Chapter - 2

Literature survey
## Chapter -2

### Literature survey

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2 Literature survey

The main object of this chapter is to know the work done by researchers on PEO-based polymer electrolytes for Li-ion batteries. This chapter deals with the literature survey of PEO-based polymer electrolytes. These results are very much useful for understanding of conduction mechanism in polymer electrolytes, structural, morphological, electrochemical, thermal, mechanical and interfacial stabilities of polymer electrolytes. It consists of four subsections namely solid polymer electrolytes, plasticized polymer electrolytes, blend based polymer electrolytes and composite polymer electrolytes. Each subsection briefly summarises results of earlier research.

2.1 Solid polymer electrolytes

A polymer electrolyte is composed of polymer host and inorganic salt. These two components play a vital role in enhancing the ionic conductivity in polymer electrolytes. Summary of literature survey on SPE electrolytes is given below.

Susan et al. [52] investigated the relation between structure and ionic conductivity of PEO/LiClO$_4$. Their XRD results showed that three crystalline phases were observed depending on the variation of lithium content in the pristine PEO. They used SANS technique for phase formation, [P(EO)$_3$-LiClO$_4$] SPE showed cylindrical form. Quantity and dimension of pure PEO lamellae was measured by using NS. QENS technique was used to determine the mobility of PEO chains directly in semicrystalline and amorphous materials. They observed that, [P(EO)$_{14}$-LiClO$_4$] SPE at 50℃ gave highest ionic conductivity.

Robitaille et al. [53] studied characterization of PEO/LiX polymer electrolytes. [PEO/LiX, where X= ClO$_4^-$, CF$_3$SO$_3^-$ and ASF] SPE were prepared and characterized with XRD, optical microscopy and interpretation of phase diagrams with complex impedance spectroscopy. They concluded that, the generation of ion-pairs was observed at low salt content and $E_a$ of the conducting species (ions) was not depending on the anion.

Mao et al. [54] investigated neutron diffraction studies on PEO/LiClO$_4$ polymer electrolytes. The local structure surrounded by Li$^+$-ions of the SPE was calculated by neutron diffraction with Li$^+$ isotope replacement. The Li-ions were coordinated with approximately 4-5 ether oxygen units present in the PEO host.
Fauteux et al. [55] studied electrochemical properties of PEO-based solid polymer electrolytes. [PEO-LiX, where X=ClO$_4^-$, CF$_3$SO$_3^-$] SPE were prepared and studied mechanical and electrical properties. They observed that, the Li$^+$ transport takes place in the amorphous of the SPE. The ionic conductivity mechanism was independent of PEO purity and depends on the ion species in the PEO. From these studies it was observed that, the conductivity mainly depends on the purity of salt and content.

Henderson et al. [56] explored characterization of polyether based SPE electrolytes. [glymes+LiX] and [PEO+LiX] where x= LiBETI, LiTFSI, LiAsF6, LiPF$_6$, LiClO4, LiI, LiBF$_4$, LiCF$_3$SO$_3$, LiNO$_3$, and LiCF$_3$CO$_2$ electrolytes were prepared and structural, morphological and thermal properties were analysed by XRD, SEM and DSC techniques. The degree of crystallinity and ionic conductivity of studied electrolytes depends on wt% of salt content.

Siqueira et al. [57] studied molecular simulations of PEO/LiClO$_4$ solid polymer electrolytes. The ion dynamical properties of SPE films were investigated by using simulation method. The results showed that Li$^+$ ion mobilities were coupled with the segmental motion of polymer chain. The structural relaxation studies showed that, on loading of salt content into the pure PEO, the polymer relaxation process significantly changed. The ionic conductivity calculated by the Nernst-Einstein formula was one order higher magnitude than the calculated conductivity by using time correlated function of charge current.

Salomon et al. [58] reported structural studies of PEO and PEG based solid polymer electrolytes. [PEO+LiClO$_4$] and [PEG+LiClO$_4$] SPE films were prepared by solution casting method. IR studies reveal that, two bands were assigned for (ClO$_4^-$) free ions at 623 cm$^{-1}$ and 635 cm$^{-1}$ respectively. From the relative amplitudes of two bands, it was found that most of the ClO$_4^-$ ions were free from Li$^+$ ions which may be due to separation of ion-pairs by the solvent. They also studied the electrical conductivities of prepared samples. The ultrasonic absorption spectra showed two relaxation processes at high frequencies.

Gorecki et al. [59] studied characterizations of PEO-based solid polymer electrolytes. [P(EO)$_x$ +LiClO$_4$] were prepared and structural and morphological properties were analyzed by XRD, DSC and NMR techniques. From NMR and DSC studies it was confirmed that there exist two phases namely crystalline and amorphous.
Munshi et al. [60] reported lithium transference number of the PEO+LiX solid polymer electrolyte system. They noticed that, $T_{Li}$ depends on the salt content, type of counter ion and thickness of the polymer film. The observed transference number for [P(EO)$_8$+LiX] system were presented in the Table 2.1.

Table 2.1 variations of Li transference number with different thickness of [PEO+LiX] system.

<table>
<thead>
<tr>
<th>System</th>
<th>Thickness of sample (μm)</th>
<th>Transference no. at 100°C</th>
</tr>
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<tbody>
<tr>
<td>P(EO)$_8$+LiAlCl$_4$</td>
<td>15</td>
<td>0.50</td>
</tr>
<tr>
<td>P(EO)$_8$+LiAlCl$_4$</td>
<td>32</td>
<td>0.49</td>
</tr>
<tr>
<td>P(EO)$_8$+LiAlCl$_4$</td>
<td>16</td>
<td>0.50</td>
</tr>
<tr>
<td>P(EO)$_8$+LiAsF$_6$</td>
<td>18</td>
<td>0.56</td>
</tr>
<tr>
<td>P(EO)$_8$+LiAsF$_6$</td>
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<td>0.54</td>
</tr>
<tr>
<td>P(EO)$_8$+LiAsF$_6$</td>
<td>49</td>
<td>0.54</td>
</tr>
<tr>
<td>P(EO)$_8$+LiPF$_6$</td>
<td>12</td>
<td>0.47</td>
</tr>
<tr>
<td>P(EO)$_8$+LiAsF$_6$</td>
<td>16</td>
<td>0.47</td>
</tr>
<tr>
<td>P(EO)$_8$+LiAsF$_6$</td>
<td>37</td>
<td>0.48</td>
</tr>
<tr>
<td>P(EO)$_8$+LiCF$_3$SO$_3$</td>
<td>8</td>
<td>0.46</td>
</tr>
<tr>
<td>P(EO)$_8$+LiCF$_3$SO$_3$</td>
<td>23</td>
<td>0.45</td>
</tr>
<tr>
<td>P(EO)$_8$+LiCF$_3$SO$_3$</td>
<td>57</td>
<td>0.46</td>
</tr>
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<td>0.38</td>
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<tr>
<td>P(EO)$_8$+LiBF$_4$</td>
<td>19</td>
<td>0.37</td>
</tr>
<tr>
<td>P(EO)$_8$+LiBF$_4$</td>
<td>28</td>
<td>0.40</td>
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Abraham et al. [61] studied ionic conductivities of various polyether based electrolytes at room temperatures. [PVdF-PEGDME-LiX wehere X= SO$_2$CF$_3$ and N(SO$_2$CF$_3$)$_2$] copolymers were prepared by solution casting method. The studied copolymers showed higher ionic conductivity in the order of $10^{-4}$ S/cm and enhanced mechanical strengths.

Magistris et al. [62] synthesized and studied thermal properties of PEO-based solvent free polymer electrolytes. [PEO+LiPF$_6$] films were prepared and studied thermal
properties at higher and lower concentrations of the LiPF$_6$ salt. The [P(EO)$_{30}$ +LiPF$_6$] SPE films showed good thermal stabilities at high temperatures and the ionic conductivity was in the order of $10^{-4}$ S/cm at 70°C.

Newman et al. [63] studied safety measure of LiClO$_4$/dioxolane electrolyte for the rechargeable batteries. The results showed that, the prepared LiClO$_4$/dioxolane polymer electrolyte was unsafe for Li-ion batteries.

Ibrahim et al. [64] studied effect of salt content on the PEO-polymer electrolytes. [PEO +x%LiPF$_6$ where x= 5, 10, 15, 20] SPE films were prepared by solution casting method. From XRD analysis it was revealed that, the PEO crystalline peaks were drastically decreased by the addition of salt content. From FTIR analysis it was proved that, the interaction between ether oxygen units with Li$^+$ ions of the LiPF$_6$ salt. The variations in the peak position shape and peak intensity represented the complete salt dissociation in the PEO polymer. From DSC studies it was observed that, the degree of crystallinity and $T_m$ changed by the addition of salt into the polymer electrolyte system. Conductivity studies revealed that, the ionic conductivity increased with the addition of 5 wt% to 20 wt% of salt content. The [PEO+20%LiPF$_6$] film exhibited maximum ionic conductivity of $10^{-5}$ S/cm at room temperature. The temperature dependence of ionic conductivity plots followed Arrhenius type behaviour.

MacGlashan et al. [65] explored the structural studies of [P(EO)-LiAsF$_6$] solid polymer electrolyte system. Their results proved that [P(EO)$_3$-LiAsF$_6$] SPE film exhibited polymer chains in the form of helical structure, where as [P(EO)$_6$-LiAsF$_6$] SPE film formed double non-helical chains which interlocked to formed a cylindrical shape. The lithium ions inhabit within these cylinders.

Litas et al. [66] studied the crystal structure of [P(EO)$_3$-LiAsF$_6$] SPE films by using XRD and neutron diffraction data using a simulated annealing technique. From structural studies it was evident that, the PEO chain exhibited helical structure. Li$^+$ ions reside within the coil of helix each Li$^+$ ion corresponding with three ether oxygen units and two fluorine atoms from each of two AsF$_6^-$ ions.

Andreev et al. [67] reported structural studies of [P(EO)$_3$-LiBF$_4$] and [Diglyme/ LiBF$_4$] polymer electrolytes. Structural studies revealed that, the PEO chain exhibited helical structure. Li$^+$ ions were resided within the coil of helix, each Li$^+$ ion
corresponding with three ether oxygen units and two fluorine atoms from each of two \( \text{BF}_4^- \) ions. Both \([\text{P(EO)}_{3}\text{-LiBF}_4]\) and \([(\text{Diglyme})/ \text{LiBF}_4\text{ where } x=1,2]\) SPE films showed same type of structure.

Bloise et al. [68] reported NMR studies of PEO-based polymer electrolytes. The polymeric chain segmental motion and ion transport effects were studied by dispersion of alumina and carbon block particles into the \([\text{PEO+LiClO}_4/\text{LiBF}_4]\) SPE systems by NMR technique. The results showed that dispersed alumina pronounced more on the polymer dynamics and cation transport. \(^7\text{Li}\) measurements showed that lineshape and relaxation were affected by combination of its quadrupolar moment to surrounding electric field gradients.

Kalita et al. [69] investigated calix[6]pyrrole added \([\text{PEO+LiBF}_4]\) solid polymer electrolyte. \([\text{P(EO)}_{20}\text{+LiBF}_4+(\text{C6P})]\) were prepared by solution casting method. DC-AC conductivity techniques and NMR results showed that, by dispersion of the C6P into the \([\text{P(EO)}_{20}\text{+LiBF}_4]\) SPE system, \(\text{t}_\text{Li}^+\) noticeably increased.

Ballard et al. [70] investigated ionic conductivity studies of amorphous polymers. Various co-monomers were added to ethylene oxide to form copolymerization of ethylene oxide. The LiTF salt added copolymerized electrolyte system showed higher ionic conductivity than \([\text{PEO+LiTF}\] electrolyte system, but it showed poor mechanical properties. \([50\%\text{PPO+PEO+LiTF}]\) copolymerized electrolyte exhibited higher mechanical strength and it is flexible with electrode-electrolyte interface. The maximum ionic conductivity of \(10^{-3}\ \text{S/cm}\) has been achieved so far.

Zardalidis et al. [71] explored local chain relaxation mechanism in the PEO-LiTF polymer electrolyte system. \([\text{P(EO)}_x+\text{LiTF}\text{ where } x=2, 4, 6, 8, 12]\) electrolytes were prepared and investigated the phase change, local chain mobilities and viscoelastic properties. Structural results revealed that, structure of the \([\text{PEO+LiTF}\] remained same on variation of the salt content. Conductivity studies showed that, the ionic conduction takes place in both crystalline phase and amorphous phase of polymer films and amorphous phase showed more conductivity. \([\text{P(EO)}_{12}\text{+LiTF}\] SPE film exhibited highest ionic conductivity at all temperatures, which would be due to local ion hop at the sub segmental levels.

Gitelman et al. [72] studied simulation studies on PEO-LiI solid polymer electrolytes. They simulated \(\text{Li}^+\)-ion transportation in a single PEO macromolecule. Their results
showed that, PEO acts like a helical structure in which Li$^+$ ions were moving and it was also solvent for the salt.

Karan et al. [73] reported conductivity and dielectric studies of PEO-LITF solid polymer electrolytes. [P(EO)$_x$+LITF where $x=8,24,30,100,200$] SPE films were prepared by solution casting method. From the studies of thermal properties they observed that, by increasing salt concentration into the PEO host, the $T_g$ value increased, which proved that Li$^+$ ions were coordinated with the ether oxygen units in the PEO host. Temperature dependence conductivity resulted in maximum ionic conductivity of [P(EO)$_{24}$+LITF] SPE film at room temperature. Relaxation peak was observed from the dielectric spectra which was associated with the segmental motion of polymer chain. The temperature dependence of the conductivity and the relaxation times followed the VTF formula.

Bernhard et al. [74] investigated thermal and electrochemical properties of low molecular weight PEG500DME/LiTFSI electrolyte system. [PEG500DME+LiTFSI] electrolyte showed high thermal stability at electrode interface and low vapour pressure. The electrical studies showed that, the electrolyte had exhibited high ionic conductivity in the order of $10^{-3}$ S/cm and high $t_{Li^+}$ (0.48). The results revealed that, [PEG500DME+LiTFSI] electrolyte was the promising candidate for the application of Li-ion battery.

Borodin et al. [75] reported ionic transportation mechanism of PEO-based solid polymer electrolyte. [PEO+LiTFSI] SPE films were prepared and studied by MD simulation method at different concentrations of salt and different temperatures. The results revealed that, Li$^+$-ion mobility increased by the addition of salt content and PEO acted as both solvent and diffusive segment for ion hopping.

Appetecchi et al. [76], fabricated and studied electrochemical properties of Li/(PEO-LiBETF)/V$_2$O$_5$ cell. [PEO-LiBETF] SPE electrolyte films were prepared by hot press technique. The constructed cell consisting of Li foil anode, [PEO-LiBETF] electrolyte and composite V$_2$O$_5$ cathode. The electrochemical properties of cell were tested.

Zhang et al. [77] synthesized and studied electrochemical properties, lithium transference number, electrode interfacial stabilities, phase transition and ionic conductivity studies of [P(EO)$_{20}$+LiTFSI] and [P(EO)$_{20}$+LiFSI] solid polymer electrolytes. [P(EO)$_{20}$+LiFSI] electrolyte showed higher ionic conductivity than the
[P(EO)_{20}+LiTFSI] electrolyte at room temperature. The comparative studies of these electrolytes observed that, [P(EO)_{20}+LiFSI] electrolyte was the promising candidate for applications of Li-batteries. Seki et al. [78] reported physical and electrochemical properties of [TG-LIFS] electrolyte 1:1 mole ratio. The TG/LiFS electrolyte exhibited high thermal properties. The cell was fabricated with [TG-LIFS] electrolyte with graphite cathode and LiFePO_4 anode. The cell showed higher charge/discharge cycles. Gao et al. [79] reported NMR studies of PEO/LiClO_4 polymer electrolyte system. [P(EO)_x+ LiClO_4 where x=3,6] SPE films were prepared by solution casting method and the phase transition, ion dynamics and conduction mechanism was studied by NMR technique.

2.2 plasticized polymer electrolytes

PEO-LiX polymer electrolyte system exhibited poor polymer chain segmental motion due to its high degree of crystallinity of PEO. The pronounced polymer segmental motion was observed in the amorphous region. To improve the ionic conductivity of PEO-based polymer electrolytes, plasticizers were added into the PEO/LiX system. The plasticization affects the decreasing degree of crystallinity and increasing of amorphous phase content of PEO/LiX system. Findings of earlier researchers are summarized below.

Niedzicki et al [80] synthesized PEO-LiTf plasticized polymer electrolytes. In their study low molecular weight PEO analogues (PEG and PEHDME) were used. LiTf salt was dissolved in the low molecular weight PEG (Mw=350g/mol) and PEGDME (Mw=500 g/mol) solvents respectively and were dried in vacuum line at 90°C for 72h. Argon dry box was used for preparation of the samples. The ionic conductivity was measured by using electrochemical impedance spectroscopy; it was found that the conductivities were in the order of 10^{-3} to 10^{-4} S/cm of 0.1-1 mol dm^{-3} concentration of salt. Bruce-Vincent method was used to estimate the Li^+ transference number; they found that this value was more than 0.5. The electrochemical interphase stability was found to be very high. Raman spectroscopy was used for structural studies and interaction between the molecular species present in the electrolyte. The ionic agglomerations for these salt concentrations were found to be less than PEO-LiClO_4 electrolytes by using Fuoss–Kraus semiempirical technique.
Wang et al [81] synthesised P(EO)$_{18}$-LiTFSI/x% PEGDME (where x = 0-24 wt%) plasticized composite polymer electrolytes by using inexpensive casting technique with acetonitrile solvent. This electrolyte system acts as a protective layer between lithium metal electrode and Li$_{1.35}$Ti$_{1.75}$Al$_{0.25}$P$_{0.9}$Si$_{0.1}$O$_{12}$ lithium ion-conducting glass ceramic. They found that, Li$^+$ transport number was doubled with the addition of plasticizer. The ionic conductivity of P(EO)$_{18}$-LiTFSI was 1.3×10$^{-4}$ S/cm at 60°C, while addition of 18 wt% PEGDME, increased conductivity by 3.8×10$^{-4}$ S/cm. The electrochemical cell was constructed and charge and discharge characterisations were studied.

Chintapalli et al. [82] reported the synthesis and infra red spectroscopic studies of PEO-LiCF$_3$SO$_3$ electrolyte system with the addition of plasticizers such as EC, TEG and TEGDME. These films were prepared by solution casting method using acetonitrile solvent. Basing on the results obtained from infrared spectroscopy was augmented with measurement of conductivity, the plasticizer would played an important role in the complexation of polymer/salt complex. PEO-LiCF$_3$SO$_3$ (EO:Li= 9:1) polymer electrolyte system, EC and TEG tend to increase the concentration of the less associated molecular species, but TEGDME increases the concentration of more associated molecular species. The final effect of plasticizer in the solid polymer electrolyte systems was to create conducting pathways for freely moving ions.

Lee et al [83] reported synthesis of modified carbonate (MC3) using starting material as adding into the PEO-LiCF$_3$SO$_3$ electrolyte system. The ionic conductivity of these plasticized electrolyte systems were higher than other plasticizers like PC and EC which were added into the PEO-LiCF$_3$SO$_3$. PEO-LiCF$_3$SO$_3$ /50wt% MC3 gives an ionic conductivity of 5×10$^{-5}$ S/cm at room temperature which is two orders of magnitude higher than the PEO-LiCF$_3$SO$_3$ system. This is also one order high magnitude than the PEO-LiCF$_3$SO$_3$ /PC electrolyte system. The thermal analysis and conductivity studies showed that this plasticizer system enhanced the ionic conductivity throughout the entire complex system. This new plasticizer system not only increased the ionic pathways in the plasticizer but also improved the ion pair dissociation which in turn enhanced the ionic conductivity.

Yang [84] studied infra red spectroscopy and Raman spectroscopy of PEO-LiCF$_3$SO$_3$/MC3 electrolyte system. From NEXAFS studies, it was evident that,
potassium salt dissociated in PC and MC3 plasticizer solutions. MC3 has stronger interaction with potassium ion pair dissociation effect than PC. The ether oxygen units in the MC3 complex K\(^+\) ions dissociated by this group stops them forming ion-pairs with SO\(_3\). 

Fan et al [85] reported synthesis and characterization of PEO- P(VDFHFP)-[LiClO\(_4\)/EC/PC] polymer blend based plasticized electrolyte system with various compositions by using solution casting technique. SEM results shows that P(VDFHFP) is very associative with the PEO. The ionic conductivity of PEO-LiClO\(_4\)/EC/PC showed high ionic conductivity but it degraded the mechanical properties. A blended plasticizer system showed improved ionic conductivity without degrading the mechanical strength of the films. This polymer blend has decreased the degree of crystallinity of the PEO. Among this systems, 25[PEO]- 50 [P(VDFHFP)]-75[LiClO\(_4\)/EC/PC] electrolyte system showed high conductivity and superior mechanical properties.

Che et al [86] synthesised and characterized two plasticized composite polymer electrolytes, namely [20%PDMAEMA +10%PEO]-x%LiTFSI/70% [EC+PC] (S1) and [20%PDMAEMA +10%PEO]-x% LiTFSI/70% [TEGDME] (S2) where x= 0, 0.3, 0.6, 0.9, 1.2, 1.5 mol/kg. These polymer composite electrolyte systems were prepared by solution casting method by varying salt concentrations. The DSC and impedance spectroscopy techniques were used for characterizing the samples at various temperatures. They studied ionic conductivities of S1 and S2 electrolyte systems and found that S2 system showed higher ionic conductivity (4.74 × 10\(^{-4}\) S cm\(^{-1}\)at 25 \(^\circ\)C) than S1. This may be due to better co-ordination of TEGDME plasticizer with ether-oxygen units in the blend, than EC and PC plasticizers. Hence it made Li-polymer interaction weaker and S2 system showing higher ionic conductivity than S1.

Pitawala et al. [87] reported preparation and conductivity studies of plasticized nanocomposite polymer electrolyte (PNCPE) system. They prepared [P(EO)\(_9\) – LiTf]+15wt %Al\(_2\)O\(_3\)+50 wt%[EC/PC] PNCPE films by varying the plasticizer concentrations using solution casting method. The ionic conductivity of [P(EO)\(_9\) – LiTf] system was of 10\(^{-7}\) S/cm. By the dispersion of 15wt% Al\(_2\)O\(_3\) into the [P(EO)\(_9\) – LiTf] system the conductivity value improved by one order magnitude (\(\sigma_{rt} =7.8\times10^{-6}\)
On further addition of plasticizers into the [P(EO)_9–LiTf]+15wt %Al_2O_3 system, ionic conductivity improved drastically. In their investigation, EC plasticizer system showed higher ionic conductivity than PC, however [P(EO)_9–LiTf]+15wt %Al_2O_3+50 wt%[75% EC+25% PC] PNCPE system gave maximum ionic conductivity (σ_r = 1.24×10^{-4} S/cm). The added plasticizers (EC, PC or EC+PC) tends to decreased the T_g, improved the amorphous phase of the PEO and [P(EO)_9–LiTf] complex, hence improved conductivity. It was shown that, the Al_2O_3 filler was also contributing to enhancing the mechanical strength and conductivity by transient hydrogen bonding of transporting Li^+ ions with O-H group at the filler surface. The DSC results observed that T_g, T_m and crystallinity values decreased on addition of plasticizers into the PNCPE system. These results also support the conductivity enhancement of studied electrolyte systems.

Dissanayake et al. [88] reported ionic conductivity studies of [P(EO)_9–LiTf]+50wt%[ EC]+x %[Al_2O_3] where x=10 and 15. These NCPE were prepared by solvent-casting method using acetonitrile as a solvent. On addition of EC, ionic conductivity enhanced but mechanical strength was not good. The combined effect of Al_2O_3 filler and EC plasticizer in the [P(EO)_9–LiTf] complex gave maximum conductivity without changing their mechanical strength. The maximum conductivity (1.5×10^{-4} S/cm) was achieved by [P(EO)_9–LiTf]+ 50wt%[ EC]+15%[Al_2O_3] complex.

Bandara et al. [89] studied synthesis and characterization of [P(EO)_9–LiCF_3SO_3] and [P(EO)_9–LiCF_3SO_3]+ 50wt%[ EC/PC] CPE systems. The CPE were prepared by using acetonitrile solvent by solution casting method. Films having a thickness of 0.1-0.5mm were obtained. The ionic conductivity increased with the loading of plasticizer content. The conductivity of the [P(EO)_9–LiCF_3SO_3] complex was 2.5×10^{-5} S/cm at 332K. On adding 50 wt% EC into [P(EO)_9–LiCF_3SO_3] complex ionic conductivity was 9.0×10^{-4} S/cm and for 50 wt% PC at 332K was 5.2×10^{-5}.

Vignarooban et al. [90] reported synthesis and electrical studies of plasticized nanocomposite polymer electrolytes. They prepared [P(EO)_9:LiTf] + x wt.% TiO_2 (where x = 0, 5, 10, 15 and 20) and [P(EO)_9:LiTf]+10 wt.% TiO_2+50 wt.% EC films by using acetonitrile as a solvent by solution-casting method. Dispersion of TiO_2 in SPE gave an enhanced ionic conductivity. The ionic conductivity of [P(EO)_9:LiTf] + 10 wt.% TiO_2 showed maximum conductivity value 4.9 × 10^{-5} S cm^{-1} at 30 °C,
which is one order magnitude higher than SPE. On addition of plasticizer into CPE, the ionic conductivity was further increased without declining the mechanical strength of the films. \([P(EO)_{90}:LiTf]+10 \text{ wt. } \% \text{ TiO}_2+50 \text{ wt. } \% \text{ EC system showed highest ionic conductivity value } 1.6\times10^{-4} \text{ S/cm at room temperature, with sustained mechanical properties. From thermal analysis, thermal properties like } T_g, T_m \text{ and } \Delta E \text{ decreased on loading of } \text{TiO}_2 \text{ and then same trend continued with } \text{TiO}_2 \text{ and EC. This additive (TiO2 and EC) supported the reduction in crystallinity of PEO and improved segmental motion of polymer chains. TiO}_2 \text{ played an important role in enhancing the conductivity, due to high dielectric constant (435) when compared with PEO (2.8-3.3), which supported dynamic (active) dissociation of lithium salt and hence increased concentration of mobile ions.}

Walker et al. [91] reported synthesis of \([\text{PEO}]_x-\text{[LiCF}_3\text{SO}_3]+ \text{[LiN(CF}_3\text{SO}_2)/\text{DEP]} \) composite polymer electrolyte (CPE) using solution casting technique. They found that plasticized electrolytes showed higher ionic conductivity than SPE. The combined plasticized salt and DEP solvent system showed highest ionic conductivity of \(4.6\times10^{-5} \text{ S/cm at temperature lower than melting point of PEO (66°C).which is two orders magnitude higher than } [\text{PEO}]_x-\text{[LiCF}_3\text{SO}_3] \) system.

Michael et al.[92] studied ion transportation properties of \([[\text{PEO-LiClO}_4]+[\text{DOP/DBP/DMP]} \) CPE system. They used different characterization techniques to study the structural, thermal and ionic conductivity of CPE. XRD analysis of \([\text{P(EO)}_8-\text{LiClO}_4]+[\text{DOP}] \) (99.9:0.1 w/o) system showed lower degree of crystallinity than SPE. This CPE showed \(9.76\times10^{-5} \text{ S/cm ionic conductivity value at room temperature. On further dispersion of } 0.01\mu\text{m sized fine particles of } \delta-\text{Al}_2\text{O}_3 \text{ into } [\text{P(EO)}_8-\text{LiClO}_4]+[\text{DOP}] \) (99.9:0.1 w/o) CPE system exhibited one order magnitude higher ionic conductivity (\(\sigma = 4.29\times10^{-4} \text{ S/cm})\). The \(\delta-\text{Al}_2\text{O}_3 \) ceramic filler incorporated polymer electrolytes exhibited high thermal and mechanical properties. From DTA and TG analysis of three plasticizer systems namely, DOP, DBP and DMP, DOP plasticized CPE system showed higher thermal stability. \([\text{P(EO)}_8-\text{LiClO}_4]+[\text{DOP}]+\delta-\text{Al}_2\text{O}_3 \) CPE system was found to be promising candidate for the secondary lithium batteries application at wide range of temperature from 29 to 100°C.

Sukeshini et al. [93] reported synthesis, thermal, vibrational and conductivity properties of \([\text{PEO-LiCF}_3\text{SO}_3]/\text{DBP} \) CPE films. They prepared x[\text{PEO}]-1-
x)[LiCF$_3$SO$_3$/DBP] where x= 0.33, 0.50, 0.67 and 0.84 by solution casting method, and the LiCF$_3$SO$_3$ salt content in DBP was (1 mol kg$^{-1}$) fixed for all samples. From DSC studies, they observed that more amount of DBP into PEO matrix, affects the thermal properties like T$_g$ and T$_m$ and also noticed from DSC plots that DBP was companionable with PEO. From infrared studies, on loading of plasticizer content into SPE, the peak broadened of the C-O-C stretching vibration on increase of salt content, shows the dissolution of salt content into the PEO matrix. The highest ionic conductivity ($\sigma = 6.0 \times 10^{-4}$ S/cm) was achieved by x=0.33 CPE system at room temperature. The plasticizer played a vital role in improving the Li$^+$ ion transport and enhancing ionic conductivity of CPE.

Li et al. [94] reported characterization of the middle MW cyclic phosphate plasticized [P(EO)$_8$ - LiTFSI] polymer electrolyte system. The middle MW cyclic phosphate not only acted as a plasticizer but also flame-retarding agent in the CPE system. Electrochemical studies revealed that, the CPE system possese high electrochemical stability and appreciable ionic conductivity.

Fan et al. [95] described electrical and mechanical properties of SN plasticized CPE system. The [xPEO+ySN+5wt%LiTFSI] (x+y=95 wt%) CPE was prepared by solution casting method by varying PEO and SN wt% concentrations. On loading SN into the CPE, the ionic conductivity increased noticeably in both lower and higher temperature regions with respect to melting temperatures of PEO and SN. DSC results showed that degree of crystallinity decreased with increase of SN content. Mechanical properties of observed [95% PEO+5% LiTFSI] and [70% PEO+25% SN+5% LiTFSI] CPE films, the mechanical strength of [95% PEO+5% LiTFSI] was 1.8Mpa and on addition of 25 wt% SN content into the [95% PEO+5% LiTFSI] system was 1.5MPa. This small loss of the mechanical strength is due to plastic nature of the SN. On observation of overall studies they believed that [70% PEO+25% SN+5% LiTFSI] CPE was the promising candidate for battery application.

Wu et al. [96] synthesized and characterized SN plasticized PEO-based composite polymer electrolytes (CPE) LIBOB salt was prepared by solid state reaction method. [[P(EO)$_{20}$:LIBOB]+x wt% SN (where x=0, 4, 8, 24 and 100)] CPE films were prepared by solution casting technique. The films were characterized by XRD, SEM, DSC and EIS techniques. From conductivity studies, the LIBOB based PEO SPE showed two
orders magnitude higher ionic conductivity than LiClO₄ based PEO SPE due to its large-size anion (BOB⁻). On incorporation of SN into the [P(EO)₂₀-LiBOB] SPE ionic conductivity further enhanced at lower temperatures. SN may be improved the polymer chain segmental mobility. The conductivity results are in consistent with results obtained from XRD and DSC. The studied CPE films showed good thermal stabilities up to 80°C.

Kyu et al. [97] described studies on ionic conductivity related to phase diagrams of PEO based composite polymer electrolytes. The composites (PEO/LiTFSI, PEO/SCN and PEO/LiTFSI/SCN) were prepared in the glow-box under nitrogen environment by solvent casting method. The ionic conductivity was optimized by using phase diagrams of (PEO/LiTFSI/SCN). The plasticizer played an important role in enhancing the ionic conductivity. The ionic conductivity was determined in three regions namely isotropic (non crystalline liquid), crystal-liquid and liquid-plasticized. EIS results showed that the conductivity in the isotropic region is higher than other regions (crystal-liquid and liquid-plasticized).

Choi et al. [98] reported studies on electrochemical stability, electrode interfacial properties and ionic conductivity of IL added PEO-based solid polymer electrolytes (SPE). [PEO+LiTFSI+x BMITFSI where x= 20, 40, 60 and 80 pbw] films were prepared by solvent casting method. On addition of BMITFSI into the [PEO+LiTFSI] complex, the T<sub>m</sub> and degree of crystallinity decreased and the ionic conductivity significantly enhanced. The maximum ionic conductivity (σ<sub>r</sub>=3. 24×10⁻⁴ S/cm) can be achieved by [PEO+ LiTFSI+ (80) BMITFSI] complex. CV characteristics of [PEO+LiTFSI+(60)BMITFSI] CPE noticeably decreased R<sub>e</sub> and R<sub>f</sub> and also supported the stabilization of Li electrode. Among all the CPEs studied, the [PEO+LiTFSI+(60)BMITFSI] system showed best optimized CPE. It exhibited strong mechanical and interfacial stabilities with the Li/LiFePO₄ electrodes at 40°C.

Zhu et al. [99] studied electrochemical characteristics of RIL based gel polymer electrolytes. [P(EO)₂₀+LiTFSI]+EMITFSI/PP13TFSI electrolytes were prepared by casting technique. On adding RIL, there was a change in the internal structure of PEO and supports more amorphous phase of the CPE. These two RIL played an important role in plasticizing [P(EO)₂₀+LiTFSI]. The highest ionic conductivity (σ =2.67×10⁻⁴ S/cm at 40°C) was achieved by [P(EO)₂₀+LiTFSI+ 1.0EMITFSI] CPE system.
Wang et al. [100] reported synthesis and electrochemical properties of IL added [PEO-Li(CF$_3$SO$_2$)$_2$N] CPEs. [P(EO)$_{18}$+LiTFSI+x% (PP13FSI) where x=0, 0.4, 0.8, 1.20, 1.44, 1.80, 2.20, 2.40] films were synthesized by solution cast technique using acetonitrile as a solvent. They have found that, on loading PP13FSI content in the SPE, ionic conductivity increased and Li$^+$ transport number decreased. The interfacial resistance of electrode-electrolyte depends on the PP13FSI content and the poor stability was obtained for x=1.20 and 1.44 content. The maximum ionic conductivity ($\sigma =6.5 \times 10^{-5}$ S/cm at 25$^\circ$C and $2.18 \times 10^{-3}$ S/cm at 60$^\circ$C) was observed at x=1.44 wt% content of PP13FSI. From diffusion coefficient calculations, it was observed that the current density and dendrite formation was decreased by adding PP13FSI content in the SPE system.

Kumar et al. [101] reported synthesis and electrical properties of PEO based electrolytes with the effect of plasticized IL. [P(EO)$_{25}$:LiTf/x(EMITf), where x=0, 10, 20, 30, 40] electrolyte films were prepared by low cast solution casting method. From XRD and SEM results, the structural modification in PEO and [P(EO)$_{25}$:LiTf] systems were observed on loading of EMITf. IR and Raman spectroscopic investigations shows that improved ion-polymer interaction and EMI$^+$ ion with ether-oxygen units present in the PEO matrix. The maximum ionic conductivity ($\sigma =3 \times 10^{-4}$ S/cm at room temperature) was obtained for 40 wt% content of EMITf in the CPE system. Thermal properties like $T_m$, $T_g$, enthalpy and $\chi$ of studied CPE systems were decreased with the increase of EMITf content. NMR studies confirmed that, the observed ionic conductivity of CPE was mainly due to Li$^+$ ions contribution.

Wetjen et al. [102] studied electro chemical properties of new composite polymer electrolyte on incorporation of both IL and ceramics filler. [P(EO)$_{20}$:LiTf+12.5 wt%(Pyr$_{1,4}$,TFSI)], [P(EO)$_{20}$:LiTf+12.5 wt%(Pyr$_{1,4}$,TFSI)+5 wt% SiO$_2$] and [P(EO)$_{20}$:LiTf+12.5 wt%(Pyr$_{2,4}$,TFSI)+5 wt% SiO$_2$] electrolytes were prepared by solvent casting technique. DSC results showed that the $T_m$, $T_g$, enthalpy and $\chi$ of studied CPE systems were decreased with the increase of EMITf content and loading of SiO$_2$ acidic filler (fumed silica). Hence the amorphous nature increased and thus enhanced the ionic conductivity and $t_{Li^+}$.The investigated films showed excellent electrochemical stabilities. The constructed cell Li/CPE/LiFePO$_4$ showed high charge and discharge capabilities in the temperature range of 49-90$^\circ$C.
Sutto et al. [103] reported preparation and electrical properties of solid gel electrolytes formed by IL plasticized PEO based composite electrolytes. [PEO-PVdF-HFP/MMPIBF₄/MMPIBF₆, with and without 0.5M Li salt] films were prepared by solution casting technique. The electrochemical stabilities and ionic conductivities of PVdF-HFP gel based electrolytes showed better results than PEO. The crystalline nature of PEO limits the interaction between ionic species and ether oxygen units present in the polymer host restricts the ion transport in the gel. Among all studied solid gel based electrolytes, 30% polymer and 70% ionic liquid electrolyte system showed maximum ionic conductivity. The nonpolar polymer corresponding with a hydrophobic electrolyte gave higher ionic conductivity and discharging of lithium ions into graphite.

2.3 Blend based polymer electrolytes

The blended polymer electrolytes were prepared by simple miscibility of two or more polymers. The amorphous nature of polymer electrolytes was improved by blending of low molecular weight polymers into the PEO host. The main intention of synthesis of blended polymer electrolyte is to enhance the ionic conductivity. By blending process, the compositional changes occur in the blended polymers and hence physical properties are easily tuneable. Many researchers explored their reports as follows.

Tsuchida et al. [104] reported preparation and electrical conductivity studies of PEO/PMMA blend based electrolytes. [PEO-PMMA]/LiClO₄ blends were prepared by using solution casting method. It was found that the ionic conductivity depends on the Mw of PEO and also LiClO₄ content in the PEO, the chain flexibility and ionic conductivity of the electrolyte membrane increased at 400 Mw of PEO. The highest ionic conductivity ($\sigma=1.3\times10^{-5}$ S/cm at 60°C) and chain flexibility was obtained for PMMA: PEO: LiClO₄ = 17:68:15 ratio.

Abraham et al. [105] studied synthesis and characterization of MEEP-PEO/Li salt blend based electrolytes. The [MEEP-PEO/(LiX)n where X= LiBF₄, LiClO₄, LiCF₃SO₃LiAlCl₄ and LiAsF₆] and [MEEP-PEO/] were prepared by solution casting method. The blend based electrolyte showed two orders magnitude higher conductivity than [PEO-LiX] solid polymer electrolyte due to the amorphous nature of MEEP. The LiClO₄ and LiBF₄ complexed blends showed higher ionic conductivity than other studied other blends.
Khan et al. [106] reported studies on electrical properties of [PEO+P2VP/P4VP+LiClO₄] blend based electrolytes. The different concentrations of blends were prepared by solution blending method. Among all prepared blend electrolytes, [85P(EO)₆+15P2VP]+LiClO₄ blend electrolyte showed high ionic conductivity at room temperature (σ=7.0×10⁻⁶ S/cm). The Li⁺ ions interacted with both oxygen units in PEO back bone and nitrogen in the pyridyl units present in the PVP. The morphological studies of the blends showed two phased microstructure stabilized by the blending effect of LiClO₄. From these studies it was observed that blend based electrolytes find applications in the microelectronic devices.

Kim et al. [107] studied preparation and characterization of PEO/PES/LiClO₄ blend based polymer electrolytes. [xPEO+yPES+LiClO₄ with fixed ratio of EO/Li =0.1 and varying the x and y values] electrolytes were prepared by blending technique. On loading of PEO into [PES+LiClO₄] electrolyte, they found a noticeable increase in the mechanical properties and decrease in its ionic conductivity. The best optimized electrolyte [40 P(EO)₁₀+60PES+LiClO₄] showed highest ionic conductivity (σ = 3×10⁻⁵ S/cm ) at room temperature and exhibited good elastic nature with high stability and low Li transport number (0.37 at 40°C).

Oh et al. [108] reported studies on electrochemical properties of PEP added solid polymer electrolytes. [PEO+x wt%PEP]/LiClO₄ where x=0, 20, 40, 60, 80,100 and EO/Li=0.1] films were prepared by solution casting method. On loading of PEP content into the [PEO+LiClO₄] complex, the ionic conductivity and polymer chain flexibility increased. Among all prepared blends the best optimized blend [60PEO+40PEP+LiClO₄] showed highest ionic conductivity at ambient temperature (σ = 2.0×10⁻⁵ S/cm). This blend exhibited rubbery nature and good electrochemical stability in wide range of temperature. The cell was fabricated by using this optimized blend electrolyte with Li anode and LiCoO₂ cathode (Li/CPE/LiCoO₂) exhibited explicit discharge ability at 40°C is 128mAh/g.

Jacob et al. [109] reported preparation and studies on conductivity of PEO/PVDF-LiClO₄ composite blend. [x%PEO/PVdF-LiClO₄, where x=0, 2, 5, 10, 20, 30, 40] blends were prepared by solution blending technique. The ionic conductivity and mechanical strength was increased on addition of PEO content into the [PVDF-
LiClO$_4$] complex. [20PEO/80(PVDF-LiClO$_4$)] blend gave maximum ionic conductivity ($\sigma = 2.63 \times 10^{-5}$ S/cm) at room temperature.

Prasanth et al. [110] studied electrochemical properties of PEO/[PVdF-LiX] electrospun fiber films. [10PEO/90PVdF-LiX, where X= ClO$_4$, TFSI, PF$_6$, CF$_3$SO$_3$] were prepared by electro spaying method. The prepared polymer gel electrolytes showed good electrochemical stabilities and high discharge ability at wide range of temperatures. They achieved higher ionic conductivity ($\sigma = 4.9 \times 10^{-3}$ S/cm on adding large anion salt (LiTFSI).

Correia et al [111] reported structural, thermal and electrical properties of P(VDF-TrFE)/PEO blend. [P(VDF-TrFE)/x%PEO where x=0, 20,40,60,80,100] blends were prepared by solvent evaporation method. They observed that, the electrical, thermal and mechanical properties of the prepared blends were not only depended on PEO wt% content but also on the molecular weight. The higher ionic conductivity was observed at PEO 60 wt% content.

Tanaka et al. [112] studied ion conductivity of [PEO/PEI] blend by uptake of lithium salt. [(PEO+PEI)/LiClO$_4$ by various ratios PEO:PEI, with fixed LiCO$_4$ content ] blends were prepared by solution casting method. The ionic conductivity of [8PEO+2PEI] blend was increased on decreasing of LiClO$_4$ content due to crystalline nature of PEO.

Das et al. [113] investigated conductivity studies of PEO/PDMS blend based composites at low ambient temperatures. [30PDMS+ P(EO)$_x$+LiPF$_6$ where x= 10, 15, 20, 25, 30] blends were prepared by solution casting method using THF as a solvent. The prepared blends showed improved ionic conductivities at room temperature and below room temperatures. The maximum ionic conductivity ($\sigma = 5.6 \times 10^{-5}$ S/cm) was obtained by [30PDMS+ P(EO)$_{10}$+LiPF$_6$] composite blend. This blend was considered as an optimized one and ionic conductivity remained unchanged up to -10°C. XRD and SEM results showed an effective miscibility between PEO and PDMS polymers and interaction with lithium salt and polymer blend.

Lalia et al. [114] studied thermo-electrical and mechanical properties of Quasi-solid polymer electrolytes (QSPE). [PEG/TEGDME/NC/PEO-LiClO$_4$ by fixed EO/Li ratio] QSPE films were prepared by solution casting method. In this blend, NC acted as thermal and mechanical stabilizer, PEO acted as binder and PEG/TEGDME gave high
amorphous phase to the binder. The 70 wt% TEGDME content added QSPE showed higher ionic conductivity in the order of $10^{-4}$S/cm.

Wong et al [115] explored studies of electrochemical and thermal properties of Low MW PEG/PFPE/LiTFSI bends. [PEG/PFPE-LiTFSI, various wt ratios of PEG/PFPE] blends were prepared by solution casting method. Thermal parameters $T_g$, $T_m$ and crystalline melting were controlled by varying the PEG/PFPE ratios. The optimized blends showed non-flammable nature and stable in the temperature range of -85 - 150°C. These blends showed ionic conductivity of the order of $10^{-4}$ range at ambient temperature.

2.4 Composite polymer electrolytes

The above research reports on SPE and plasticized-based electrolytes are not promising candidates for Li-ion batteries due to its low ionic conductivity of SPE and poor mechanical stability of plasticized-based polymer electrolytes. Researchers have been investigating a novel method to solve this issue. Among those solutions, preparation of composite is composed of filler (ceramic, metallic oxide) and mixture polymer is a promising candidate for Li-ion batteries. The research reports are summarized as follows.

Cheung et al. [116] synthesized and characterized ceramic fillers doped composite polymer electrolytes. They prepared PEO-based SPE and PEO-based CPE at different contents of salts and metal oxides. They investigated various salts (LITFS, LiClO$_4$ and LITF) and different filler (Al$_2$O$_3$, TiO$_2$ and SiO$_2$) based PEO electrolytes. The conclusions of their research work are as follows.

a. The particle size of the additives affect the ionic conductivities and mechanical properties of the electrolyte.

b. The salt content and Mw of polymer influenced the electrochemical stabilities and conductivities of SPE.

c. [PEO+LITF] SPE system showed the best mechanical and electrochemical properties before and after heating.

d. The dispersed metal oxide fillers into the [PEO-LITF] system also showed enhanced mechanical and ionic conductivities at above and below melting point of PEO host.
e. The NMR spectroscopy studies reveal that, the diffusive coefficient was higher for ceramic filler doped CPE systems. Chung et al. [117] reported NMR studies of composite polymer electrolytes. [P(EO)₈+LiClO₄+ 10%TiO₂] and [PEG+LiClO₄+10%(Al₂O₃)ₓ where x= acid, base and neutral] CPE films were prepared and investigated by ¹H and ⁷Li NMR. They determined molecular and ionic diffusive coefficients of all prepared films.

Johansson et al. [118] reported effect of ceramic fillers doped composite polymer electrolytes. Raman spectroscopy results showed that there was small effect of TiO₂ on the composite electrolyte system. When small amount of filler was added into polymer-salt system, the width of a Raman line showed enhanced disorder of anions. DSC results showed that, loading of TiO₂ filler into the SPE system decreased the degree of crystallinity.

Scrosati et al. [119] explored their research work on the composite polymer electrolytes for Li-batteries. [PEO+LiTFS+SiO₂/Al₂O₃/LiAlO₃] composite electrolytes were prepared and characterized by various characterization techniques. The filler played an important role in enhancing electrode-electrolyte interference stability with the anode. It also enhanced transportation properties of Li-ions in the polymer-salt system.

Yang et al. [120] studied SAP dispersed PEO- based composite polymer electrolytes. [PEO+LiClO₄+SAP] films were prepared by solution casting technique. SEM images, showed that, SAP nanoparticles were dispersed uniformly in the SPE films. The prepared films were characterized by XRD, FTIR, DSC and NMR techniques. Impedance studies showed that, dispersion of SAP into the [PEO+LiClO₄] SPE enhanced the ionic conductivity and lithium transference number. [P(EO)₆+LiClO₄+2%SAP] showed highest ionic conductivity which was three order higher magnitude than [P(EO)₆+LiClO₄] SPE. Further lithium transference number also enhanced.

Kim et al. [121] investigated electrical properties of MCM dispersed composites. [PEO+LiClO₄+MCM-14] were prepared and characterized by XRD, SEM and DSC techniques. MCM-14 nano particles influenced the ionic conductivity and ion transference number of CPE films. The optimized [P(EO)₁₆+LiClO₄+8%MCM-14] CPE film showed highest ionic conductivity (1.2×10⁻⁴ S/cm) at room temperature.
which was two order higher magnitude of $[\text{PEO+LiClO}_4]$ composite. The results showed that the degree of crystallinity also decreased (30.4%). This 8% MCM-14 filler dispersion in SPE gave highest Li-transference number of $t_{Li} =0.5$ and the electrochemical stabilities also increased considerably.

Samir et al. [122] investigated nanosized cellulose particles doped in the POE-based composites. The cellulose whiskers filler based $[\text{POE+LiTFSI}]$ composites polymer electrolyte (CPE) films were prepared and characterized by various characterization techniques like XRD, SEM, DSC and Impedance spectroscopy. From their results, the ionic conductivities and electrochemical stabilities of CPE were enhanced considerably. NMR studies revels that, reinforcing effect would not affect the Li-ion transference number. The filler provided high mechanical strength to the CPE film.

Best et al. [123] studied electrical properties of polyether based composite polymer electrolytes. $[\text{PEG+x%LiTFSI/LiClO}_4 + \text{TiO}_2]$ where $x=1.0, 1.25, 1.5, 2.0]$ films were prepared by solution casting method. The filler $\text{TiO}_2$ has not considerably enhanced the ionic conductivity of $[\text{PEG+x%LiTFSI/LiClO}_4]$. However $[\text{PEG+1.5%LiClO}_4]$ film showed higher ionic conductivity. From their Raman spectroscopic studies, it was evident that, only single peak was assigned to the composite electrolyte.

Bloise et al. [124] reported studies on electrical and NMR properties of composite polymer electrolytes. They investigated space charge formation of $\text{TiO}_2$ dispersed composite polymer electrolytes and $[\text{PEO+LiClO}_4]$ SPE system by using NMR and impedance spectroscopy. They measured $^1\text{H}$ and $^7\text{Li}$ line shapes and spin-lattice relaxation times as a function of temperature. From NMR results it was found that, the Li-Li interactions were more strengthened in the composite than SPE.

Forsyth et al. [125] synthesized and characterized $\text{TiO}_2$ doped copolymer-based polymer electrolytes. Their results are summarized as follows: the Raman spectroscopy, NMR, impedance spectroscopy and positron annihilation techniques showed that noticeable interactions between $\text{TiO}_2$ nanoparticles and amorphous polyether composite electrolytes. The results showed that there was an interfacial region affected by both lithium salt and polyether with the surface groups of $\text{TiO}_2$ nano filler. IR spectroscopy studies showed that filler affects the DLAM in the case of polyether and implied the interaction between polymer and surface of the filler. From
impedance spectroscopy analysis, the TiO$_2$ filler would play an important role in enhancing the ionic conductivity.

Karlsson et al. [126] investigated ion-dynamics of TiO$_2$ nanocomposite polymer electrolytes. The microscopic polymer dynamics of prepared composite films were carried out by QSN experimental technique. Two dynamical processes were observed from their QSN results: local chain motion and slower diffusive segmental motion. No changes of the quasielastic peak widths could be observed between the filled or unfilled composites; however, the elastic scattering of the sample was found to increase upon addition of the filler to the polymer electrolyte.

Pylahan et al. [127] synthesized and fabricated self supported Li-batteries based on TiO$_2$ nanotubes. The fabricated cell consists of [PEO+LiTFSI] solid polymer electrolyte, TiO$_2$ nanotube as an anode and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ as cathode. It showed an operating voltage of 2.1 V and performed steady discharge ability of 30 μA h cm$^{-2}$ μm$^{-1}$. The fabricated cell was good compatible with the integrated circuit.

Xia et al. [128] studied luminescence and ionic conductivities of ZnO doped composite polymer electrolytes based on low molecular weight PEGME. [ZnO+PEGME] composite was prepared by sol-gel method and LITFSI was dissolved into the [ZnO+PEGME] composite. They studied various characterization techniques to determine the structural and morphological properties of both the samples. From their investigations it was observed that, the physically mixed [ZnO+PEGME] composite system showed higher electrochemical stability than SPE system. The ZnO nanoparticles possessed good photoluminescence properties and SPE system gave highest ionic conductivity.

Xia et al. [129] investigated ZnO doped composite polymer electrolytes for Li-battery applications. [PEO+LITFSI+ZnO(PEGME)/ZnO(Ac)] films were prepared and characterized by various techniques. Their results were summarized as follows: HRTEM results showed that the ZnO nanoparticles were uniformly dispersed in the [PEO+LITFSI+ZnO(PEGME)] grafted-polymer electrolyte system. Whereas ZnO particles were not homogenously dispersed in the [PEO+LITFSI+ZnO(Ac)] system. From AFM results it was concluded that, the [PEO+LITFSI+ZnO(PEGME)] system possessed a small amount of tiny crystalline phase at room temperature after one month storage. The [PEO+LITFSI+ZnO(Ac)] system showed dendrite structure and
their original phase changed. Their conductivity results and cyclic discharge performance of cell showed that, polyether-grafted polymer electrolytes were promising candidates for applications in the Li-batteries.

Xiong et al. [130] investigated ZnO doped PEO-based composite polymer electrolytes. [PEO+ZnO] and [PEO+LiClO$_4$+ZnO] films were prepared by solution casting technique. From Luminescence studies it was observed that, by the dispersion of ZnO nanoparticles into PEO matrix the photoluminescence intensity decreased. Conductivity results showed the dispersion of ZnO nanoparticles into the [PEO+LiClO$_4$] system. The co-ordination effect of PEO with LiClO$_4$ changed as a unidentate coordination form with acidic surface group of ZnO nanoparticles. These changes suggested that, PEO segments, Li$^+$ and acetate surface groups on the ZnO nanoparticles forms cross-linking structures. Due to this, more number of free Li$^+$ ions was released from Li$^+$ ClO$_4^-$ ion-pairs and hence ion transport increased in the [PEO+LiClO$_4$+ZnO] composite films.

Samir et al. [131] reported electrical and mechanical properties of cellulose doped cross-linked composite polymer electrolytes. The prepared CPE films were characterized by DSC, SEM and DMA techniques. The cellulose doped composites showed better ionic conductivities than unfilled cross-linked composite films. The cellulose doped CPE showed enhanced mechanical stability.

Schroers et al. [132] synthesized and studied electrochemical stability of nanocomposite cellulose doped EO-EPI copolymer. [(EO-EPI) + LiClO$_4$+cellulose] CPE were prepared by solution-casting method by using THF solvent. The studied CPE films showed improved mechanical strength than the [(EO-EPI) + LiClO$_4$] SPE films. Conductivity results showed that, on loading of filler into the SPE has been decreased slightly.

Samir et al. [133] reported electrochemical properties of nanocrystal reinforced PEO-based composite polymer electrolytes. [POE+cellulose whiskers] and [POE+LiTFSI+cellulose whiskers] composites were prepared and characterized by XRD, DSC and SEM techniques. The added filler affected the degree of crystallinity, $T_m$ and $T_g$ of CPEs. SEM images showed that spherulitic nature was not observed throughout the sample and filler would not affect the growth rate of the spherulites.
The filler gave good mechanical strength to the SPE films and it showed moderate ionic conductivity at room temperature.

Kumar et al. [134] studied synthesis and characterization of PEO based composite polymer electrolytes. \([P(EO)_{x}+\text{LiBF}_4]/\text{MgO}/\text{BaTiO}_3\) films were prepared by melt-casting method. From their studies CPE showed enhanced ionic conductivity by ether filled micro or nano sized fillers. However nano sized fillers gave higher ionic conductivities than micro sized fillers incorporated into the \([\text{PEO-LiBF}_4]\) SPE. The nano sized filler gave better coordination with ether-oxygen units in the PEO. Incorporation of nanosized MgO or BaTiO\(_3\) into the \([P(EO)_{x}+\text{LiBF}_4]\) SPE gave conductivity of the order of \(10^{-4}\) S/cm at around room temperature.

Zhang et al. [135] synthesized and carried out electrochemical studies of nano MgO doped PEO based composite polymer electrolytes. \([\text{P(EO)_{20}+LiBOB+5wt\%MgO}]\) films were prepared by solvent casting. They observed that, incorporation of nano MgO filler into \([\text{P(EO)_{20}+LiBOB}]\) SPE, improved anode stability and decreased interface resistance. LiBOB played an important role in improving kinetic permanence and reactive ability towards the negative electrode.

Angulakshmi et al. [136] studied synthesis and electrochemical characteristics of MgAl\(_2\)O\(_4\) doped CPE. \([\text{PEO+LiPF}_6+\text{MgAl}_2\text{O}_4]\) electrolytes were prepared by hot-pressed method. On dispersion of MgAl\(_2\)O\(_4\) filler into \([\text{PEO+LiPF}_6]\) SPE, noticeable increase in the ionic conductivity was observed in their studies. Among all the studied CPE, \([85\%\text{PEO}+10\%\text{LiPF}_6+5\%\text{MgAl}_2\text{O}_4]\) composite possessed higher ionic conductivity and good electrolyte-electrode interface stability. This optimized composite gave higher discharging capacity of 127mAh\(^{-1}\).

Angulakshmi et al. [137] studied electrical properties of MgAl\(_2\)SiO\(_6\) doped PEO-based electrolytes. \([\text{PEO+LiPF}_6+\text{MgAl}_2\text{SiO}_4]\) electrolytes were prepared by hot-pressed method. On dispersion of MgAl\(_2\)SiO\(_4\) filler into \([\text{PEO+LiPF}_6]\) SPE, noticeable increase in ionic conductivity was observed. Among all studied CPE, \([80\%\text{PEO}+8\%\text{LiPF}_6+12\%\text{MgAl}_2\text{O}_4]\) composite exhibited higher ionic conductivity (\(\sigma = 1.3\times10^{-3}\) S/cm at 70\(^\circ\)C) and noticeable thermal stability was observed in this report.

Kim et al. [138] reported the incorporation of various fillers into the PEO-based electrolytes. \([\text{P(EO)_{16}+LiClO}_4/10\text{wt}\%X, where X was various metal oxides}]\) films
were prepared by solution casting method. It was observed from their conductivity results that, at 100°C all CPE exhibited predominant amorphous phase and almost same ionic conductivity even though there is variation in their particle size and chemical compositions. These ceramic fillers may not have much coordination between the Li⁺ - ether oxygen units of PEO and ceramic surfaces. At low temperatures, they observed the variations in the ionic conductivities of CPEs. This may be an effect of added filler on the morphology of [Pt(EO)₁₆+LiClO₄] SPE and hence the degree of crystallinity and PEO chain flexibility has changed. They also investigated thermal and electrical properties and concluded that the relation exist between Tₘ and Tₖ only.

Yang et al. [139] reported the characterization of ceramic filler dispersed gel type polymer electrolytes (GPE). [PVdF+PEDA+PMMA+LiPF₆/LiCF₃SO₃+10%(Al₂O₃/ BaTiO₃/TiO₂) with LiPF₆/ LiCF₃SO₃ ratio=10/1 wt%] GPE were prepared by solution casting method. The ionic conductivity, electrochemical stability, discharge capacity and interface stability with electrode were discussed elaborately in their report. From their results it was observed that, the optimized GPE gave higher interfacial stability and ionic conductivity. They also constructed cell with optimized GPE with LiCoO₂ as cathode and MCMB as an anode, which exhibited good discharging ability.

Rajasudha et al. [140] investigated preparation and characterization of CuO doped Polyindole based composite polymer electrolytes. [Polyindole+LiClO₄/ CuO] CPE films were prepared by sol-gel method. They observed that, dispersion of CuO into [Polyindole-LiClO₄] system showed enhanced ionic conductivity and XRD results showed decreased degree of crystallinity of CPE. The highest ionic conductivity of 1.95×10⁻⁵ S/cm was observed for CuO at room temperature to monomer ratio was 2:1, which may be due to highest amorphous phase of CPE.

Johan et al. [141] synthesized and studied the conductivity of plasticizer and inorganic filler effect on PEO based SPE. [PEO+LiCF₃SO₃ +x%DBP where x=0, 5, 10, 15, 20] and [PEO+LiCF₃SO₃ +10%DBP+x%CuO where x= 5, 10, 15] films were prepared by solution casting technique using HFT solvent. From their observation [PEO+13%LiCF₃SO₃] SPE films exhibited high ionic conductivity σ=3×10⁻⁵ S/cm at room temperature. On loading of 10 wt% DBP content into the [PEO+13%LiCF₃SO₃]
SPE, the ionic conductivity further increased to \( \sigma_n = 1.6 \times 10^{-4} \) S/cm. This may be due to the plasticizer which has encouraged made more dissociation of salt into ions. On further dispersion of nanosized 5 wt% CuO content into the [PEO+13%LiCF₃SO₃ +10%DBP], plasticized composite polymer electrolyte exhibited highest ionic conductivity \( (\sigma=2.62 \times 10^{-4}) \) at room temperature. These observed results showed that, the variation of ionic conductivity with wt% content (DBT or CuO) of studied CPE was non-linear in nature.

Karmakar et al. [142] explored electrical conductivity studies of PEO-base CPE for lithium ion batteries. \([\text{P}(\text{EO})_{12}+\text{LiI}+x\%\text{CdO} \text{ where } x=0,0.05,0.10,0.15]\) films were prepared by solution casting method. The prepared films were characterized by XRD and DSC results showed that, on loading of nano sized CdO into the \([\text{P}(\text{EO})_{12}+\text{LiI}]\) SPE, the \( T_g \), the degree of crystallinity decreased noticeably and enhanced conducting path ways in the PEO host. From their SEM results it was observed that an average CdO particle size 2.5 nm was incorporated in the PEO host. \([\text{P}(\text{EO})_{12}+\text{LiI}+0.10\% \text{CdO}]\) film exhibited highest ionic conductivity which was in the order of \( 10^{-4} \) S/cm which was due to higher amorphous phase. On further addition of CdO content into the \([\text{P}(\text{EO})_{12}+\text{LiI}]\) SPE, the conductivity decreased due to aggregation of CdO and it has blocked the ions for transportation. The temperature dependence of conductivity results showed that, all studied CPE plots followed Arrhenius and VTF conductivity behaviour.

Kumar et al. [143] synthesized and studied characterization of PEO based composite polymer electrolyte. \([\text{P}(\text{EO})_{8.5}+\text{LiBETI}+\text{BN/Li}_2\text{O}]\) films were prepared by energy-milling technique. On incorporation of ceramic fillers BN/\( \text{Li}_2\text{O} \) into the \([\text{P}(\text{EO})_{8.5}+\text{LiBETI}])\) SPE enhanced ionic conductivities, improved interfacial stability with electrodes and also increased lithium transference number. The charge-transfer resistance was decreased noticeably on loading of both BN and Li₂O into the \([\text{P}(\text{EO})_{8.5}+\text{LiBETI}]\). They also measured the time and temperature- dependent electrical properties of prepared samples.

Appetecchi et al. [144] reported electrode-electrolyte interfacial stability of PEO based composite electrolytes. \([\text{P}(\text{EO})_{20}-\text{LiCF}_3\text{SO}_3/\text{carbon/Al}_2\text{O}_3]\) CPE films were prepared by using melt-mixing technique and investigated interfacial stability of Li-electrode. They found that interfacial stability depends on many factors like sample
preparation technique, which atmosphere the sample was prepared and cell fabrication procedure. They also noticed that, dispersion of filler content would affect the compatibility of lithium electrode interfacial stability.

Appetecchi et al. [145] investigated electrochemical properties of large scale procured PEO- based composite polymer electrolytes. \([\text{P(EO)}_{20}+\text{LiCF}_3\text{SO}_3+16.7\%\gamma\text{-Al}_2\text{O}_3]\) films were prepared by melt-mix method. They observed that prepared films were electrochemically compatible with the lithium electrode and ionic conductivity was also higher than \([\text{P(EO)}_{20}+\text{LiCF}_3\text{SO}_3]\) SPE films. The ionic conductivity of \([\text{P(EO)}_{20}+\text{LiCF}_3\text{SO}_3+16.7\%\gamma\text{-Al}_2\text{O}_3]\) CPE films at 70°C was \(10^{-4}\) S/cm.

Zhang et al. [146] reported synthesis and characterization of PEO-based composite polymer electrolytes. \([\text{P(EO)}_{20}+\text{LiTF}+x\%\text{Urea where } x= 0.2, 0.5, 1, 1.5, 2.0]\) CPE films were prepared by solution casting method. They observed \([\text{P(EO)}_{20}+\text{LiTF}+1.5\%\text{Urea}\] films which showed highest ionic conductivity at room temperature \((\sigma = 5.1\times10^{-6} \text{ S/cm})\) which was two order magnitude higher than \([\text{P(EO)}_{20}+\text{LiTF}]\) SPE film. DSC and ATR-IR techniques were used for explanation of the enhancement of conduction mechanism. The enhanced ionic conductivity was due to interaction of urea molecules with LiTF salt via carboxyl group. They observed that electrochemical stability and lithium transference number was higher in the optimized \([\text{P(EO)}_{20}+\text{LiTF}+1.5\%\text{Urea}\] CPE system. They constructed lithium cell with the optimized electrolyte and examined discharge capacity.

Kim et al. [147] synthesized and characterized organic clay based composite polymer electrolytes. MMT clay dispersed PEO+LiClO₄ films were prepared by solution casting method using acetonitrile solvent. They observed that, dispersion of various wt% MMT clay would affect the structural modifications of the PEO host and also enhanced the ionic conductivity of PEO+LiClO₄ SPE system. Their XRD measurements showed that, the interlayer distance between MMT clays were much wider than the Na-MMT. The ionic conductivity of organic MMT clay based polymer electrolytes showed higher ionic conductivity than that of Na-MMT clay based polymer electrolytes.

Kim et al. [148] investigated electrochemical characterization of the Li-MMT doped composite polymer electrolytes. PEO+LiClO₄+\(x\%\text{Li-MMT where } x= 0, 2, 5, 10, 15, 20\] CPE were prepared by solution-casting method. From their results it was found
that, the ionic conductivity and lithium transference number was increased on loading of Li-MMT clay into the [PEO+LiClO$_4$] system. The optimized [PEO+LiClO$_4$+20%Li-MMT] CPE system showed highest ionic conductivity ($\sigma=5.3\times10^{-5}$ S/cm) and lithium transference number ($t_{li}=0.55$). The increased ionic conductivity of this optimized system maybe due to the dispersed Li-MMT which changed the structural and morphological properties of PEO and hence decreased the degree of crystallinity of PEO host. They also observed that ionic conductivity verses inverse temperature plots followed Arrhenius behaviour.