Chapter- 4B

Characterization of CoO dispersed [PEO-LiClO$_4$] solid polymer electrolyte system
## Chapter 4B

**Characterization of CoO dispersed [PEO-LiClO₄] solid polymer electrolyte system**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of the sub-title</th>
<th>Page. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4B.1</td>
<td>Introduction</td>
<td>89</td>
</tr>
<tr>
<td>4B.2</td>
<td>Characterization techniques</td>
<td>90</td>
</tr>
<tr>
<td>4B.3</td>
<td>Results and discussion</td>
<td>91</td>
</tr>
<tr>
<td>4B.3.1</td>
<td>XRD analysis</td>
<td>91</td>
</tr>
<tr>
<td>4B.3.2</td>
<td>FTIR analysis</td>
<td>92</td>
</tr>
<tr>
<td>4B.3.3</td>
<td>DSC analysis</td>
<td>95</td>
</tr>
<tr>
<td>4B.3.4</td>
<td>Impedance and ionic conductivity studies</td>
<td>97</td>
</tr>
<tr>
<td>4B.3.5</td>
<td>Temperature variation of ionic conductivity</td>
<td>101</td>
</tr>
<tr>
<td>4B.3.6</td>
<td>Dielectric studies</td>
<td>103</td>
</tr>
<tr>
<td>4B.3.7</td>
<td>AC conductivity studies</td>
<td>107</td>
</tr>
<tr>
<td>4B.4</td>
<td>Conclusions</td>
<td>108</td>
</tr>
</tbody>
</table>
4B.1 Introduction

Solid polymer electrolytes (SPE) are very important polymer substances in the area of material science and engineering. The SPE are also called as polymer in salt complexes generally prepared by dissolving polymer and inorganic salt in familiar dipolar solvents like methanol, acetonitrile followed by solution cast method. The superiority of SPE samples over the ceramic and liquid electrolytes are in terms of their leak-proof, high flexibility, light weight, ease of synthesis and tailor made geometry. SPE are the most suitable materials for the squashed design of all the solid state ion conducting electrochemical devices, especially in the fabrication of the solid state high energy density rechargeable batteries to run portable electronic equipment for longer duration. Among many polymer hosts, polyethylene oxide (PEO) based complexes have been importantly studied, because PEO forms more steady complexation with inorganic salts and having its high solvating capacity of salt than that of other hosts like polypropylene oxide (PPO) and polyethylene glycol (PEG) polymers. PEO contain ether oxygen atoms which act as a Lewis base to coordinate the cations (Lewis acid sites), and thus the dissolution of inorganic salt such as LiSCN, LiI, LiCF$_3$SO$_3$, LiClO$_4$, LiBF$_4$ and LiAsF$_6$, etc takes place [47]. To improve the ionic conductivity ($\sigma_{dc}$) of SPE, numerous modifications have been proposed such as addition of plasticizers, addition of ionic liquids, copolymer, blending, addition of nano clay, dispersion of inorganic oxides, and ceramic powders [48].

Composite polymer electrolytes (CPE) have received technological importance in the field of electrochemical cells and high energy density lithium batteries since the last two decades. CPE are more advantageous than liquid and gel electrolytes in terms of flexibility, shape, leak proof nature, good interfacial contact with electrodes, high mechanical strength etc [49]. CPE are obtained by the dispersion of micro/nano inert inorganic fillers such as ceramic and metal oxide fillers in the solid polymer electrolytes. PEO-based CPE are having gained technological importance because of their commercial availability in various molecular weights, low cost and high solvating power [50]. In CPE systems, the dielectric properties and thermal treatment of fillers play significant task. For example, in PEO electrolytes the loaded fillers influence the PEO dipole orientation to align polarized dipolar moments. Dispersal of
micro/nano sized inorganic fillers like MgO, Al₂O₃, Fe₂O₃, SnO₂, ZrO₂, Sm₂O₃, SiC, SiO₂, TiO₂ etc., are improves the overall performance of SPE [51]. The improved ionic conductivity and transference number of the CPE can be explicated on the concept of Lewis acid-base model. From this model, the structural modification is possible by addition of above said inorganic fillers in to the PEO matrix. The dispersed filler behaves like a cross-linking centre to lithium anions and the segments of PEO chain, which leads to preventing the PEO crystalline reorganization tendency, may be promotion of Li⁺ conducting tracts at the surface of dispersed filler. Polar groups on the surface of the inorganic filler may act as Lewis acid-base interaction centres with the electrolyte ions which lead to more salt dissociation by forming ion-ceramic complex[171].

In the present chapter, Composite polymer electrolytes (CPE) were prepared by dispersing of cobalt oxide (CoO) along with LiClO₄ in PEO (See chapter-3, section 3.4.2 synthesis of polymer electrolyte system-2). The structural and thermal characteristics of the CPE system were evaluated. The systematic study of the impedance spectroscopy and complex dielectric permittivity of CPE are also elaborated in this chapter. The CPE shows an enhanced ionic conductivity at ambient temperature.

### 4B.2 Characterization techniques

<table>
<thead>
<tr>
<th>Characterization technique</th>
<th>Instrument</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD</td>
<td>SHIMDZU XRD 7000</td>
<td>X-ray diffractometer in 2θ range of 10-60° using CuKα radiation</td>
</tr>
<tr>
<td>FTIR spectra</td>
<td>JASCO 400</td>
<td>Infrared spectrometer with a resolution of 2 cm⁻¹. The spectra were obtained in the wave number range 4000 – 400 cm⁻¹.</td>
</tr>
<tr>
<td>DSC</td>
<td>DSC7 (Perkin Elmer)</td>
<td>Over a temperature range of -80 to +100°C at a heating rate of 10°C min⁻¹. CPE samples of about 10–12 mg are kept in an aluminium pan and all experiments were carried out under nitrogen gas atmosphere.</td>
</tr>
<tr>
<td>Characterization technique</td>
<td>Instrument Description</td>
<td></td>
</tr>
<tr>
<td>----------------------------</td>
<td>------------------------</td>
<td></td>
</tr>
</tbody>
</table>
| Complex impedance studies  | LCR-Bridge (HIOKI-3532-50) | The CPE films were placed between two electrodes in the sample holder and kept in a computer controlled oven. Frequency range of 100Hz to 5MHz in the temperature range 303K-353K.

**4B.3 Results and discussion**

**4B.3.1 XRD analysis**

X-ray diffraction plots of PEO-LiClO$_4$ and PEO-LiClO$_4$/CoO CPE system are shown in Fig. 4B.1. The XRD graph of pure PEO have two dominant diffraction peaks (ref Fig.4A.1 in chapter-4A) located at $\theta = 19.2^\circ$ and $23.34^\circ$, indicating the semicrystalline nature of the polymer. The semicrystalline nature of PEO is due to the ordered arrangements of polymer chains [163, 172]. On incorporation of LiClO$_4$ into PEO, the diffraction peaks become weaker and broader signifying that the ordering of the PEO polymer chain is disturbed due to co-ordinate interactions in between the Li$^+$ ions and C-O-C group of ether oxygen atoms of PEO [141]. The peaks corresponding to CoO in the PEO-LiClO$_4$ complex are not seen because their peak intensities became very low and broad. On loading of CoO filler into PEO-LiClO$_4$ complex, the peak intensities of PEO decreases and broaden further, due to the chain reorganization happening in PEO which is a consequence of the interaction between PEO and CoO. These results may also supports that the structure of the PEO has locally changed into disordered form as confirmed from calculated values of degree of crystallinity from DSC result shown in Table 4B.2. From Fig.4B.1 it is observed that the peak intensity is lesser in CPE with 3 wt% CoO filler (PLCo-3) as compared to all other CPE films, possibly because of high dispersions of CoO filler in the PEO-LiClO$_4$ complex, which changes the chain reorganization and facilitates for higher ionic conduction.
Fig. 4B.1 XRD pattern of PEO-LiClO$_4$/CoO CPE films

4B.3.2 FTIR analysis

FTIR spectra recorded for pure PEO is shown in Fig. 4B.2 the most important vibrational bands present in pure PEO are presented in Table 4B.1. All these bands exhibited by pure PEO are very sensitive to macromolecular conformations and provide evidence of semicrystalline phase. FTIR spectra of PEO –LiClO$_4$/CoO CPE films are shown in Fig. 4B.3. The vibrational bands between 1000-1200 cm$^{-1}$ corresponding to C-O-C symmetric and asymmetric stretching vibrations of a PEO [173] are more important for our study because the cations of LiClO$_4$ as well as CoO filler added to PEO are more likely to complex with ether oxygen of this C-O-C bond, thereby resulting in a polymer chain reorientation form, a more amorphous phase. This is further supported to favour the conductivity of PEO films.
Fig. 4B.2 FTIR spectra of pure PEO

Table 4B.1 Wave number and assigned IR bands of pure PEO.

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>Vibrational mode of functional groups</th>
<th>Label no.</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>528</td>
<td>C-O-C bending</td>
<td>1</td>
<td>174</td>
</tr>
<tr>
<td>843</td>
<td>CH$_2$ rocking</td>
<td>2</td>
<td>175</td>
</tr>
<tr>
<td>960</td>
<td>CH$_2$ stretching and asymmetric rocking</td>
<td>3</td>
<td>175</td>
</tr>
<tr>
<td>1147, 1094, 1059</td>
<td>A triplet C-O-C asymmetric stretching</td>
<td>4</td>
<td>176</td>
</tr>
<tr>
<td>1279, 1239</td>
<td>CH$_2$ asymmetric and symmetric twisting</td>
<td>5</td>
<td>177,178</td>
</tr>
<tr>
<td>1360, 1341</td>
<td>CH$_2$ wagging</td>
<td>6</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>CH$_2$ bending</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1468</td>
<td>CH$_2$ scissoring</td>
<td>7</td>
<td>180</td>
</tr>
<tr>
<td>2872</td>
<td>C-H symmetric stretching</td>
<td>8</td>
<td>180</td>
</tr>
</tbody>
</table>
On incorporation of LiClO$_4$, the peaks corresponding to C-O-C vibrations shifted to 1144, 1095 and 1059 cm$^{-1}$. This indicates that Li$^+$ cation is interacting with ether oxygen C-O-C of PEO. On loading of CoO into PEO-LiClO$_4$ solid electrolyte system, the position of the IR spectrum changes significantly (Fig.4B.3 loading of 1 to 5 wt% CoO). The triplet band corresponding to C-O-C stretching vibrations became a single band with absorption maximum shifting down from 1095 to ~ 1070 cm$^{-1}$. This confirms that the interaction in PEO-LiClO$_4$/CoO leads to formation of cross-links that further weaken the C-O bond[130]. In addition, the split band of CH$_2$ wagging mode at 1360 and 1340 cm$^{-1}$ of PEO degenerates into a single band, as a result of the PEO-LiClO$_4$/CoO composite becoming more amorphous. The peaks found in between 500- 510 cm$^{-1}$ are ascribed to stretching vibrations of CoO [173].

The peak of ν ClO$_4^-$ bands in the range of 650 - 600 cm$^{-1}$ is generally used to study the ion–ion interaction in PEO/LiClO$_4$ based CPE systems. Literature revels that the ν (ClO$_4^-$) band centred in between 635 and 630 cm$^{-1}$ is assorted with the presence of contact-ion pairs whereas the band at about 623 cm$^{-1}$ can be represented to free ClO$_4^-$ anions [58]. From Fig. 4B.3, it is clear that a new peak is found at 623 cm$^{-1}$ in CPE.
films which can be assigned to spectroscopically free ν (ClO$_4^-$) anion. This suggest that the Lewis acid-base type of interactions between the CoO and oxygen atoms present in PEO segments and as well as ClO$_4^-$ anions can weaken its interactions with Li$^+$ and result to release of more free lithium ions[181].

**4B.3.3 DSC analysis**

In the DSC curve of pure PEO (Fig 4A.4ref Chapter4A) the endothermic peak representing to the melting temperature ($T_m$) of pure PEO occurs at 341K. $T_m$ is identified as the peak minimum of endothermic process, which is ascribed to the melting of crystalline phase. DSC graphs of PEO+LiClO$_4$ and PEO+LiClO$_4$/CoO films in the presence of heat scans are represents in Fig.4B.4. The $T_m$ of crystalline PEO decreases from 341 to 327K on addition of LiClO$_4$. The composite system shows the lowest $T_m$ value (315K) with the 3 wt% CoO (PLCo-3) system. The melting enthalpy ($\Delta H$) is represented as heat energy absorbed per unit weight of the polymeric electrolyte sample. The degree of percentage of crystallinity ($\chi_c$) is calculated by following equation by considering the absolute crystalline nature of host PEO.

$$\chi_c(\%) = \frac{\Delta H}{\Delta H(\text{PEO})}$$  \hspace{1cm} (4B.1)

where $\Delta H(\text{PEO})$ is melting enthalpy of 100% crystalline PEO which is equal to 203 J/g [182]. The calculated degree of crystallinity ($\chi_c$), melting enthalpy ($\Delta H$) and melting temperature ($T_m$) are presented in Table. 4B.2. It is observed from Fig.4B.4 and Table.4B.2 that crystallinity and melting temperature of PEO decreased noticeably when LiClO$_4$ is added into PEO polymer. The co-ordination interaction in between the ether oxygen units of PEO and Li$^+$ ions, which restrain restructuring of PEO chain efficiently and hence, decreases the crystallization. The DSC studies further complement XRD results indicating that the PEO crystallinity gets weakened by LiClO$_4$ and further by the dispersion of CoO. The decreased values of $T_m$ and $\chi_c$ indicates improved segmental motion and flexibility of PEO with filler incorporation. However the crystallinity, melting temperature are not linearly varied with the addition of CoO content. This type of non linear behaviour was observed in [PEO-LiAsF$_6$/MCM-41] composite polymer electrolyte system by Subba Reddy et al [
Minimum crystallinity (18.4\%) and minimum melting enthalpy (38.53 J/g) are observed at 3 wt \% CoO (PLCo-3) and increases further from 3 to 5 wt \% CoO.

![DSC curves of PEO-LiClO$_4$/CoO CPE system](image)

**Fig. 4B.4 DSC curves of PEO-LiClO$_4$/CoO CPE system**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (K)</th>
<th>Melting enthalpy ($\Delta H_m$, J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PO) Pure PEO</td>
<td>342.0</td>
<td>153.72</td>
<td>75.6</td>
</tr>
<tr>
<td>PL</td>
<td>327.0</td>
<td>54.95</td>
<td>27.1</td>
</tr>
<tr>
<td>PLCo-1</td>
<td>319.3</td>
<td>41.22</td>
<td>19.7</td>
</tr>
<tr>
<td>PLCo-2</td>
<td>316.1</td>
<td>40.96</td>
<td>19.5</td>
</tr>
<tr>
<td>PLCo-3</td>
<td>315.2</td>
<td>38.53</td>
<td>18.4</td>
</tr>
<tr>
<td>PLCo-4</td>
<td>322.2</td>
<td>60.87</td>
<td>29.1</td>
</tr>
<tr>
<td>PLCo-5</td>
<td>323.2</td>
<td>64.04</td>
<td>30.6</td>
</tr>
</tbody>
</table>
4B.3.4 Impedance and Ionic conductivity studies

Complex impedance measurement has an important technique for determining the ionic conductivity of the CPE films. The impedance plots of the PEO-LiClO₄ (PL) and PEO-LiClO₄/CoO CPE films at various temperatures are represented in Fig.4B.5. It is observed that all samples exhibit a similar type of behavior i.e., a semicircular portion (arc) at higher frequency region represents bulk properties of samples and a straight line having an angle less than 90° at low frequency part is represent the ascendancy of EP effect for each sample [183, 184]. The bulk resistance ($R_b$) of the CPE is generally measured from the equivalent circuit or directly obtained from the graphs i.e., the point where the common intercept of the low frequency end of the semicircular arc and high frequency end of the inclined straight line coincides with the real axis ($Z'$). It is also observed from the Fig 4B.5 that, the common intercept point on the real axis ($Z'$) shifted towards origin; which indicates that $R_b$ of the sample decreases with increase of temperature in all the samples. The frequency value of these common intercept point separates the bulk properties of samples from that of EP influenced low frequency region [185]. The $R_b$ values are presented in Table 4B.3. The dc ionic conductivity of the CPE films can be calculated from the relation.

$$\sigma_{dc} = \frac{d}{AR_b} \quad (4B.2)$$

Where $d$ is the thickness, $A$ is the area of the electrodes contacting with CPE film and $R_b$ is the bulk resistance, which is determined from the impedance spectra. The calculated ionic conductivity ($\sigma_{dc}$) values are presented in the Table 4B.3, which shows that $\sigma_{dc}$ values increases with increasing temperature. The viscosity of CPE plays an important role here, the decrease in viscosity may increase of the polymer chain flexibility [186]. Due to availability of this free-volume, hopping carriers takes place in the localized states [187].

The impedance spectra of the PEO-LiClO₄ and PEO-LiClO₄/CoO CPE films at room temperature are shown in Fig.4B.6. It can be clearly observed that the impedance spectrum of PEO-LiClO₄/CoO is an asymmetrically compressed semicircular arc with the high frequency region and an inclined straight line in the low frequency region due to dominance of EP. As shown in Fig. 4B.6, on addition of 1 to 3 wt% CoO the
bulk of 4 to 5 wt% CoO, $R_b$ values changes 124.4 $\Omega$ and 233.89 $\Omega$ respectively. With the increase of CoO content up to 3 wt%, the intersections of the straight line with real axis gradually move to a higher frequency direction. Thus, bulk resistance of the electrolyte gradually decreases.

Fig.4B.5 Impedance spectra of PEO-LiClO$_4$/CoO CPE system at different temperatures (PL, PLCo-1, PLCo-2, PLCo-3, PLCo-4 and PLCo-5 electrolyte films)
The ionic conductivity of PEO-LiClO$_4$/CoO composite polymer electrolyte at different temperatures is shown in Fig. 4B.7 and conductivity data is summarized in Table. 4B.3. CoO plays an important role in the enhancement of ionic conductivity. The ionic conductivity increase with the CoO content and optimum value is found at 3 wt% CoO at all temperatures. Then afterwards, the conductivity decreases with further increase of CoO content due to massive dispersion of CoO content, blocking the conduction pathways. Reduction of crystallinity resulted in increase of ionic conductivity of composite polymer electrolyte with the homogenous dispersion of CoO filler particles.

![Impedance spectra of PEO-LiClO$_4$/CoO CPE system at room temperature](image)

Fig. 4B.6 Impedance spectra of PEO-LiClO$_4$/CoO CPE system at room temperature
Table 4B.3 Bulk resistance and ionic conductivity of PEO-LiClO₄/CoO CPE system at various temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Bulk resistance ($R_b$) (ohm)</th>
<th>Ionic conductivity ($\sigma_{dc}$) (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PL</td>
<td>PLCo-1</td>
</tr>
<tr>
<td>303</td>
<td>236.40</td>
<td>124.46</td>
</tr>
<tr>
<td>308</td>
<td>195.00</td>
<td>103.01</td>
</tr>
<tr>
<td>313</td>
<td>145.30</td>
<td>81.13</td>
</tr>
<tr>
<td>318</td>
<td>116.20</td>
<td>61.91</td>
</tr>
<tr>
<td>323</td>
<td>94.10</td>
<td>47.15</td>
</tr>
<tr>
<td>328</td>
<td>67.00</td>
<td>36.64</td>
</tr>
<tr>
<td>333</td>
<td>60.00</td>
<td>29.23</td>
</tr>
<tr>
<td>338</td>
<td>51.80</td>
<td>24.18</td>
</tr>
<tr>
<td>343</td>
<td>45.20</td>
<td>20.10</td>
</tr>
<tr>
<td>353</td>
<td>34.50</td>
<td>14.46</td>
</tr>
</tbody>
</table>
Fig. 4B.7 Composition dependent of ionic conductivity of [PEO+LiClO₄]/CoO CPE films at different temperatures

Segmental motion of PEO is increased due to polymer chain flexibility in the amorphous region. The dc ionic conductivity is increasing in a nonlinear manner. The ionic conductivity achieves maximum value of 2.48×10⁻⁴ S/cm at ambient temperature with the addition of 3wt.% CoO, which is very close to application standards. However above 3 wt. % CoO, the ionic conductivity begins to decline as the metallic oxide filler particles lean to hinder ion transport by acts as an agglomerator [181].

4B.3.5 Temperature variation of ionic conductivity

The temperature variation of the ionic conductivity of CPE films are shown in Fig.4B.8. It is observed that the linear variation above and below Tₘ follows an Arrhenius-type behaviour of thermal activated system. The Arrhenius relation is given by

$$\sigma_{dc} = \sigma_0 \exp \left( \frac{-E_a}{K_B T} \right)$$  \hspace{1cm} (4B.3)

where $\sigma_0$ is the pre-exponential factor, $E_a$ the activation energy, $K_B$ the Boltzmann constant and $T$ is the absolute temperature. The temperature dependence of
conductivity follows Arrhenius forms signifying that the process of conduction is thermally activated.

Table 4B.4. $R_b$, $\sigma_{dc}$ and $E_a$ of PEO-LiClO$_4$/CoO at room temperature.

<table>
<thead>
<tr>
<th>CPE films</th>
<th>$R_b$ (Ohm)</th>
<th>$\sigma_{dc}$ (S cm$^{-1}$)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>236.4</td>
<td>$6.64\times10^{-5}$</td>
<td>0.15</td>
</tr>
<tr>
<td>PLCo-1</td>
<td>124.46</td>
<td>$1.35\times10^{-5}$</td>
<td>0.15</td>
</tr>
<tr>
<td>PLCo-2</td>
<td>71.35</td>
<td>$2.36\times10^{-4}$</td>
<td>0.12</td>
</tr>
<tr>
<td>PLCo-3</td>
<td>67.9</td>
<td>$2.48\times10^{-4}$</td>
<td>0.11</td>
</tr>
<tr>
<td>PLCo-4</td>
<td>189.3</td>
<td>$8.88\times10^{-5}$</td>
<td>0.17</td>
</tr>
<tr>
<td>PLCo-5</td>
<td>233.89</td>
<td>$7.19\times10^{-5}$</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The activation energies of CPE films are evaluated by linear fitting in the temperature region of 303 - 353 K and the results are presented in Table 4B.4.

Fig.4B.8 Arrhenius plots of PEO-LiClO$_4$/CoO CPE system
The conductivity of CPE increases with temperature, which is due to the promoted segmental motion by the high temperature. The activation energy decreases as conductivity of the sample increases implying that the ions in highly conducting samples require lower energies for migration.

**4B.3.6 Dielectric studies**

The real ($\epsilon'$) and imaginary parts ($\epsilon''$) of permittivity of CPE films, were calculated using the following formulae,

$$\epsilon^*(\omega) = \epsilon' - j \epsilon''$$  \hspace{1cm} (4B.4)

$$\epsilon' = \frac{d\varepsilon}{A\varepsilon_0}$$  \hspace{1cm} (4B.5)

$$\epsilon'' = \epsilon' \tan\delta$$  \hspace{1cm} (4B.6)

where d is the thickness of the CPE films, A is the area of electrode contacting with CPE film and $\varepsilon_0 (8.854 \times 10^{-12} \text{ Fm}^{-1})$ is permittivity of free space. The real ($\epsilon'$) and imaginary ($\epsilon''$) parts of dielectric permittivity of PEO-LiClO$_4$/CoO CPE films at room temperature (303 K) are shown in Fig. 4B.9. The Frequency scan of CPE offers in depth understanding of polarization processes and constituent elemental dynamics in polymer electrolyte. Large magnitude of $\epsilon'$ and $\epsilon''$ observed at low frequencies is due to electrode polarization (EP) effect [166,189]. During slow time variation of fields, charge accumulates at the electrode- electrolyte interface, forming electric double layers resulting in EP. This kind of non-Debye behaviour with frequency was also reported by R. Baskaran et al [189] for PVAc-LiClO$_4$ composites.

Eventually as the frequency increases, ions cannot follow the ac applied fields and stop responding. For the present series of CPE films this has occurred at 100 KHz frequency. In addition to this, the electric double layer formed at the interface also decreases the effective dielectric constant. This steady $\epsilon'$ at high frequency is usually termed as limiting dielectric constant $\epsilon_\infty$. However an increase in $\epsilon'$ is noted up to a loading of 3 wt% CoO beyond which it decreased till 3 wt% CoO. These dielectric results are in co-relation with ionic conductivity studies presented in the earlier section.
The real ($\varepsilon'$) and imaginary (dielectric loss) ($\varepsilon''$) parts of dielectric permittivity of CPE films as a function of frequency at different temperature are plotted. Fig.4B.10 shows dielectric constant ($\varepsilon'$) of PLCo-1, PLCo-3 and PLCo-5 CPE films. Fig.4B.11 shows dielectric loss ($\varepsilon''$) of PLCo-1, PLCo-3, and PLCo-5 CPE films. It is observed that, at low frequency region both $\varepsilon'$ and $\varepsilon''$ values of CPE films increases with increase of temperature, which can be ascribed to the increase in charge carrier density and polarization of ions as added contribution of electrode-polarization. At high frequency region, $\varepsilon'$ and $\varepsilon''$ values of CPE films are found to be almost constant with increase of temperature, which indicates that the effective contribution is due to dipoles of ion species of CPE films[179]. The $\varepsilon''$ values of CPE films shows higher values at low frequencies which may be due to the free charge movement in the polymer electrolyte samples [190].
Fig 4B.10 Dielectric permittivity ($\epsilon'$) of PLCo-1, PLCo-3, and PLCo-5 CPE films at different temperatures.
Fig. 4B.11 Dielectric loss ($\varepsilon''$) of PLCo-1, PLCo-3 and PLCo-5 CPE films at various temperatures.
4B.3.7 AC conductivity analysis

The AC conductivity ($\sigma_{ac}$) of CPE film was obtained from the relation,

$$\sigma_{ac} = \frac{Gd}{A} \quad (4B.7)$$

where $d$ is the thickness, $A$ is the area of the electrodes contacting with CPE film and $G$ is the conductance. Frequency scan of ac conductivity $\sigma_{ac}$ and loss tangent ($\tan\delta$) of PEO-LiClO$_4$/CoO CPE films at room temperature (303 K) are shown in Fig. 4B.12. The frequency dependence of ac conductivity follows Jonscher’s universal power law [166] given in relation (4B.8). It is observed that $\sigma_{ac}$ is increasing with increase in frequency. It is also noticed that there is a slope change in the higher frequency region. The low frequency region I, is taken till the slope change and after the slope change the region is assumed as region II. Slope change is observed exactly at the peak ($f_{EP}$) values of $\tan\delta$ on the frequency line. Such type of behaviour was observed in similar systems by ShobhnaChoudhary et al [188].

![Image](image.png)

Fig.4B.12 Frequency dependence of conductivity and $\tan\delta$ of PEO-LiClO$_4$/CoO
They suggested that $\sigma_{ac}$ in low frequency region I is dominated by electrode polarization effects as mentioned earlier in the dielectric section. The Jonscher exponents $n_1$ and $n_2$ and the pre-exponent functions $A$ and $B$ are estimated by fitting these curves to the power law and the values are tabulated in Table 4B.5.

$$\sigma_{ac}(\omega) = \sigma_{dc} + A \omega^{n_1} + B \omega^{n_2}$$  \hspace{1cm} (4B.8)

where $A$, $B$ are pre-exponential functions and $n_1$, $n_2$ are the fractional exponents which varies between 0 and 1. Dyre et al [191] suggested that hopping mechanism is universal in conduction phenomenon. Thus in the present system the conduction mechanism may be attributed to thermally activated ion hopping mechanism. The activation energy ($\Delta E$) in the two regions is calculated using following equation [192].

$$\Delta E = \frac{6T k_B}{1-n}$$  \hspace{1cm} (4B.9)

Where $T$ is temperature, $k_B$ is Boltzmann constant and $n$ is exponent; these values are tabulated in Table 4B.5 Activation energy represents the inter site hopping energy required by an ion in the polymer matrix.

Table 4B.5 $n_1$, $n_2$ and $A$, $B$ and $\Delta E$ values of PEO-LiClO$_4$/CoO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Region-I</th>
<th>Region -II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A x10$^{-5}$</td>
<td>$n_1$</td>
</tr>
<tr>
<td>PL</td>
<td>2.99</td>
<td>0.37</td>
</tr>
<tr>
<td>PLCo-1</td>
<td>1.61</td>
<td>0.22</td>
</tr>
<tr>
<td>PLCo-2</td>
<td>3.18</td>
<td>0.07</td>
</tr>
<tr>
<td>PLCo-3</td>
<td>2.58</td>
<td>0.20</td>
</tr>
<tr>
<td>PLCo-4</td>
<td>1.59</td>
<td>0.17</td>
</tr>
<tr>
<td>PLCo-5</td>
<td>1.91</td>
<td>0.11</td>
</tr>
</tbody>
</table>

4B.4. Conclusions

The PEO-LiClO$_4$/CoO CPE films were prepared by solution casting method. The structural, thermal and compositional studies were analyzed by XRD, DSC and FTIR.
characterization techniques. XRD studies reveal that, the reduction of crystallinity is observed on dispersion of CoO filler into the PEO-LiClO$_4$ system. The peak intensity is lesser in CPE with 3 wt% CoO filler (PLCo-3) as compared to all other CPE films, possibly because of high dispersions of CoO filler in the PEO-LiClO$_4$ complex, which changes the chain reorganization and facilitates for higher ionic conduction. FTIR studies reveals that, the appearance of some new peaks in the spectra and with modifications in the existing peaks gives direct evidence of dissolution of salt with PEO and also change in the crystallinity of PEO. DSC studies reveals that, the degree of crystallinity and melting enthalpy values are found to be lesser at 3 wt.% CoO (PLCo-3). The ionic conductivity enhancement observed in the PEO-LiClO$_4$/CoO polymer electrolyte evidently results from the effect of CoO filler. The increased conductivity is found to be one order higher and the optimum value is found at 3 wt.% CoO (PLCo-3). This can be explained in terms of reduction in crystallinity and leading to the maximum segmental motion of the lithium ions. The ionic conductivity achieves maximum value $2.48 \times 10^{-4}$S/cm at room temperature with the addition of 3wt.% CoO, which is very close to application standards. The temperature dependence of ionic conductivity plots follows Arrhenius behaviour. The decline in ionic conductivity at higher filler contents is attributed to the development of an oxide-lithium aggregation phase. The frequency dependent dielectric constant has shown the presence of electrode polarization effect at lower frequencies. Further study of ac conductivity as a function of frequency confirms electrode polarization effect at lower frequency.