CHAPTER II

REVIEW OF LITERATURE

The explosive demand for portable electronic devices requires lithium ion batteries, since they are light and offer high voltage and high energy density. Due to the importance of polymer electrolytes in Li-ion batteries, many efforts have been made to optimize the electrochemical properties of PEs to satisfy the need of all solid-state lithium polymer electrolyte batteries. A number of methods have been reported for improving the mechanical and morphological characteristics of polymer electrolytes in the higher temperature range, and for improving conductivity in the lower temperature range. A review of the significant research findings on polymer electrolytes is reported in this chapter.

2.1 PEO Based Polymer Electrolytes

PEO is a crystalline polymer. The oxygen in PEO acts as a donor for the cation and the anion generally of large dimension stabilizes the PEO alkali salt complex.

The polymer electrolytes composed of a blend of poly (ethylene oxide) (PEO) and poly (acrylonitrile) (poly (EO/AN)) as a host polymer, mixture of ethylene carbonate (EC) and γ-butyrolactone (BL) as plasticizer and LiClO₄ as a salt were prepared by Choi et al. [1]. High ionic conductivity \(1.2 \times 10^{-3} \text{ S cm}^{-1}\) was estimated for 10PEO–40PAN–12LiClO₄–38EC:BL. The beneficial effects
of PEO blending with PAN-based electrolytes are comparable ionic conductivity, better dimensional stability and wider electrochemical stability.

Xi et al. [2] aimed to improve ionic conductivity with a novel approach using PEO and PVdF as host polymers by phase inversion technique. The room temperature conductivity was measured as a function of PEO content. As the weight ratio of PEO was increased from 40 to 50%, the ionic conductivity also increased more than one magnitude from 0.15 to $1.96 \times 10^{-1}$ Scm$^{-1}$ which is mainly due to the increasing of pore connectivity. This is very important for the transport of charge carriers in microporous polymer membrane.

Fan et al. [3] investigated the plasticizer effect on PEO-salt complex using succinitrile (SN) as a plasticizer, LiClO$_4$, LiPF$_6$ and LiCF$_3$SO$_3$ as lithium salts. It was found that the addition of plasticizer was responsible for high ionic conductivity which could be attributed to the high polarity and diffusivity of succinitrile. Activation energy of the electrolytes was also estimated from Arrhenius plot.

Cha et al. [4] synthesized a novel plasticized polymer electrolytes based on poly(N,N-dimethylamino-ethyl-methacrylate) (PDMAEMA), polyethylene oxide (PEO), LiTFSI as a salt, tetraethylene glycol dimethyl ether (tetaglyme), EC/PC and DEP as plasticizers. The ionic conductivity of various compositions of polymer electrolytes was investigated as a function of temperature, various concentrations of LiTFSI, plasticizers and various ratio of PDMAEMA/PEO. The ionic conductivity of PDMAEMA/PEO/LiTFSI with DEP as a plasticizer was found to be $1.5 \times 10^{-4}$ Scm$^{-1}$. By increasing the PDMAEMA
concentration up to 13.3%, the ionic conductivity decreased rapidly which may be due to high viscosity.

Poly (ethylene oxide) / poly (triethylene glycol) was prepared by Itoh et al. [5] incorporating benzoate, BaTiO₃ and lithium imides. The ionic conductivity value was estimated as $1.6 \times 10^{-3} \text{ S cm}^{-1}$ at 80 °C and the electrochemical stability window as 4.0 V. The membrane was also characterized by TG/DTA and is thermally stable up to 307 °C.

### 2.2 PAN Based Polymer Electrolytes

Kim et al. [6] prepared highly porous polymer electrolyte employing P(VdF-co-HFP) and PAN with a view to attain high ionic conductivity and good mechanical strength. Lithium-ion polymer battery using these gel polymer electrolytes was assembled, and its charge – discharge characteristics were also reported.

Tsutsumi and Kitagava [7] synthesized a new type polymer electrolyte films based on poly (acrylonitrile) and Cyanoethylated poly (vinyl alcohol) (CN-PVA) and its conductivity behaviour was also investigated. They found the ionic conductivity value as $14.6 \times 10^{-3} \text{ S cm}^{-1}$ at 30 °C for PAN (10)-CN-PVA (10)-LiClO₄ (8)-PC (4) complex system. The interactions of Li⁺-ion and nitrile groups of PAN in the matrix were confirmed by FTIR analysis.

Perera et al. [8] reported the system based on PAN–ethylene carbonate (EC)–propylene carbonate(PC) –lithium trifluoromethane sulfonate (LiCF₃SO₃). The composition 15 mol% PAN–42 mol% EC–36 mol% PC–
7 mol% LiCF$_3$SO$_3$ has shown a maximum room temperature conductivity of $1.2 \times 10^{-3}$ Scm$^{-1}$. They also extended their investigation on cells in the form, Li/PAN–EC–PC–LiCF$_3$SO$_3$/ polypyrrole (PPy) alkylsulfonate (AS). Cyclic voltametry studies and continuous charge–discharge tests were carried out to study the performance of the cell.

Subramania et al. [9], reported a micro-porous PAN based polymer blend electrolytes by phase-inversion technique. The ionic conductivity of the micro-porous polymer blend electrolyte films was studied by varying the PAN content in the (PVdF-co-HFP) matrix. Charge–discharge studies were carried out in an assembled cell with carbon anode and LiSr$_{0.25}$Mn$_{1.75}$O$_4$ cathode and micro-porous polymer blend electrolyte in between the above electrodes.

Chen et al. [10] prepared the hydrophobic clay, ALA-MMT by the ionic exchange reaction of MMT with a carboxy-terminal alkyl ammonium salt. Using the prepared ALA-MMT as filler, they reported a series of composite electrolytes based on poly(acrylonitrile) and LiClO$_4$. The effect of the addition of ALA–MMT on the properties of the composite polymer electrolytes (CPEs) was investigated. The best ionic conductivity at room temperature was obtained from the CPE with 7 wt% of the modified clay and 0.6 M LiClO$_4$ per PAN repeat unit (CPE-7) and was more than seven times higher than that from the corresponding PAN/LiClO$_4$ polymer electrolyte (CPE-0). The mechanical property and the cation transference number of CPE-7 were largely increased compared to that of CPE-0. They were electrochemically stable up to 4.75 V
and the corresponding cell exhibited excellent electrochemical stability and cyclability over the potential range between 0 V and 4.0 V vs. Li/Li⁺.

The ionic conductivity and FTIR studies were carried out on PAN based gel electrolytes with EC: PC and EC: DMC mixtures as plasticizers, LiClO₄ or LiBF₄ as the salt by Armand et al. [11]. High ionic conductivity (1.47×10⁻³ Scm⁻¹) was estimated for 20:28:45:7 molar ratio of PAN-PVA: EC: DMC: LiBF₄ system. Charge/discharge performance of the maximum ionic conductivity complex was also studied.

2.3 PMMA Based Polymer Electrolytes

Ali et al. [12] reported the electrical properties of polymer electrolytes comprising PMMA, PC, EC as plasticizer and different lithium salts LiCF₃SO₃ and LiN(CF₃SO₂)₂. The polymer electrolytes exhibited high ionic conductivity at room temperature in the range of 10⁻⁶ to 10⁻⁴ Scm⁻¹. The temperature dependence studies confirmed that the conduction in electrolyte is only by ions and seemed to obey the VTF rule. FTIR spectroscopy studies confirmed the polymer salt interactions.

Andersson et al. [13] investigated the transition behaviour of PMMA-based gels with and without nano-particle filler at elevated pressures up to 0.9 GPa and in the temperature range 220–310 K. Both gels had molar ratios of 53.9:22:5.2:18.9 of ethylene carbonate (EC), propylene carbonate (PC), lithium perchlorate, PMMA and one gel contained 8 wt.% TiO₂ nano-particles. The results show a sluggish transition between a low-pressure (high temperature)
state and a high-pressure (low temperature) state. The nano-particle filler facilitated the kinetics of the transition, yielding a significantly lower transition pressure as well as a better homogeneity in the sample after a transition back to the low-pressure state. These results can be explained by a filler-induced increase of the nucleation rate, which yields smaller crystallites. The transition was observed also by differential scanning calorimetry and Raman spectroscopy at ambient pressure and was likely associated with crystallization of the EC–PC solvent. The logarithmic pressure derivative of the conductance and, consequently, the activation volume changes a factor of 3 as a result of the transition.

FTIR spectroscopic investigations coupled with ionic conductivity and viscosity measurements on Lithium imide LiN(CF₃SO₂)-propylene carbonate (PC)-poly(methyl methacrylate) (PMMA) based liquid and gel electrolytes over a wide range of salt (0.025-3M) and polymer (5-25 wt%) concentration were reported by Deepa et al. [14] and found that the high ionic conductivity occurs at salt concentrations ≥1.25M.

Polymeric gel electrolytes, based on a blend of poly(methylmethacrylate)/ poly (vinylidene fluoride) (PMMA/PVdF), ethylene carbonate/ propylene carbonate (EC/PC) as plasticizer and lithium perchlorate as salt, had been studied [15] as a function of the different polymeric ratios to obtain the best compromise between ionic conduction and mechanical properties of the systems involved. Ionic conductivity and the lithium self-diffusion coefficient were measured by the PFG–NMR method, which revealed
a maximum of lithium mobility for the composition PMMA 60%–PVdF 40%.
The Raman spectroscopic study revealed a change of the interaction between
that of the lithium cations and the plasticizer molecules for different
PMMA/PVdF ratios. Oscillatory rheological tests showed better mechanical
properties for the intermediate compositions of the blend.

Ramesh et al. [16] investigated the effect upon addition of SiO₂ on the
ionic conductivity of the composite polymer electrolyte systems composed of
poly (methyl methacrylate) (PMMA) as the host polymer and Lithium triflate
(LiCF₃SO₃) as dopant salt. Addition of 2 wt. % fumed silica on the composite
polymer electrolyte complexes exhibited the maximum ionic conductivity.
Interfacial stability of composite polymer electrolytes also enhanced at ambient
temperature. FTIR studies revealed the occurrence of complexation between
PMMA, LiCF₃SO₃, and SiO₂ in the composite matrix polymer. The
incorporation of fumed silica increased the thermal stability of the composite
polymer electrolyte systems.

2.4 PVC Based Polymer Electrolytes

Polymer electrolytes composed of a blend of polyvinyl chloride–
 polyethylene oxide (PVC–PEO) as a host polymer, lithium triflate (LiCF₃SO₃)
as a salt, mixture of ethylene carbonate (EC) and dibuthyl phthalate (DBP) as
plasticizers and silica (SiO₂) as the nanocomposite filler were studied by
Ramesh et al. [17]. Results suggest that PVC–PEO blending exhibits improved
mechanical strength compared to that of pure PEO. The introduction of
LiCF$_3$SO$_3$ changed the mechanical properties of PVC–PEO blends from hard and brittle to soft and tough. In PVC–PEO: LiCF$_3$SO$_3$ (70:30) system, the Young’s modulus value decreased from $5.30 \times 10^{-1}$ MPa to $4.78 \times 10^{-4}$ MPa and the elongation at peak value increased from 3.71 mm to 32.09 mm with the incorporation of DBP and EC. Incorporation of 5% SiO$_2$ increased the Young’s modulus value from $4.78 \times 10^{-4}$ MPa to $1.51 \times 10^{-3}$ MPa. The improvement of the mechanical properties revealed greater dispersion of SiO$_2$ particles in PVC–PEO blend based polymer electrolytes.

Composites of polyaniline with poly(vinyl chloride) and poly styrene had been prepared by Gupta et al. [18] and concluded that the IR, TGA and XRD spectra of the composites were superimposed on their parent materials, indicating that the composites were just the physical mixture of their constituents. These composites were semiconducting in nature with electrical conductivities in the range of $10^{-2}$ to $10^{-13}$ Scm$^{-1}$.

The effect of ceramic fillers such as ZrO$_2$, TiO$_2$ and Al$_2$O$_3$ on the room temperature conductivity in PVC-LiClO$_4$ based composite polymer electrolyte was carried out by Ahmad et al. [19]. The samples were prepared with different percentage (%) by weight of ceramic filler. The highest ionic conductivity achieved was $3.7 \times 10^{-7}$ Scm$^{-1}$ for the sample prepared with 20% of ZrO$_2$. The glass transition temperature decreased with the filler concentration due to the increasing amorphous state while the decomposition temperature increased with the filler concentration. Both of these thermal properties influenced the enhancement of the conductivity value.
2.5 PVAc Based Polymer Electrolytes

Structural, thermal and transport properties of PVAc- LiClO₄ based complexes were studied by Baskaran et al. [20]. The bulk conductivity was found to vary between $7.6 \times 10^{-7}$ Scm⁻¹ and $6.2 \times 10^{-5}$ Scm⁻¹ at 303 K with an increase in salt concentration. The amorphous nature of polymer complexes was confirmed by XRD and SEM analysis.

Animitsa et al. [21] enhanced the ionic conductivity of PEO-LiClO₄ using amorphous poly(vinyl acetate) (PVAc) as additive. Ionic conductivity increased with the increase of PVAc content. Morphological studies were also reported for this system.

Rajendran et al. [22] prepared the polymer electrolytes comprising poly(vinyl acetate) (PVAc), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP), Ethylene Carbonate (EC) and different lithium salts (LiBF₄, LiClO₄ and LiCF₃SO₃) by solution casting technique. Ionic conductivity was obtained as a function of frequency at various temperatures ranging from 302 to 363 K. The maximum room temperature ionic conductivity was found to be $1.18 \times 10^{-3}$ Scm⁻¹ for the film containing LiBF₄ and the temperature dependent ionic conductivity values seem to obey VTF relation.

2.6 Other Polymer Electrolytes

Aravindan et al. [23] measured the ionic conductivity and coherence length of PEMA/PVdF-HFP blend based polymer electrolytes with DEC/EC as plasticizers and sodium trifluoromethanesulfonate (NaCF₃SO₃) as salt and
nanosized Sb$_2$O$_3$ as filler by solution casting technique. The highest ionic conductivity was obtained for the film with 10wt% of Sb$_2$O$_3$ filler.

Subba Reddy et al. [24] synthesized vanadium oxide (V$_2$O$_5$) intercalating with a conducting polymer polyethylene glycol (PEG), by simple hydrothermal process. XRD, FTIR, SEM and CV studies were carried out. The V$_2$O$_5$ nanobelts exhibited a high specific discharge capacity of 397.61 mAh g$^{-1}$.

Choe et al. [25] reported that the PVdF based electrolytes plasticized with a solution of LiN(CF$_3$SO$_2$)$_2$ in PC had a conductivity of $1.74 \times 10^{-3}$ Scm$^{-1}$ at 30 °C and potential limits between 3.9 and 4.3V vs Li$^+$/Li.

A polymer blend electrolyte based on polyvinyl alcohol (PVA) and polyacrylonitrile (PAN) was prepared by Subramania et al. [26]. The ionic conductivity of polymer blend electrolytes was investigated by varying the PAN content in the PVA matrix. The ionic conductivity of polymer blend electrolyte increased with the increase of PAN content. The effect of lithium salt concentrations was also studied for the polymer blend electrolyte of high ionic conductivity. A maximum ionic conductivity of $3.76 \times 10^{-3}$ Scm$^{-1}$ was obtained in 3M LiClO$_4$ electrolyte solution. Linear sweep voltammetry and DC polarization studies were carried out to find out the stability and lithium transference number of the polymer blend electrolyte.

**Scope of the work**

From the literature survey, it is found that among the host polymers, PAN provides rigidity, high room temperature ionic conductivity
and thermal stability to the polymer electrolytes. However, PAN-based electrolytes have undesirable effects such as liquid extraction from the gel, which results in decrease in ionic conductivity for the PEs upon long term storage. Also the porous PAN membranes are very brittle for the reason that the interaction of adjacent cyanide groups increases the resistance of interior rotation of the main chain and thus decreases the flexibility of the polymer chain [27]. These drawbacks can be overcome by blending PAN with other polymers. Also, it is noted that PMMA, a common thermoplastic polymer, is a potential candidate for polymer electrolyte applications. Its amorphous structure is beneficial to ionic conduction and PMMA-based gel electrolytes have shown excellent interfacial stability towards lithium metal. The pendant COOCH$_3$ is not likely to crystallize around Li$^+$ as PEO does. PMMA based PEs exhibit high electrolyte uptake, ionic conductivity and good electrochemical stability [28]. Unlike PAN, PMMA has ability to make chemical cross-linking, which will remarkably increase the mechanical strength and the electrolyte solution retention ability of the PE [29, 30]. Also it has been reported that gel electrolytes based on cross-linked PMMA can suppress lithium dendrite formation [29]. In this view, it is proposed to use homogeneous blend of the polymers PAN and PMMA as matrix polymer to prepare the porous membranes exploiting the beneficial characteristics of individual polymers. The various compositions of the polymer electrolytes are given below:
### System I: Compositional effect of PAN/PMMA (in wt %)

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<tr>
<td>PAN (100)/PMMA (0)/LiClO₄ (5)</td>
<td>PAN (75)/PMMA (25)/LiClO₄ (5)</td>
<td>PAN (50)/PMMA (50)/LiClO₄ (5)</td>
<td>PAN (25)/PMMA (75)/LiClO₄ (5)</td>
<td>PAN (0)/PMMA (100)/LiClO₄ (5)</td>
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### System II: Effect of Salt Concentration (in wt %)

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<tr>
<td>PAN (75)/PMMA (25)/LiClO₄ (2)</td>
<td>PAN (75)/PMMA (25)/LiClO₄ (5)</td>
<td>PAN (75)/PMMA (25)/LiClO₄ (8)</td>
<td>PAN (75)/PMMA (25)/LiClO₄ (11)</td>
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### System III: Effect of Plasticizer Concentration (in wt %)

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<tr>
<td>PAN (24.75)/PMMA (8.25)/LiClO₄ (8)/PC (59)</td>
<td>PAN (22.5)/PMMA (7.5)/LiClO₄ (8)/PC (62)</td>
<td>PAN (20.25)/PMMA (6.75)/LiClO₄ (8)/PC (65)</td>
<td>PAN (18)/PMMA (6)/LiClO₄ (8)/PC (68)</td>
<td>PAN (15.75)/PMMA (5.25)/LiClO₄ (8)/PC (71)</td>
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### System IV: Role of Different Plasticizers (in wt %)

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<tr>
<td>PAN (18)/PMMA (6)/LiClO₄ (8)/EC (68)</td>
<td>PAN (18)/PMMA (6)/LiClO₄ (8)/DMC (68)</td>
<td>PAN (18)/PMMA (6)/LiClO₄ (8)/DEC (68)</td>
<td>PAN (18)/PMMA (6)/LiClO₄ (8)/GBL (68)</td>
<td>PAN (18)/PMMA (6)/LiClO₄ (8)/PC (68)</td>
</tr>
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</table>
System V: Effect of Different Li Salts (in wt %)

E1: PAN (18)/ PMMA (6)/LiBF₄ (8)/EC (68)
E2: PAN (18)/ PMMA (6)/LiCF₃SO₃ (8)/EC (68)
E3: PAN (18)/ PMMA (6)/ LiN(CF₃SO₂)₂ (8)/EC (68)
E4: PAN (18)/ PMMA (6)/LiClO₄ (8)/EC (68)

System VI: Effect of Filler Concentration (in wt %)

F1: PAN (18)/ PMMA (6)/ LiN(CF₃SO₂)₂ (8)/EC (68)/BaTiO₃(0)
F2: PAN (18)/ PMMA (6)/ LiN(CF₃SO₂)₂ (8)/EC (68)/BaTiO₃(5)
F3: PAN (18)/ PMMA (6)/ LiN(CF₃SO₂)₂ (8)/EC (68)/ BaTiO₃(10)
F4: PAN (18)/ PMMA (6)/ LiN(CF₃SO₂)₂ (8)/EC (68)/ BaTiO₃(15)
F5: PAN (18)/ PMMA (6)/ LiN(CF₃SO₂)₂ (8)/EC (68)/ BaTiO₃(20)
References


