LITERATURE SURVEY &

SCOPE OF THE PRESENT INVESTIGATION

CHAPTER-II
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In this chapter literature survey on several important types of polymer electrolytes based on poly (ethylene oxide) PEO, poly (acrylonitrile) PAN, poly (methyl methacrylate) PMMA, poly (vinylidene difluoride) PVdF and poly (vinylidene fluoride-co-hexafluoropropylene) PVdF-co-HFP have been focused besides the scope of the present investigation.

2.1 LITERATURE SURVEY

2.1.1 PEO based polymer electrolyte

In 1973, the first measurements on ionic conductivity of poly (ethylene oxide) (PEO) complexes with alkali metal salts were made [1,2]. The potential of these new materials were realized for battery applications [3]. These electrolytes combine the advantages of solid state with the ease of casting as thin films. However PEO based electrolytes offer very low ionic conductivity that ranges from $10^{-4}$ to $10^{-6}$ Scm$^{-1}$ at temperature between 40°C and 100°C. PEO is a semi crystalline polymer and about 60% of the bulk is crystalline at room temperature with a melting point (Tm) of 65°C was usually employed as the polymer host to form complexes with lithium salts. Apart from the ability of the sequential oxyethylene group, -CH$_2$-CH$_2$-O- in PEO to complex with lithium salts, polymer hosts containing oxygen atoms in the backbone can solvate the lithium salts [4].

PEO has been found to complex with lithium salts such as LiBr, LiI, LiSCN, LiClO$_4$, LiCF$_3$SO$_3$, LiBF$_4$ and LiASF$_6$ [4] out of which PEO: LiCF$_3$SO$_3$ [5, 6] and
PEO:LiClO₄ [6, 7] have been the most widely studied. The concentration of lithium salt in PEO a lowered the conductivities and lithium transference numbers [8]. This was considered as due to hindrance of polymer chains motion accompanying ion mobility and formation of ion pairs which lowered the amount of free lithium ions availability for conduction [9]. Using NMR techniques, the ion pair formation has been shown to form at high salt concentration [10]. In PEO complexes, ion pairing was found to set which cation:ether oxygen ratio was greater than 1:8, where as for 1-cation:4-ether oxygen ion aggregates were generally formed [10]. The maximum ionic conductivity in PEO complexes is obtained by limiting the amount of salt (or charge carrier) allowed in the host polymer.

The complete phase diagram of PEO-LiCF₃SO₃ was determined by XRD and DSC analysis [11]. The existences of three different molecular adducts involving the polymer and the salt was deduced from the phase diagram and a transition of phase of higher symmetry of a salt was identified at 179°C.

The lithium salt complexes with poly (ethylene oxide), PEO [12] and poly (propylene oxide), PPO [13] are the most widely investigated solid polymer electrolyte systems. The main reason to select these two polymer hosts is they form more stable complexes and possess higher ionic conductivities than any other group of solvating polymers without the addition of organic solvents.

Complex formation in PEOₙ - salt (n=number of ether oxygens per mole of salt) is governed by competition between salvation energy and lattice energy of the polymer and the inorganic salt [14]. Low lattice energies of both the polymer and the complexing salt have been found to increase stabilities in the resultant polymer electrolyte.

Watanabe et al [15] investigated various PEO-alkali salt complexes and informed that the ionic motion in PEO is promoted by the polymer segmental
relaxation. It is well established that increase of pressure decreases the free volume fraction and increased the Tg of the polymer. This could also reduce the mobility of ions and decrease of conductivity with pressure [16]. However, it was found that the bulk conductivity of PEO-LiCF$_3$SO$_3$ electrolyte decreased with increasing the pressure over 60 to 300MPa. When a cell was held at a constant pressure and temperature, the conductivity was again seen to fall with time [17]. These effects were attributed to structural changes at higher pressure and possibly due to increased crystallization [18].

The preparation and characterization of a new type of polymer-inorganic nanocomposite films of PEO-ZnO and PEO-ZnO-LiClO$_4$ is known [19]. Interaction between the PEO and ZnO nanoparticle decreased the photoluminescence intensity of the PEO film to a great extent, which were manifested by XRD. The cooperative effect of PEO and LiClO$_4$ forms cross-linking structures, providing free ions as charge carrier in the electrolyte thereby decreasing the films crystallinity to produce more amorphous regions for charge carriers to transfer and to the conductivity of the film.

The synthesis and the characterization of PEO based composite polymer electrolytes prepared by hot-pressing technique a solvent-free procedure was reported [20]. The characterization in terms of ionic conductivity was done in the 30°C to 105°C range. The electrolytes reached the conductivity value of 10$^{-4}$Scm$^{-1}$ at 70°C. They concluded that there was no practical effect on conductivity enhancement at high filler contents (above around 5wt%). A novel lithium composite solid polymer electrolyte based on a PEO and a rare earth metal oxide Sm$_2$O$_3$ (Samarium oxide) was prepared [21]. The incorporation of lithium salt and samarium oxide to PEO showed a dramatic modification of surface morphology. In addition to this SEM micrographs showed the reduction of crystallinity and it confirmed the fact that the salt acts as the compatibilizer. The conductivity in the composite electrolyte is one order of magnitude higher compared with pure PEO/Li electrolyte and the value...
decreased with increasing content of Sm$_2$O$_3$ to over 10wt%. The thermal stability and electrochemical stability of PEO-LiCF$_3$SO$_3$ and PEO-LiN(CF$_3$S0$_2$)$_2$ based polymer electrolytes, thermal stability up to 300°C, which are more safe as compared to liquid electrolyte were also reported [22]. They became unstable and underwent thermal runaway reaction when in contact with cathode materials; Both LiNiO$_2$ and LiCoO$_2$ exhibited significant exothermic reaction and also electrochemically stable up to 5V vs Li/Li$^+$ at a blocking electrode, while it decomposed at ca3.8V with a carbon composite electrode.

Glass as a filler for PEO-LiC(CF$_3$SO$_2$)$_2$ was used [23]. Room temperature conductivities as high as $10^{-4}$ S cm$^{-1}$ and good mechanical stabilities were observed for x=13%, in a (100-x):x system, where, (100-x) and x are respective volume percent of the glass electrolyte, (0.56Li$_2$S-0.19B$_2$S$_3$-0.25LiI) and the polymer electrolyte. The ionic conductivity [24], transference number [25,26], DSC and NMR [27], thermal [28] polarization [29] and cycling performance [30,31] of PEO and co-polymer of P(EO-MMA) based electrolytes [32] have been reported. A novel PEO electrolyte was prepared [33] with lithium 4,5-dicyano-1,2,3-triazolate as salt. A higher ionic conductivity, electrochemical stability, thermal stability and high transference number have been achieved with this host than other PEO systems. The possibility of using low cost lithium-ion batteries comprising LiFe$_6$PO$_4$/PEO gel electrolytes/natural graphite system was also explored [34]. This system has shown excellent capacity retention and was found to be more suitable for hybrid electric vehicle applications.

The composite solid polymer electrolyte of (PEO)$_{10}$ LiClO$_4$-Al$_2$O$_3$ was known [35]. The room temperature ionic conductivity of CSPE can be enhanced by the addition Al$_2$O$_3$ particles. After the addition of Al$_2$O$_3$ particles, a little decrease of Tg is observed from $-39.43^\circ$C to $-40.3^\circ$C and the decrease of Xc is from 13.15% for (PEO)$_{10}$ LiClO$_4$ to 12.39% for(PEO)$_{10}$ LiClO$_4$-Al$_2$O$_3$ SPE. Although the decrease of Tg and Xc as a result of Al$_2$O$_3$ addition are less than 1°C and 1% respectively, the trend
of the changes is the same [36] and also the change in the micro structure and morphology are due to the reactions of various Lewis acids and bases occurring among Lewis base centers of the polyether.

A structure-conductivity correlation in the PEO: LiClO$_4$ – MgO composite polymer electrolyte system was proposed [37]. The role of MgO is to depress the PEO melting temperature and to retard the kinetic of its crystallization. A concentration around 30wt % of ceramic phase adversely affected the conductivity. The highest conductivity in the 0-100°C temperature span ranged from $10^{-5.4}$ to $10^{-3.1}$ Scm$^{-1}$ for the PEO: LiBF$_4$ (8:1) -MgO (10wt%) specimen. There was a slight reduction in conductivity over the entire temperature range when [O]:[Li] ratio decreased to 6:1 and 7:1. A higher concentration (30wt%) of MgO leads to its segregation and reduction in conductivity resulting from crystallization of PEO.

Thermal stability and electrochemical stability of PEO-LiCF$_3$SO$_3$ and PEO-Li[N(CF$_3$SO$_2$)$_2$ based polymer electrolytes, thermal stability upto 300°C, which are more safe as compared to liquid electrolyte are reported [38]. They become unstable and undergo thermal runaway reaction when in contact with cathode materials: Both LiNiO$_2$ and LiCoO$_2$ exhibited significant exothermic reaction and also electrochemically stable upto 5V vs Li/Li$^+$ at a blocking electrode, while it decomposed at ca3.8V at a carbon composite electrode.

The morphological, electrical and mechanical characteristics of the PEO based composite polymer electrolytes with alumina whisker as fillers was reported [39]. Addition of alumina whisker effectively prevented the formation of the microcracks. The alumina whisker were homogeneously dispersed in the polymer electrolyte matrix and exhibited excellent interconnection with PEO-LiClO$_4$ polymer electrolyte. The addition of whisker additives improved the ionic conductivity, when the content of the whisker was less than 20wt%. LiClO$_4$, P(EO)$_{10}$ and
LiCF$_3$SO$_3$-P(EO)$_{10}$ EC plasticizer samples, the enhanced conductivity of the as prepared films in transient and it is not maintained on thermal cycling under vacuum [40]. In particular all the complexes of LiCF$_3$SO$_3$ showed a hysteresis loop, whilst it was absent in the complexes of LiClO$_4$.

The effect of varying factors such as salt and PEO molecular weight and the nature of the oxide nanoparticles (different compounds and different particle sizes) was explored [41]. It was found that polymer electrolytes containing the trifluoromethanesulfonimide salt had higher conductivity, this advantage was offset by poor electrochemical stability. In addition to improving mechanical properties at elevated temperature, there were cases in which the ceramic additives improved Li-ion diffusivity and ionic conductivity without a corresponding increase in polymer segmental mobility.

A composite polymer electrolyte based on PEO with a hyperbranched polymer poly[bis(triethylene glycol)benzoate] capped with an acetyl group (HBP) and a ceramic filler BaTiO$_3$ was examined as electrolyte [42]. The conductivity of the composite polymer electrolyte PEO-10wt% HBP with Li(CF$_3$SO$_2$)N -10wt% LiPF$_6$ as a lithium salt and 10wt% BaTiO$_3$ was found to be 1.6 X 10$^{-4}$ S cm$^{-1}$ at 25°C and 1.5 X 10$^{-3}$ S cm$^{-1}$ at 60°C in a O/Li ratio of 10. The cyclic performance can be improved by revising the electrode and the electrolyte interface with the addition of filler into the polymer electrolyte.

An increase in the ionic conductivity from 10$^{-7}$ - 10$^{-8}$ S cm$^{-1}$ to 2.3 X 10$^{-5}$ S cm$^{-1}$ at room temperature is obtained through the addition of nano-sized SiO$_2$ filler to a PEO:LiClO$_4$ composite electrolyte by post heat treatment [43]. The nano-sized SiO$_2$ particles appeared to play two roles, the simultaneous arrangement of dipoles in the composite electrolytes and interruption of the crystallization of PEO. The PEO and the inorganic filler generally tend to orient their dipoles to minimize their total energy, so that PEO chains were forced to rotate and orient in a direction parallel to the
applied field. It is proposed that the organic and inorganic hybrid electrolyte may be a new promising candidate for lithium rechargeable batteries.

The ion conduction of polymer electrolytes confined in cylindrical pores having diameters ranging from 400 to 30nm was investigated [44]. The confinement of PEO polymer electrolytes in nanopores increases ionic conduction as the pore size decreased with the greatest conductivity occurring in pores that were 30nm in diameter where the specific conductivity of 2.43 X 10^-4 S cm^-1 was observed. In addition to the advantages of enhanced conduction, these membranes had enhanced conduction perpendicular to the plane of the thin film electrolyte unlike other oriented films that are made by stretching polymer electrolyte films [45, 46] where increased conduction was parallel to the film surface.

(PEO)_{16}-LiClO_{4} based composite polymer electrolytes containing silane modified SiO_{2} have been evaluated [47]. Compared with unmodified SiO_{2}, modified SiO_{2} in PEO based polymer electrolytes effectively led to higher enhancement in ionic conductivity and mechanical stability. The enhancement was attributed to the good dispersion of silane modified SiO_{2} in polymer electrolyte.

The nanocomposite polymer electrolyte based on synthetic lithium hectorite (SLH) and different mass ratio of PEO was described [48]. The conductivity of the nanocomposite with a nominal ratio of PEO:SLH 1:1 showed a conductivity of 4.324 X 10^-3 S cm^-1 and the thermal stability of polymer electrolyte around 206.6°C (55.5% weight as PEO) and the remaining material corresponded to SLH. AC conductivity measurements and NMR study of lineshape and relaxation rates in PEO lithium salt and TiO_{2} composite polymer electrolytes was reported [49].

PEO, lithium salt (LiCF_{3}SO_{3}, LiClO_{4} and LiPF_{6}) and nano-sized ceramic powder (TiO_{2}, SiO_{2} and Al_{2}O_{3}) based composite polymer electrolytes prepared using stirring or high-energy ball milling technique [50]. High-energy ball milling also
increased the ionic conductivity greater in the order of magnitude compared with unmilled samples by lowering the glass transition temperature of the composite polymers. The highest ionic conductivity was reported when using LiPF₆ and Al₂O₃ as dispersed particles and its electrochemical stability in the range of 2-5V.

The composite polymer electrolyte of PEO/BaTiO₃/LiN(CF₃CF₂SO₂)₂ salt with poly[bis(triethyleneglycol)benzoate] as hyperbranched polymer capped with an acetyl group as a plasticizer was described [51]. The optimized polymer electrolyte showed the ionic conductivity of 1.3 X 10⁻⁴ Scm⁻¹ at 30°C and 1.6 X 10⁻³ Scm⁻¹ at 80°C respectively. The electrochemical stability window of 4V and also it was stable until 307°C under air. Interfacial stability of the LiN(CF₃CF₂SO₂)₂ based composite polymer electrolyte for a lithium metal electrode was found to be better than that of LiN(CF₃SO₂)₂.

A new class of polymer electrolytes based on semi interpenetrating polymer network of PEO-poly urethane and polyacrylonitrile doped with LiClO₄. With varying amount of PAN and LiClO₄, room temperature conductivity increased over four orders of magnitude from 10⁻¹⁰ to 10⁻⁶ Scm⁻¹. The semi IPN structure improved the tensile strength and modulus while retaining the flexibility of the host polymer [52].

A simple visualization method is used to understand the difference between two composite polymer electrolyte systems based on PEO, LiBF₄ and SiO₂ [53]. In one of the systems, the OH groups on the SiO₂ filler are replaced by inactive phenyl groups in a silanization reaction with the purpose of reducing the Lewis acid base interaction between the ceramic particles, the polymer host and lithium salt. Two type of SiO₂ particles had similar morphology and dispersion in the polymer and were expected to amorphitize the polymer to the same extent. The ceramic surface groups which affects the Lewis acid-base interaction in the composite electrolytes, the decrease in conductivity with temperature for the modified SiO₂-PEO system
between 60°C and 90°C was speculated as arising from the steric hindrance of the phenyl groups on the silica surface.

The properties of homogeneous polymer gel electrolyte membranes prepared by a new concept involving the swelling process of linear PEO-LiClO₄ based composite matrix was described [54]. The swelling a P(EO)₁₀LiClO₄:10wt%SiO₂ composite matrix in an EC/DEC solvent mixture was achieved. The impedance analysis gave an ionic conductivity of the order of 10⁻³ Scm⁻¹ in the -10°C/+25°C temperature range.

Poly ethylene glycol (poly urethane)/polyethylene oxide based polymer electrolyte [55] showed ionic conductivity of the order of 6.4 X10⁻⁴ Scm⁻¹ at room temperature and also electrochemical stability in the working voltage ranging from 2 to 4.5V. Cyclic performance of Li/PE/LiCoO₂ cell revealed that when the cyclic number increased the charge transfer in the lithium electrode difficult and Li⁺ ion diffusion rate in the Li/PE interface became very slow. This is a convincing indication of the reaction between PC and lithium metal to result a passive layer which caused loss of capacity on cycling due to degradation of Li/PE interface.

The effect of carbon black and ceramic (αAl₂O₃ and γAl₂O₃) particles on the cationic and polymer chain mobility have been investigated in PEO –LiClO₄ and LiBF₄ salts using NMR techniques [56]. ¹H and ⁷Li data indicated that the lineshape and spin lattice relaxation times were measured as a function of temperature. The ⁷Li lineshape in PEO based lithium salt polymer electrolyte was influenced by both the dipolar and quadrupolar interactions, where as the spin-lattice relaxation mechanism was dominated by the quadrupolar interaction. The result showed that the addition of αAl₂O₃ influenced both the relative cation mobility and the polymer chain motion.
Two cross-linked polymers, poly(ethylene oxide-propylene oxide) [poly(EO-PO)] and with and without LiN(SO₂CF₃)₂ on the polymer structure, segmental motion (¹H NMR), lithium hoping motions (⁷Li NMR), the anion diffusion (¹⁹F NMR) and the ionic conductivity was studied [57]. The ionic conductivity was observed between 2 X 10⁻⁵ and 4 X 10⁻⁴ S cm⁻¹ and the interaction between the polymer chain and lithium ions is stronger in poly(EO-GE) than in poly(EO-PO). From the NMR diffusion and relaxation measurements, it was inferred that the dynamics of the lithium ions are strongly correlated with the polymer segmental motion.

DSC, AC conductivity and ⁷Li NMR experiments were held to study the behaviour of PEO₆-LiClO₄ with different quantities of αAl₂O₃ or γAl₂O₃ [58]. DSC result showed that the presence of the filler did not change the glass transition temperature of the electrolyte but on the other hand, modified the quantity of its crystalline phase. The conductivity, calculated from impedance data, could therefore be related to change in the interaction between the Li-ions and the filler when αAl₂O₃ replaced by γAl₂O₃ due to changes in PEO crystallinity or with the formation of a space charge zone in the region near the filler particles.

Ceramic containing electrolytes exhibited better lithium/electrolyte interfacial stability. Such improvement has been noted with simple PEO-LiN(CF₃SO₂)₂- γLiAlO₂ electrolytes too [59]. The interactions between ceramic particles and other components are not well understood [60]. Possible effects including suppression of crystalline PEO or PEO salt phases which led to an increase in electrical conductivity [61]. In highly salt concentrated PEO complexes, the presence of the inorganic additive improved transport through grain boundaries parallel to the current flow in the electrolyte [62]. Among the less understood is the effect of grain boundary in enhancing lithium/electrolyte interfacial stability [63, 64].
2.1.2 PAN based polymer electrolyte

As compared to PEO based electrolytes, PAN based compositions offer advantages like high ionic conductivity. In fact, as early as 1975 it was known that electrolytes consisting of PAN and hydrated perchlorate salts with ionic conductivity in the range of $10^{-7}$ to $10^{-2}$ Scm$^{-1}$ [65]. In these systems hydration water acted as a plasticizer.

PAN based polymer salt complexes using ethylene carbonate and propylene carbonate as plasticizer, the conductivity correlated with the mole ratio [plasticizer]/[salt] in the hybrid films was studied [66-68]. An increase in this ratio increased the conductivity due to the fact that the ionic mobility increased with the high dielectric constant plasticizer content. Conductivities in the range of $10^{-3}$ to $10^{-4}$ Scm$^{-1}$ were obtained at room temperature [69,70] with electrochemical stability windows exceeding 4.5V vs Li$^+/Li$ and lithium transport number exceeding 0.6 [71].

An increase in ionic conductivity of PAN based electrolytes comprising of 38 m/o EC, 33m/o PC with 8m/o LiClO$_4$ and 21m/o of PAN was found [72]. A fully amorphous gel of PAN-LiClO$_4$ (1:02) in EC showed room temperature conductivity of the order of $1 \times 10^{-3}$ Scm$^{-1}$ at ambient temperature was reported [73]. The PAN based gels were found to have lithium ion transference numbers more than 0.5 because of the absence of oxygen atoms in the matrix. The transference number was enhanced to 0.7 when the lithium salts like LiTFSI and LiTFSM were used.

The conductivity changed slightly with changes of salt concentration in PAN was reported [74]. The conductivity, however changed markedly with the amount of salt in the plasticizer as shown by Abraham [71, 72] who investigated PAN based electrolyte containing EC and PC. It was concluded that the PAN host did not actively participate in the transport mechanism, but only served as a stable structural matrix.
The variation of conductivity with temperature of LiClO₄ in DMF and LiClO₄ in PAN was compared and found that the conductivity of the latter increased markedly with temperature indicating that the conductivity increase did not originate from the polymer electrolytes residual organic solvent, but from the polymer backbone's segmental motion. The ionic conduction in solid polymer electrolytes occurred primarily through the non-crystalline phase for which reason PAN based electrolytes should exhibit good ionic conductivity [76, 77].

The conductivity of PAN based lithium salt complexes had been reported for various temperatures ranging from -15°C to 55°C [78]. The room temperature conductivity was the order of 10⁻⁴ Scm⁻¹ and the transference number was found to be 0.66. However, the compatibility with metallic lithium was proved to be rather good. Using ternary solvent mixtures consisting of EC, PC and 3-methyl-2-oxazolodinon (MEOX), the low temperature conductivity of PAN based gel polymer electrolyte had been improved [79].

The elevated conductivity is a favourable characteristic of gelled electrolytes based on PAN. Lithium metal electrodes may undergo passivation when in contact with PAN based gel electrolytes and the passivation increased with time [80]. Addition of 5wt% zeolite to the gels effectively reduced the rate of growth of the resistive layer on the lithium surface. It was believed that this beneficial interface. The dispersion of ground zeolite trapped impurities and prevented them from reacting at the interface. Another possible reason for the improved interface may be due to the composite film being more viscous than the gel electrolyte, thus preventing the flow of corrosive solvents to the interface [81]. A details discussion regarding the electrochemical stability of PAN based electrolyte was prepared [82]. Salt concentration, PAN concentration and the mixture ratio between PC and EC had no effect on the anodic stability. The anodic stability was usually limited by the
decomposition of PAN and the lithium salt, while cathodic stability was more complex.

The PAN based electrolytes were prepared by encapsulating Li-salt solutions obtained by dissolving LiN(CF₃SO₂)₂, LiAsF₆, LiCF₃SO₃ and LiPF₆ in plasticizer mixture of EC and PC [83]. Cyclic voltammetry studies revealed that the electrolytes had an inherent oxidation stability window exceeding 5V vs Li⁺/Li. The electrochemical properties of gel polymer electrolytes by immobilization of PAN matrix with different lithium salts such as LiClO₄, LiAsF₆, Li(CF₃SO₂)₂ was reported. These electrolytes exhibited high ionic conductivity and high lithium transference number. Their applications in rechargeable lithium polymer batteries was hinderance and was attributed to the instability with lithium electrode interface.

Co-polymer of poly(acrylonitrile-co-lithium methacrylate) based polymer electrolyte was described [85]. The polymer electrolytes based on the PAN ionomer with 4mol% LiMA content exhibited ionic conductivity of 1.9x10⁻³ Scm⁻¹ at 25°C and 2.4 X 10⁻⁴ Scm⁻¹ at -10°C when only EC was used as a plasticizer. The suppression of the EC crystallization was expected to result from the strong ion-dipole interaction between the LiMA groups in the ionomer and the polar groups of EC. It was the factor for the increase in ionic conductivity with increase in LiMA content as the crystalline phase of EC could not transport the charge carrier and hindered the motion of the charge carrier [86, 87]. The interfacial resistance of PAN ionomer was also observed to be much lower than that for the PAN based polymer electrolyte.

Gel polymer electrolyte composed of PAN/EC/PC/ lithium (trifluoromethanesulfone) imide (LiTFSI) was known [88]. Room temperature ionic conductivity was of the order of 2.5x10⁻³ Scm⁻¹ is obtained for PAN(15.4%)/EC(41.0%)/PC(41.0%)/LiTFSI(2.6%) by weight system.
Micro-porous polymer membrane by phase inversion technique was developed [89]. It was expected that an uptake of the electrolyte solution might result in swelling or gelation of the polymer rather than dissolution. They showed high ionic conductivity of $2.8 \times 10^{-3} \text{Scm}^{-1}$ at room temperature and electrochemical stability over 5V vs Li$^+$/Li.

A novel fire retardant gel polymer based on PAN was reported [90] to optimize the ratio of polymer, with a combination of ethylene carbonate and propylene carbonate and LiPF$_6$. The incorporation of LiPF$_6$ significantly reduced the carbonizing point of the gel electrolytes and increased the residue of carbonaceous materials after burning.

A series of novel solid type $\alpha$Al$_2$O$_3$ containing PAN based CPE was developed [91]. The high ionic conductivity of $5.7 \times 10^{-4} \text{Scm}^{-1}$ at room temperature was obtained with 7.5wt% $\alpha$Al$_2$O$_3$ and 0.6LiClO$_4$ per PAN repeating unit. It possesses high yield stress (73kgcm$^{-2}$) suitable for serving as separators in the solid-state lithium battery. But trapping a LiPF$_6$ – PC solution into a PAN with Al$_2$O$_3$ dispersed ceramic powder, had ionic conductivity of $0.8 \times 10^{-3} \text{Scm}^{-1}$ at 25°C and of the electrochemical window of 5.5V Li$^+$/Li [92].

NMR and Raman spectroscopic investigation on a novel fast ion-conducting polymer –in-salt electrolyte based on LiCF$_3$SO$_3$ and PAN was carried out [93]. They concluded that the significant ionic motion occurred at temperatures close to Tg of polymer-in-salt electrolytes where as in dilute salt-in-polymer regime, ionic motion appeared mainly to local salt-rich domain.

NMR spectroscopic studies was used to determine the self-diffusion coefficient of lithium ions in PAN based gel electrolytes [94]. The result indicated that the self diffusion coefficient of lithium ions dependent on the mass ratio of lithium salts and have a maximum at 10% in the range of 5-20%.
The performance of GPEs in terms of the affinity between polymer matrix and plasticizing solvent molecules was followed [95]. Four different polymers were studied; among them PAN based gel polymer electrolytes showed poor solvent retention ability compared with the other gel polymer electrolytes based PVDf, PMMA etc. However, the PAN based polymer electrolytes showed good mechanical properties.

The spectroscopic and NMR studies on PAN complexed with LiCF₃SO₃ was reported [96]. Significant ionic motion was found at temperature close to the glass transition temperature. Lithium metal electrode might underwent passivation when in contact with PAN based gel electrolytes [97]. They observed an expansion of impedance semicircle, which implied that the lithium electrode was passivated with time.

A composite polymer electrolyte which consisted of zeolite powders, dispersed in PAN based gel with LiAsF₆ was studied [98]. Addition of small amounts of zeolite prevented the crystallization leading to the formation of amorphous domains. Preliminary polarization effect of Li/PAN-Li⁺ (LiPF₆ and LiBF₄) interface by analyzing the surface film compositions with XPS measurement was investigated [99]. A layer consisted of mainly LiF and LiOH was formed on voltage cycling and the layer stabilizes the interface.

Inhibition effects of PAN based gel polymer electrolytes in lithium dendrite formation was studied. The dendrites formation was suppressed in gel electrolytes containing 5-17% PAN. It was systematically investigated that PAN based gel using different solvent mixtures and reported high ionic conductivities in the order of 2.5 X 10⁻³Scm⁻¹ to 4.7 X 10⁻³Scm⁻¹ along with good compatibility with a lithium metallic electrode [101, 102].
Electrical properties of the plasticized polymer electrolytes composed of acrylonitrile-methyl methacrylate copolymer (AN-MMA) and a liquid electrolyte solution was known [103]. The ionic conductivity of these systems reached an order of $10^{-3} \text{Scm}^{-1}$ in presence of 80wt% of liquid electrolyte solution at room temperature having homogeneous films with good dimensional stability. The cyclic performance of rechargeable cells based on AN-MMA-Styrene (AMS) polymer electrolytes had been reported [104-107]. Good cycling performance was witnessed for a lithium-ion polymer cell comprised of carbon anode prepared with mesocarbon beads AMS based polymer electrolyte and LiNi$_{0.83}$Co$_{0.17}$O$_2$ cathode.

Positron annihilation life time spectroscopy was used to estimate the free volume behaviour of PAN based electrolyte complexed with LiCF$_3$SO$_3$ [108]. The relative free volume cavity size at room temperature was shown to decrease with increase in salt concentration.

The electrochemical characteristics of Li/LiMn$_2$O$_4$ cell with GPE composed of AN-MMA co-polymer and LiClO$_4$ with PC and EC were reported [109]. The cell had a reversible capacity of 132mAh/g in the voltage range of 3-4.5V at C/5 rate showed a good cycling performance with the columbic efficiency greater than 99%. GPE with porous membrane based on AN-MMA co-polymer were prepared by phase inversion method [110]. The membrane thus formed could encapsulate the electrolyte solution without leaking and have good mechanical properties with an ionic conductivity is greater than $6 \times 10^{-4} \text{Scm}^{-1}$ at room temperature.

A polymer electrolyte consisted of AMS terpolymer was prepared and characterized for its application in lithium ion polymer cells [111]. Gel polymer electrolyte of this type showed better rate capacity and cycling efficiency. Dual phase polymer electrolyte composed of poly(acrylonitrile-co-butadiene) was reported [112].
These electrolytes showed enhanced tensile strength of about 3.0Mpa with the conductivity of above $1 \times 10^{-3}$Scm$^{-1}$.

2.1.3 PMMA based polymer electrolyte

Poly(methyl methacrylate) began to be investigated [113] in 1985 of its use as gelatinization agent providing appreciable conductivity of $1 \times 10^{-4}$Scm$^{-1}$ at 25°C for a PMMA content of 45wt%. However, this electrolyte suffered from a gel like mechanical property and it did not form freestanding film at high plasticizer content.

A room temperature conductivity of $2.3 \times 10^{-3}$Scm$^{-1}$ for 20% PMMA –PC composition containing 1MLiClO$_4$ was demonstrated [114]. The presence of high molecular weight PMMA imparted a high macroscopic viscosity ($\sim$335Pa.S) to the system without significantly diminishing the conductivity i.e. the conductivity of gel remains very closer to that of a liquid electrolyte. PMMA acted primarily as a "stiffening" agent that ion transport occurred through a continuous conduction path of PC molecules and that the presence of PMMA did not affect the electrochemical stability of the electrolyte. The conductivity of the system decreased with increasing the amount of polymer. Depending on the amount of polymer in the electrolyte, conductivity varied from $5 \times 10^{-5}$Scm$^{-1}$ to $5 \times 10^{-3}$Scm$^{-1}$.

The model that emphasized the importance of PC and/or PMMA lithium salvation effect of ion pairing and the cross linking action of cations at high PMMA concentration have also been reported [115]. To 20 w/o of PMMA gels were considered as a liquid electrolyte encaged in an inert polymer matrix. On the other hand, very strong interaction between the polymeric chains and the ionic species was observed when the concentration of PMMA was increased to 45w/o of the gel.

The PMMA based gel electrolytes using DSC and NMR spectroscopy was studied [116]. The DSC analysis showed a single glass transition temperature, exhibiting the homogeneous nature of the PMMA film. Gel polymer electrolyte based
on PMMA/PC containing various Li, Na, Mg and Zn perchlorates were investigated and compared [117]. The conductivity of gel containing cations of smaller ionic radii such as lithium and magnesium was lower than that of long term structural stability, which determined a reduction of the contact area with the electrode and caused lowering of conductivity. Long term structurally stable PMMA based GPEs were prepared [118]. Structural modifications were induced in the system by annealing for several months at room temperature.

Studies on gel electrolytes based on PMMA and non-aqueous solution of lithium salt, LiClO₄ in the mixed solvent of PC and EC was carried out [119]. Influence of polymer concentration and the ratio of mixed solvent on the properties of electrolyte was reported. Conductivity decreases with addition of beyond 2:1 ratio of EC:PC.

PMMA based electrolytes containing EC-PC-LiX [X=ClO₄, AsF₆ or N(CE3SO₂)₂] were shown to exhibit conductivities as high as 0.5 X 10⁻³ S cm⁻¹ at 60°C [120]. Transference number of PMMA based electrolytes were higher than those obtained for conventional PEO based electrolyte. PMMA based electrolyte had been shown to be compactable with reactive metals like lithium and to be stable up to a little more than 4.5V [121].

PMMA based GPEs with various solvents was investigated and the gel could have good mechanical stability, solvent retention and high electrical conductivity [122, 123]. Molecular and ionic interactions of PMMA and GPEs were determined using Vibrational Raman and FT-IR spectroscopy [124]. No spectroscopically detectable interactions between the polymer matrix and the electrolyte could be noticed.

Gel polymer electrolytes composed of porous MMA-styrene copolymer membrane were prepared [125]. The ionic conductivity was found to be about 1.0 X
10⁻³ S cm⁻¹. Transparent and polymeric electrolytes based on poly(ethylene glycol) methyl ether blend with PMMA and doped with LiClO₄ were prepared and investigated [126]. Maximum ionic conductivity at room temperature was measured to be around 6 X 10⁻⁴ S cm⁻¹ for PMMA concentration of 17 w/w. The decrease in the overall ionic conductivity of PEGMe-PMMA blend with increasing PMMA concentration was observed, which may be due to dilution effect arising from the phase separation of PMMA.

GPEs were prepared and investigated with MMA-styrene copolymers and LiPF₆ or LiBF₄ in EC/DMC [127]. Depending on the molar composition of the copolymer these GPEs exhibited a different range of mechanical and electrical properties. Spectroscopic and electrochemical studies of PMMA based GPEs that was modified with interpenetration networks [128]. An increase in ionic conductivity was noticed due to enhancement in both free-ion fraction and the ionic mobility.

The electrochemical and physical properties of composite polymer electrolytes based on a blend of PMMA and PEGDA were investigated [129]. The addition of nano-sized TiO₂ filler in the polymer matrix decreased the crystallinity with improved ionic conductivity and the interfacial resistance between the electrodes and the electrolyte.

The effect of ionic conductivity on the addition of clay to PMMA polymer matrix was investigated [130]. The addition of optimum content of dimethylidioctadecylammonium chloride modified montmorillonite clay enhanced the ionic conductivity by nearly 40 times and promotes the dissociation of the lithium salt and thus the specific interaction was enhanced between C=O and free lithium cation. The ion conduction behaviour of the plasticized polymer electrolyte based on PMMA-co-sodium methacrylate was studied using in situ FT-IR spectroscopy and ac electric field [131]. It was found that the transport of charge carrier was dependent on
the ion content of the ionomer. Ionic aggregates were formed when the ionomer content was about 7 mol%.

The transport properties of gel type ionic conducting membranes consisting of PMMA blend with PEO, LiClO₄, LiBF₄, LiCF₃SO₃ and dimethyl phtahlate were studied [132]. The highest conductivity at room temperature was about $0.64 \times 10^{-4}\, \text{S/cm}$ for the blend electrolyte. This hybrid polymer electrolyte on PMMA – PEO appeared to very promising for lithium battery applications. Three types of modified natural rubber, namely PMMA grafted natural rubber, 25% and 50% epoxidised natural rubber were investigated [133]. Adhesive and transparent polymer blend electrolytes were synthesized by the free radical polymerization of MMA with PPG complexed with LiCF₃SO₃ [134]. The physical characteristic of the polymer blend electrolytes were found to depend on the PPG molecular weight, salt concentration and PMMA content. SEM studies indicate the a phase separated morphology of the polymer blend.

The optical properties of electrochromic smart window type displays using the polymer blend of PMMA-PEG-LiClO₄ as electrolyte was studied [135]. The electrolyte showed ionic conductivity of about $2 \times 10^{-6}\, \text{S/cm}$ at room temperature and the light transmittance was approximately 89% for a 25μm thick layer and show low optical scattering. Composite electrolyte composed of a blend of PEGDA, PVdF and PMMA together with a non-woven fabric were prepared by means of UV cross linking [136]. Such composite electrolyte had good integrity upon an initial liquid electrolyte uptake of 100 (%) EC-DMC-EMC-LiPF₆. The ionic conductivity of the composite electrolytes reached $4.5 \times 10^{-3}\, \text{S/cm}$ at a temperature of around 18°C and was electrochemically stable upto 4.8V vs Li/Li⁺.

The compatibility of duel phase polymer electrolyte (DPE) was prepared [137]. The ionic conductivity of DPE increased with in the ratio of PMMA/Poly(MMA-
The ionic conductivity varied from $2.44 \times 10^{-4}$ Scm$^{-1}$ to $2.67 \times 10^{-3}$ Scm$^{-1}$ with the weight ratio of PMMA:poly(MMA-g-PVC) increased from 2:1 to 10:2. The electrochemical stability of 1:1 PMMA:poly(MMA-g-PVC) electrolyte exhibited 4.8V vs Li/Li$^+$.  

2.1.4 PVDF based polymer electrolyte

PVdF based polymer electrolytes are highly anodically stable to the presence of strong electron withdrawing functional group (-C-F) and the polymer itself has a dielectric constant ($\varepsilon$=8.4) which helped for greater dissolution of lithium salts and subsequently supported high concentration of charge carriers. The earlier report indicated a homogeneous hybrid film could be obtained with PVdF when EC and or PC with lithium salt of proper propositions [138].

It was reported that both the crystallinity and melting temperature of PVdF were decreased with increasing salt content and by blending with TiO$_2$ particles [139]. Polymer electrolyte by using PVdF matrix, LiPF$_6$ as the mobile ions source and nano-size particles of high dielectric constant in the polymer served to develop amorphous phase of the PVdF polymer to enhance free volume was prepared. These properties confirmed by DSC and XRD results. SEM micrograph was also consistent with DSC and XRD.

The plasticized PVdF with 30mol% of LiClO$_4$ was examined and the viscosity played a major role in the conductivity rather than the dielectric constant of the plasticizer [140, 141]. However, these electrolytes exhibited low ionic conductivity of the order of $10^{-5}$ Scm$^{-1}$ at room temperatures.

In order to explain the carrier migration mechanism of gel polymer electrolyte through the dynamic behaviour of diffusion co-efficient and conductivity, polymer electrolyte composed of PVdF and PEO was prepared [142]. The diffusion co-efficient of the ionic species decreased with the increase in the polymer fraction in
the gel. Cation migration was closely associated with the polymer, showing the reduced activation energy for diffusion with polymer in contrast of the increasing feature of the activation energy of the anion diffusion. Due to the swelling saturation of PVdF gel electrolyte, the diffusion showed two components. One was the fast migration of the carriers similar to that in the solution and relatively slow migration in the swollen region. The latter was influenced by the polymer due to the physical blocking and chemical interactive effect.

The electrochemical properties of PVdF based electrolyte with 1:1 EC and PC as the plasticizer and LiBF₄ as the salt was studied [143, 144]. The gel polymer electrolyte showed high ionic conductivity, good mechanical stability and was stable for a wide electrochemical window. Gel polymer electrolyte based on PVdF a ternary solvent mixture consisting of PC, EC and dimethylacetamide as the solvent and different (-ortho, -para and -meta) hydroxyl substituted carboxylic acid have been studied [145]. The conductivity value depended upon the concentration of acid and the conductivity was of the order of 10⁻⁴ S cm⁻¹ at 20°C. The conductivity of the gel polymer electrolytes was found to be higher than that of the corresponding liquid electrolytes at all acid concentrations. A study was made on the electrical and electrochemical characteristics of PVdF based polymer electrolytes [146].

A novel polymer electrolyte comprising of PVdF-EC-PC and a lithium salt like LiCF₃SO₃, LiPF₆ or LiN(SO₂CF₃)₂ was prepared by thermal extrusion method [147]. The mechanical strength of the polymer electrolyte film varied depending on the PVdF content. The viscosity of the medium and the concentration of the charge carriers, which are directly related to the weight ratio of PVdF-EC-PC and the kind of lithium salt studied, mainly influenced the conductivity of the electrolyte. Although, the PVdF based polymer electrolyte offered excellent electrochemical properties and this fluorinated polymer formed LiF upon cycling. The compatibility study of lithium metal anode with PVdF-EC-PC-imide polymer electrolyte revealed that these electrolytes
may have good shelf life at room temperature. Also the cyclic voltammetry studies suggested PVdF based polymer electrolytes are more suitable for primary than secondary batteries when lithium metal is employed as anode. Gel polymer electrolyte consist of PVdF and mixtures of PC and DMF, lithium salts and small amounts of plasticizer, either diethylphthalate or dibutylphthalate was investigated [148]. It showed the electrical conductivity of about $3 \times 10^{-4}$ Scm$^{-1}$ at 25°C.

The conduction mechanism of gel polymer electrolyte composed of PVdF produced by the phase inversion method with EC/DEC solution of LiN(CF$_3$SO$_2$)$_2$ were investigated [149]. Ionic conductivity of new ternary and quaternary solvent mixtures containing significant amount of toluene was reduced upon the addition of PVdF host matrices [150]. However, the ionic conductivity remained sufficiently high yield down at least -40°C. These results revealed that the addition of toluene in the quarternary mixture solvents not only increased the stability of the anodic film but also reduced the solubility and swelling of PVdF. The capacity retention of cells using PVdF mixed with quaternary solvent at -40°C is 50% of nominal capacity at ambient temperature. Very recently, the electrochemical and dielectric properties of PVdF polymers have been reported [151].

New kind of porous PVdF-PEO based blend membrane was prepared by a simple phase inversion process, in which the addition of PEO can obviously improved the pore configuration [152]. The highest porosity of about 84% and ionic conductivity of about $2 \times 10^{-3}$ Scm$^{-1}$ at room temperature can be obtained when the weight ratio of PEO to PVdF is 50%. In addition, the tensile modulus decreased from ~85MPa (for pure PVdF) to ~30MPa (for PVdF-50% PEO). However, this value was still same as that of pure PVdF-co-HFP co-polymer electrolyte [153].

PVdF-PEO-ZSM5 based micro-porous polymer blend electrolyte with a phase inversion technique was prepared [154]. ZSM5 molecular sieves improved the
mechanical strength and ionic conductivity of PVdF-PEO blend. The increase in ionic conductivity was due to absorb liquid electrolyte, ZSM5 particles formed a special conducting pathway in PVdF-PEO matrix. However, PEO could improved the pore configuration of PVdF matrix and hence, the ionic conductivity enhanced at room temperature.

2.1.5 PVDF-co-HFP based polymer electrolyte

In general, PVdF based polymer electrolytes suffered from the mechanical properties and the films had to be hardened by either chemical or physical curing. Besides this, the main shortcoming was that it had to be carried out in a completely moisture-free atmosphere. This resulted in high processing costs. These difficulties were overcome by choosing a co-polymer of vinyldene fluoride with hexafluoropropylene (PVdF-co-HFP) rather than choosing commonly used gel electrolyte [155, 156]. This contained amorphous domains capable of trapping large amounts of liquid electrolytes and crystalline regions, which provided sufficient mechanical integrity for the processing of freestanding films and thereby, eliminated the need for cross linking.

The PVdF-co-HFP based gel polymer electrolyte and the solution of ethylene carbonate (EC), diethyl carbonate (DEC) and LiN(CF₃SO₂)₃ as salt were prepared [157], by changing the content of the polymer. The change in the range of 10⁻² to 10⁻⁸ Scm⁻¹.In addition diffusion co-efficient of lithium (Dₐₐ) and fluoride species (Dₓ₃) decreased with increase of the polymer content. The use of polymer electrolyte in lithium ion batteries based on PVdF-co-HFP was studied [158]. It was observed that the porosity of the PVdF-co-HFP matrix increases with increase of EC content in the PVdF-co-HFP film and it was most significant at the EC content of 62.6 wt(%) due to the formation of bulk EC phase. Thermal and spectroscopic investigations showed that most of the EC interact with PVdF-co-HFP and the EC content being below 60wt(%). The micro-porous structure of the PVdF-co-HFP matrix also provided stable
cycle performances at the charge/discharge rate of 1C/1C and good-rate capability of the MCMB/PE/LiCoO₂ cells.

Conduction properties of PVdF-co-HFP based gel polymer electrolytes composed of lithium imide salts such as Li(N(CF₃SO₂)₂, Li(N(C₂F₅SO₂)₂ were investigated using NMR spectroscopy and complex impedance technique [159]. It was found that the diffusion co-efficient of the gel polymer electrolyte decreased with an increase in the polymer fraction in the gel.

The ionic conductivity, thermal stability and compatibility of PVdF-co-HFP with combination of EC and PC as plasticizers and three different lithium salts (LiCF₃SO₃, LiBF₄, LiClO₄) have been examined [160]. The ionic conductivity of the gel polymer electrolyte increased with the addition of polymer in the gel. Among the salts studies, the film, which possessed LiBF₄ as salt exhibited maximum conductivity and was attributed to the low lattice energy of the salt. On contrary, the films, which possess LiBF₄ exhibited poor compatibility with lithium metal anode and were identified due to the formation of LiF in the layer.

The gel polymer electrolytes based on PVdF and PVdF-co-HFP membranes with different morphology and porosity have been prepared by phase inversion technique. Porous PVdF-co-HFP displays two diffusion co-efficient, depending on the level of porosity and the film morphology. However, one component was slow in diffusion compared with the value of swollen polymer and was assigned to the restricted solution in the not well connected cavities as a result opposite behaviour between the cation and anion species [161].

Ionic conductivity, interfacial stability with the lithium electrode and electrochemical stability window of the PVdF-co-HFP-PVAc based polymer blend electrolyte were investigated [162] by varying the PVAc content in the polymer matrix. It was found that the ionic conductivity decreased with increase of PVAc
content. This behaviour was related to mobility of lithium ion and concentration of the charge carrier in the polymer electrolyte. The bulk and interfacial resistance of the polymer electrolytes based on kynar for the lithium symmetric cell were gradually increased with storage. The polymer electrolyte based on the kynar 2801/PVAc (7/3, w/w) blend was electrochemically stable up to 5.0 V vs Li/Li⁺.

PVdF-co-HFP based gel polymer electrolytes was prepared [163] supported with a polyolefin membrane for lithium-ion polymer batteries. The membrane exhibited high ionic conductivity and mechanical properties and was electrochemically stable up to 5.0 V vs Li/Li⁺. Films with and without silicon dioxide (SiO₂), addition of SiO₂ into the PVdF-co-HFP/PS system raised the conductivity to nearly 4 X 10⁻² S cm⁻¹.

A highly porous polymer membrane with high affinity for electrolyte solution was prepared and characterized [164]. A blend of PVdF-PAN was used as a matrix polymer to have high ionic conductivity and good mechanical strength. Systematic studies on the ionic conductivity and transport properties of polymer electrolytes comprising of the co-polymer of PVdF-co-HFP-PC-DEC-LiClO₄ and PVdF-PC-DEC-LiClO₄ separately was made [165]. The film which possessed PVdF-HFP host exhibited higher conductivity and transport number than film with PVdF. The films were also subjected to FTIR and XRD analysis. The higher ionic conductivity of PVdF-co-HFP film was attributed to the higher amorphocity as there are two randomly mixed monomers providing the more free mobile Li⁺ ions. On the other hand, PVdF has higher degree of crystallinity, which resulted in lower ionic conductivity.

Gel polymer blend electrolyte consisted of a PVdF-co-HFP polymer, PE thermoplastics resin, and 1.0 mol/dm³ LiClO₄/PC/DEC or LiPF₆/PC/DEC was reported [166]. By the SEM observation, it was found that the PE particles uniformly dispersed in the PVdF-co-HFP gel polymer electrolyte could be fused and formed...
into a continuous film at or near the PE melting point. An ambient temperature Li-ion conducting solid polymer electrolyte using the concept of polymer electrolyte alloying upon blending two thermoplastic polymers, PVdF-co-HFP and poly(N-vinylcarbozole) was developed [167]. A system of porous, chemically cross-linked, PVdF-co-HFP as a polymer matrix, PEG as a plasticizer, and PEGDMA as a chemical cross-linking oligomer was also synthesized [168].

The electrochemical and cycling profile of Li/ LiCoO$_2$ and MCMB/ LiCoO$_2$ cells comprising gel polymer electrolyte (PVdF-co-HFP) (25%), EC-PC (65%) and LiN(CF$_3$SO$_3$)$_2$ have been reported [169]. The cell comprising MCMB /GPE/ LiCoO$_2$ were found to delivered higher capacity and cumblic efficient than the Li /GPE/ LiCoO$_2$ cells. The polymer electrolytes composed of the blend of PVdF-co-HFP and poly(MMA-co-lithium methacrylate) ionomer with EC and DMC-LiPF$_6$ salts were prepared and investigated [170]. The introduction of the ionomer into the polymer matrix was found to enhance the compatibility of the polymer with the liquid electrolyte. The uptake of the liquid electrolyte into the porous matrix and the ionic conductivities at ambient temperature were also enhanced.

The conduction mechanism of the porous PVdF-co-HFP based polymer electrolyte was investigated [171]. The results reveal that the homogeneous distribution of the ion conduction paths through the network of the swollen polymer chains was dominant for high ionic conductivity than the conduction paths of the solution in the electrolyte.

Thermally annealed micro-porous PVdF-co-HFP/P(EO-EC) electrolyte membrane by phase inversion technique was prepared [172]. But the existence of viscous P(EO-EC) matrix led to a decrease in the mechanical strength and had a maximum conductivity value of $3.5 \times 10^{-5}$ Scm$^{-1}$ at room temperature. However, the mechanical properties of porous membrane was improved by the thermal annealing
without risking any deterioration of porosity, uptake of electrolyte solution and electrochemical performance.

PVdF-co-HFP based micro-porous polymer membrane with a phase inversion techniques using water as the non-solvent was prepared [173]. As prepared porous membranes had the porosities of 70% to 90% and the ionic conductivity of $1.2 \times 10^{-3}$ Scm$^{-1}$ at room temperature. A Li/MPGPE/LiCoO$_2$ coin type cell was fabricated which showed very stable charge-discharge behaviour and little capacity loss. PVdF-co-HFP and PEO based gel polymer electrolyte was prepared [174].

N-ethyl-N-methly morpholinium bis (trifluoromethane sulfonyl) imide (Mor$_{1,2}$TFSI) and PVdF-co-HFP based ionic liquid-polymer gel polymer electrolyte [IPGEs] was prepared [175, 176]. From this ac-impedance spectroscopy analysis reveals that the IPGs increased as the temperature and concentration of the Mor$_{1,2}$TFSI increased which gave highest ionic conductivity of $1.1 \times 10^{-2}$ Scm$^{-1}$ at 60°C. Further, the thermal analysis revealed that IPGE composed of an ionic liquid-gel polymer electrolyte has high thermal stability.

Highly ionic conducting PVdF-co-HFP/P123 based membrane was prepared with a phase inversion technique [177]. It was found that small amount of P123 (polymer surfactant) was added into the polymer matrix, meso-pores with well defined sizes were formed. The increase in the content of P123 into the PVdF-co-HFP matrix, increased the ionic conductivity upto $4 \times 10^{-3}$ Scm$^{-1}$ at room temperature. Further, blending of P123 (>50Wt(%)) in PVdF-co-HFP reduced the pore size of the polymer membrane, therefore the solution leakage was also reduced. These polymer electrolytes were electrochemically stable upto 4.5V vs Li/Li$^+$ when LiCoO$_2$ used as the cathode and MCMB used as anode.

Composite polymer electrolyte based on PVdF-co-HFP-AlO[OH]$_n$-LiN(C$_2$F$_3$SO$_2$)$_2$ was prepared using solvent casting technique [178]. The incorporation
of AlO[OH]_n did not reduce the crystalinity of the polymer matrix and act as solid plasticizer capable of enhancing the transport properties but also provided a better interfacial stability towards a lithium metal anode. The incorporation of nano-size AlO[OH]_n (14nm) greatly enhanced the ionic conductivity and electrochemical properties of the composite polymer electrolyte rather than micro-size fillers (7μm) used. The inert particles depending upon the volume fraction would tend to minimize the area of the lithium electrode exposed to polymers consisting of O, -OH species and thus reduce the passivation process. LiCr_{0.2}:Mn_{1.99}O_4/PVdF-co-HFP- AlO[OH]_n-LiN(C_2F_5SO_2)2/Li cell which possess the membrane with micron sized fillers underwent a slight higher fade in capacity rather than nano-size ceramic filler was due to high interfacial resistance of the system.

Highly conductive gel polymer electrolyte comprising of 25wt(%)PVdF-co-HFP-65wt(%)EC-10wt(%)PC-10wt(%)LiN(CF_3SO_3)_2 was prepared [179]. The ionic conductivity of such polymer electrolyte exhibited 1.2 × 10^{-3} Scm^{-1} at room temperature and their electrochemical stability window was around 4.8 V vs Li/Li^+. The lithium transference number, t_L^+, of the gel polymer electrolytes calculated from t_L^+={Rb}/[V/I(α)-Ri] and was found to have a value of to 0.4. Li/GPE/LiCoO_2 cell delivered a specific discharge capacity of 17.6 and 136.7 mAh/g with a coulombic efficiencies of 99.8% and 99.2% on the first and then 20^{th} cycle, respectively. But the rate capability of the LiCoO_2/GPE/MCMB cell was better than that of Li/GPE/ LiCoO_2 cell, and its specific discharge capacity was higher than 140 mAh/g for up to 20^{th} cycles at all current densities.

PVdF-co-HFP-SiO_2 composite membrane based on hydrolysis of tetraethoxysilane through phase inversion method was developed [180]. In situ preparative method enhanced the overall properties of porous polymer electrolyte such as ionic conductivity, electrochemical stability and interfacial stability against lithium electrodes than the direct composite silica.
2.2 SCOPE OF THE PRESENT INVESTIGATION

Through the careful analysis of literature, it is known that the use of micro-porous poly (vinylidene difluoride-co-hexafluoro propylene) based polymer electrolytes have several advantages compared with other analogs. Hence, the object of the present investigation is to develop PVdF-co-HFP based micro-porous polymer membrane with different processes such as: (a) Phase inversion (b) Non-solvent extraction and (c) novel preferential polymer dissolution followed by soaking the membranes 1M LiClO₄ containing 1:1 (v/v) ratio of EC and DEC electrolyte solution.

The prepared micro-porous gel polymer electrolytes would be characterized by following techniques to choose the best and an efficient process.

- Scanning electron microscopy studies to be carried out to find out surface morphology of polymer films/membranes.
- 1-butanol absorption/desorption experiments are to be carried out to determine the porosity of the polymer membranes.
- Ionic conductivity studies are to be carried out using ac-impedance spectroscopic method.
- Thermal behaviour of micro-porous gel polymer electrolyte membranes are to be studied by differential scanning calorimetry analysis.
- X-ray diffraction analysis to be carried out to find out crystallinity nature of micro-porous gel polymer electrolyte membranes.
- Electrochemical stability of micro-porous gel polymer electrolyte membranes are to be tested by linear sweep voltammetry technique.
- The electrochemical charge-discharge behaviour of micro-porous gel polymer electrolyte membranes are to be studied by fabricating a cell with a
configuration of carbon/LiMg$_{0.10}$Mn$_{1.90}$O$_4$ using galvanostatic method in the range of 3.2V-4.8V at C/10 rate.

- Dielectric permittivity of micro-porous gel polymer electrolyte membranes are to be studied using dielectric spectroscopic method.

- Further the effect of blending of PMMA with PVdF-co-HFP to the development of micro-porous gel polymer blend electrolyte membranes are also to be studied extensively using one of the best chosen processes besides the incorporation of ZrO$_2$/LiAlO$_2$ nano-particles onto a PVdF-co-HFP based micro-porous nano-composite polymer electrolyte membranes.
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