (2.5 \times 10^{19} \nu). \quad (\text{units cm}^2)$$

Calculated values of r are listed in the table 2. For PL 10 the value of r is in agreement with the value reported by D.F. Howarth et.al for Li-O³⁵.

The rate constant (k_e) for emission (probability per unit time), according to classical theory, is related to the molar extinction coefficient for absorption by,

$$(8) \quad k_e = 3 \times 10^{-9} \nu^2 \int \epsilon d\nu \equiv \nu^2 f,$$

where ν is the energy corresponding to the maximum wavelength of absorption, the values of calculated rate constant are listed in the table 2.

Inherent emission life time (τ) which is defined as $1/k_e$ ^[36] for corresponding radiative transition. The total area under the curve gives the integrated absorption intensity $\int_{\nu_l}^{\nu^2} \epsilon d\nu \approx \epsilon \Delta\nu$ where $\Delta\nu$ is the half band width.

3.1.3. Transmittance

The transmittance spectra of the pure and Li_2SO_4 doped PEO films are shown in figure 5. The fundamental absorption, which corresponds to electron excitation from the valance to conduction bands, can be used to determine the nature and value of the optical band gap. From figure it is observed that the spectrum involves deep dip corresponding to absorption

bands in the ranges 400–330 nm corresponding to the absorption with the minimum transmittances. The maximum transmittance is 142% at $\lambda = 399\text{nm}$ for Li_2SO_4 doped PEO. The optical transmittance in the visible region approached 120%, confirmation that the polymer electrolyte film is still transparent in the visible region [37].

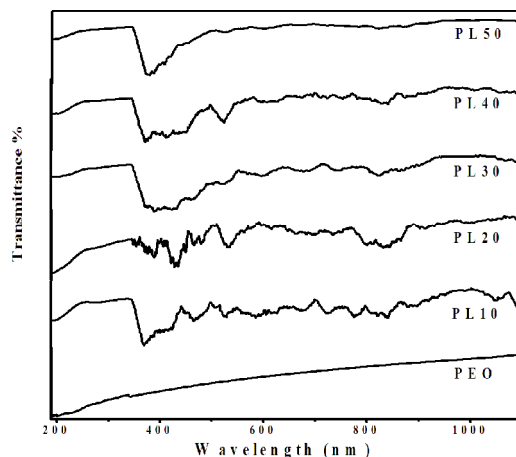


Figure 5. Optical Transmittance versus wavelength Li_2SO_4 doped PEO of PL10(PEO: Li_2SO_4 = 90:10), PL20(PEO: Li_2SO_4 = 80:20), PL30(PEO: Li_2SO_4 = 70:30), PL40(PEO: Li_2SO_4 = 60:40), PL50(PEO: Li_2SO_4 = 50:50)wt %

It is evident that, in the vicinity of the minimum of the transmittance spectrum in the range 400–330 nm is consequent to maximum in the absorption. In generally, it can be interpret that only photons with energy greater than band gap of the materials will be absorbed more and that of longer wavelength will pass through (i.e. be transmitted) having just sufficient energy to excite electrons. This means that light can be transmitted in wavelength regions confined by the band gap [38]. Figure 5 show that there is a slight decrease in transmission with increasing of Li_2SO_4 doping concentration, it can be explained in terms of a reduction in cross linking, which decreases light transmission and increases light absorption [39]. It is clear that the transmittance exhibits a steep decrease at high photon energy of the spectrum, indicating the existence of strong absorption bands in the UV-region⁴⁰.

3.3. The D C Conductivity

Measurements made on pure PEO and Li_2SO_4 doped PEO polymer electrolytes in the temperature range from 30-62°C are shown in the figure 10. The conductivity is found to be $6.85 \times 10^{-8} \text{scm}^{-1}$ in pure PEO. Increase in the

conductivity was observed with the increasing concentration of O/Li^{2+} as well as temperature. The conductivity σ may be expressed⁴¹ as

$$(9) \quad \sigma_t = \sigma_0 e^{\left(\frac{-E_a}{KT}\right)},$$

where σ_0 is a pre exponential factor, E_a the activation energy and k is Boltzmann constant. The calculated values of σ_t are given in the table1. Plots of all polymer films shows the increase in conductivity with temperature, indicating that these electrolytes exhibit an enhanced the amorphous nature. The increase in conductivity with temperature can be linked to the decrease in viscosity and, hence, increased chain flexibility.

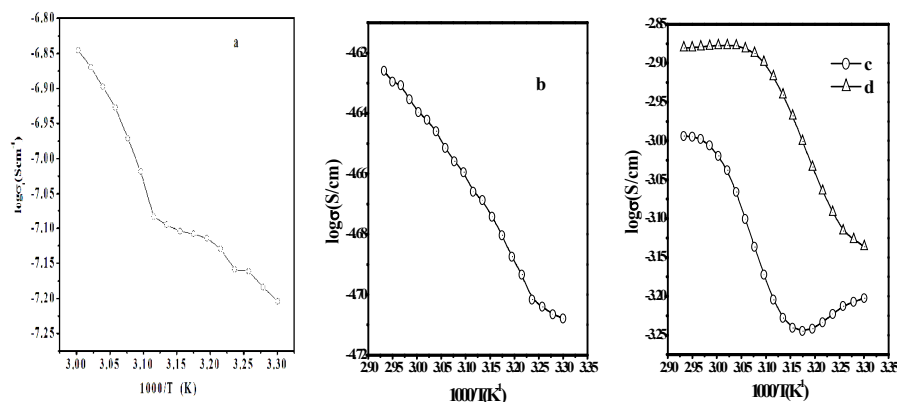


Figure 6. Conductivity vs. temperature plots of a) PEO, b) PL5, c) PL20 and d) PL30

In the plots, it is clear that the conductivity is found to increase with increasing of temperature in pure PEO as well as in the entire doped polymer. The increase in the conductivity versus temperature plots may be attributed to the transitions from crystalline/semi-crystalline phase to amorphous phase.

3.4. Transference number

The transference number's corresponding to ionic (t_{ion}) and electronic (t_{ele}) were evaluated using Wagner's polarization method. In this technique the dc current is monitored as a function of on application of fixed dc voltage across the cell. The current versus time plot was obtained for PEO/ Li_2SO_4 electrolyte. The transference numbers were calculated from the polarization current versus time plot using the equations

$$(10) \quad t_{ion} = \frac{(I_i - I_f)}{I_i}; t_{ele} = \frac{I_f}{I_i},$$

where I_i is the initial current, I_f is the final residual current.

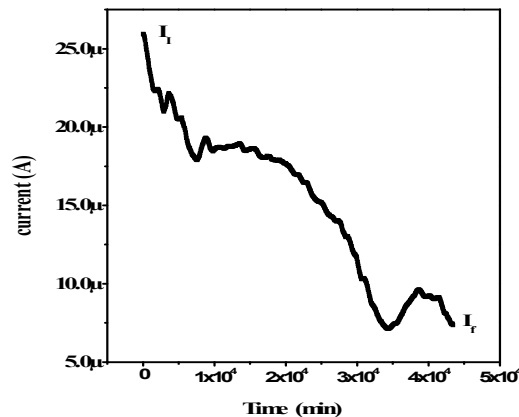


Figure 7. Polarization current vs. time Plot of (PEO:Li₂SO₄) (70:30) electrolyte film

The calculated transference number for PL 10 is $t_{ion} = 0.14$, $t_{ele} = 0.86$; for PL 30 $t_{ion} = 0.62$, $t_{ele} = 0.38$; and for PL50 $t_{ion} = 0.27$, $t_{ele} = 0.73$. From these values it suggests that the transference number for polymer electrolyte is purely Ionic.

the polymer matrix is more mobile and the lithium ions associated with the polymer can have higher transference number, leading to a higher conductivity as found by Sand et. al.⁴².

3.5. Discharge Characteristics

The electro chemical cell Na-(PEO+Li₂SO₄)-(I₂+C+Electrolyte) discharge characteristics are studied at room temperature for a load of 1k Ω and plotted in the figure 8. The open circuit voltages (OCV) and short circuit currents (SCCs) were found to be 1.62V and 273 μ A for PEO+Li₂SO₄ (70:30). And several other parameters⁴³ are given in the table 4.

Table 4. Cell parameters for (PEO+Li₂SO₄) electrochemical cell

Parameter	value
Area of the Cell (cm ²)	4.71
Wt. of the cell (g)	2.00
OCV (V)	1.62
SCC (μ A)	273
Current density (μ Acm ⁻²)	57.96
Discharge time for plateau region (h)	7.00
Discharge capacity (μ Ah ⁻¹)	39.00
Power density (Wkg ⁻¹)	0.77

Energy density (Wkg^{-1}h)	5.40
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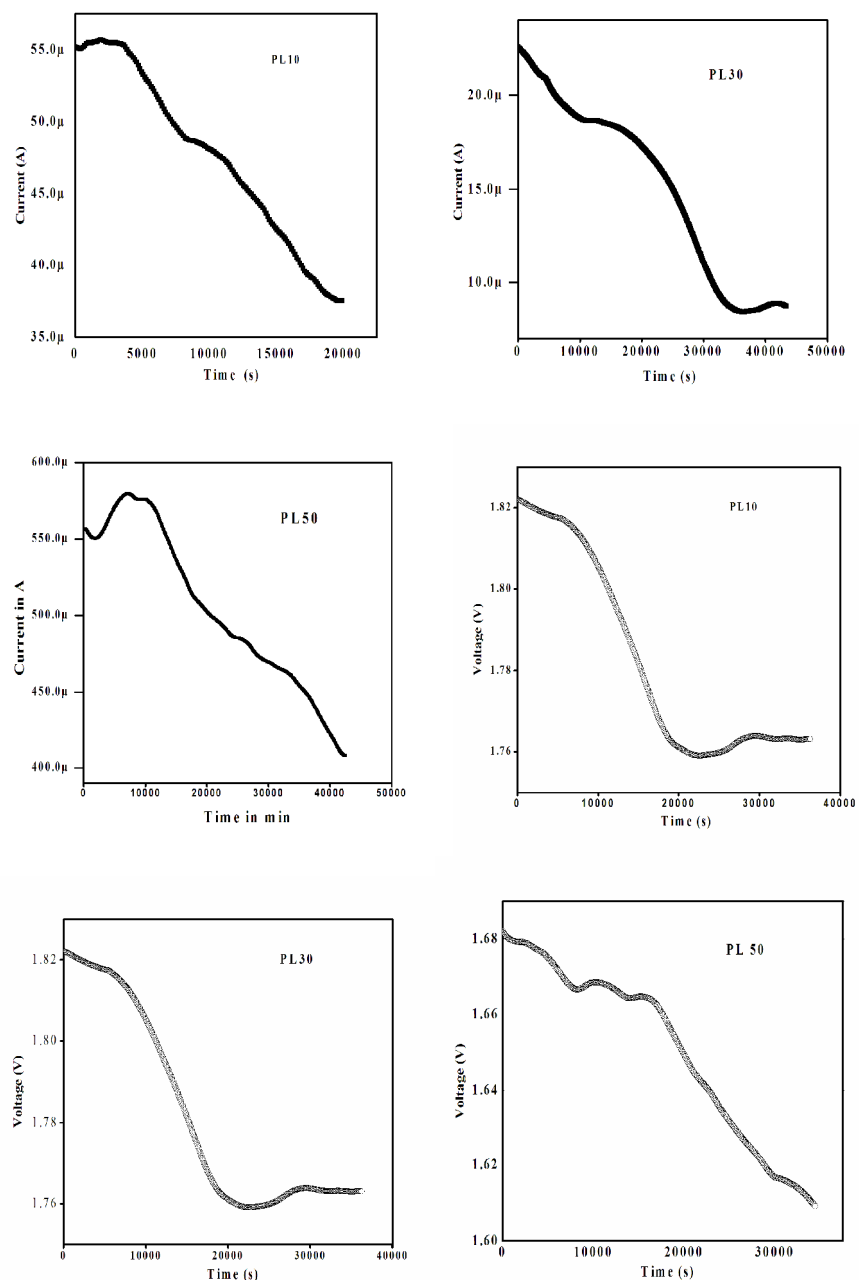


Figure 8 Discharge characteristics of a) $\text{PEO}+\text{Li}_2\text{SO}_4$ (90:10), b) $\text{PEO}+\text{Li}_2\text{SO}_4$ (70:30), c) $\text{PEO}+\text{Li}_2\text{SO}_4$ (50:50) electrochemical cell

From the table and plots it is clear that PEO+Li₂SO₄ complexed electrolytes are suitable for solid state batteries.

3.6. Mobility

The mobility of lithium ions has been evaluated using a transient ionic current measurement technique. A peak has been observed at $t=40$ s in the transient ionic current, it against time, t , plot the formula used for mobility is

$$(11) \quad \mu = \frac{d^2}{tV}$$

where d is the thickness of the sample, t is time of flight and V is applied voltage. The value of mobility has been evaluated to be $\mu=4.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

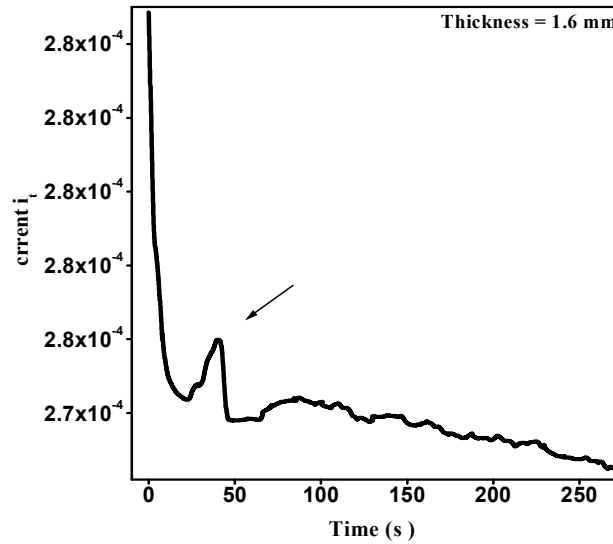


Figure 9 The transient ionic current i_t against time (t) plot of PEO+Li₂SO₄ (70:30) polymer complex

In case of PEO+LiSO₄ electrolytes, it favored to form more transient cross links with dimensional Stable morphology due to large cation–anion association effects, increase in transient cross links and the smaller amount of scattering of electrons by phonons in the more ordered medium⁴³, the mobility of Li⁺ increases so that the conductivity is increased in mixed polymer electrolytes⁴⁴.

4. Conclusion

1. The red shift is due to unsaturated centered double or triple bonds of, C=O and/or C=C mainly in the polymer and increase in the concentration of Li₂SO₄ in the Polymer electrolytes.
 2. Decrease in the energy gap indicates an increase in the conductivity of doped polymer electrolytes.
 3. Optical Properties shown good candidature for optical devices.
 4. The magnitude of the electric conductivity increases with dopant.
 5. The transference number for these polymer electrolytes shows the conductivity is maximum contribution from ions and less from electrons.
- Using those films, Electrochemical cells have been fabricated for which OCV and SSC are 1.62 V and 273 μ A respectively. The cell parameters are comparable with earlier reported vales for various other cells. Thus, (PEO+Li₂SO₄) electrolytes are possible candidates for solid-state batteries.

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