Chapter -1

Introduction
### Chapter - 1

**Introduction**

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1.1 Introduction to polymer electrolytes

Since time immemorial, polymers played a major role in human life. Man made polymers have seen the light in 18th century. Swedish chemist Jakos Berzilius proposed the word polymer in 1833. Vulcanized rubber is the first commercially successful polymer. Stickiness is prevented in polymers by adding sulphur to natural rubber by the process of vulcanization. Polymer electrolytes (PE) play a major role in developing various thin and flexible solid state electrochemical devices because of their tremendous technological potentials. PE possesses high conductivity due to ions (< 10⁻⁴ S/cm) at ambient temperature.

Polyethylene oxide (PEO) doped with alkali metal salt polymer complex is the first conducting polymer discovered in 1973 [1-4]. The PEO/lithium salt based solid polymer electrolyte system (SPE) has been demonstrated in 1979 [2]. This led a path to pursue research intensively in the field of conducting polymer composites. Many varieties of transporting ions like Li⁺, Na⁺, K⁺, Ag⁺, H⁺, Mg²⁺ etc. involved in PE were reported. PE was used in varieties of all solid state electrochemical power sources like mini/micro, primary/secondary, super capacitors, fuel cells etc. Due to these applications, an extensive exploitation of PE has been done in electrochemical devices in various research laboratories. The mechanism of ion transport can be concluded by studying the physical and chemical changes involved at electrode-electrolyte interfaces in the PE materials. Regarding materials designing and techniques adopted in material, structure, thermal and ion transport of PE systems, large number of books as well as research articles have been published [3-7]. There was pre-conceived notation that fast ion transport in SPE was mainly due to amorphous phase and the degree of amorphosity in the polymer matrix of SPE [8]. As a result, the present work is to develop large and stable amorphous phase in the polymer matrix of low glass transition temperature (Tg). Improvement of flexibility in the polymer chains through ion transport mechanism. Gadjourova et al. [9] had overturned this concept by experimentally demonstrating a static and ordered crystalline environment in polymer matrix which could support high ion conduction in SPE systems. The PE materials which are preferred in solid state electrochemical devices must possess the following properties
a. Ionic conductivity (σ)

Ionic conductivity of the PE material composite must be approximately equal to that of a system with liquid electrolyte based, σ should be greater than $10^{-4}$ S/cm.

b. Ionic transference number ($I_n$)

This should be approximately 1. In order to find their applications in batteries, PE should be single ion conducting system meant for both ion conducting medium and an electronic separator. However, numbers of PE systems studied so far show that the $I_n \leq 0.5$ even though showing negligible electronic conduction [10]. Naturally the cation current $I_n$ is inversely proportional to concentration polarization effect in the electrolyte during charge discharge procedures leading to availability of higher power density in the battery.

c. High thermal, chemical and electrochemical properties

By sandwiching the PE membranes between anode and cathode materials, the solid state electrochemical devices have been fabricated. They should have a high chemical stability to avoid unwanted chemical reaction at electrode-electrolyte interface. They should have excellent thermal stability to have wide temperature range for battery operation. They should possess electrochemical stability for the voltage of 0V to 5V.

d. High mechanical strength

PE should be mechanically stable for the realization of the scaling to bulk and for large scale production of devices,

e. compatibility

In order to have compatibility, a variety of non-toxic electrode materials and cathode materials should be identified.

Now a day’s CPE membranes incorporated with Li$^+$ ions were used widely for manufacturing of rechargeable batteries to the commercial requirements. It is emphasized that lithium batteries apart from providing very high specific power, they are economical, very safe to operate and handle, flexible in packing in a desired shape and size. Therefore lithium ion PE exhibits a great promise as future energy materials for wide range of small and large scale requirements.

1.2 Characteristics of polymer host:

In order to use polymer as a host for PEs, it should have the following characteristics.
To form coordinate bond with cations, a polymer repeat unit should possess an atom with at least one lone pair of electron.

Low barriers to make bonds and permitting segmented motion to the charge carries in the polymer chain.

Optimization of the distance between the coordinating centers to form a multiple inter-polymer ionic bonds.

Various polymer hosts with wide potentials have been exploring for usage in SPEs. Polyether lime PEO, Polypropylene oxide, PEO – PPO, PEO – PPO – PEO etc., found to possess reasonable conductivities. Care must be taken while designing a PE that the branches of the polymer backbone should not add rigidness to the overall chain and the glass transition temperature should not be reduced due to chemical constitutions. Even though a number of macro molecules satisfy the above criteria, PEO is the widely studied polymer host because of its characteristic features like easy processing, high chain flexibility, good solubility of different metallic salts, low cost, nontoxicity, abundancy, easily manufacturing, high dielectric constant, low glass transition temperature leads to better plasticity. All these features make PEO a facile material. Another point is polymer backbone should be flexible enough to spiral around the cation and the monomer units must be placed at optimum distance from each other. This is evident from the fact that though PEO co-ordinates number of cations, -CH₂-O and -CH₂-CH₂-CH₂-O- are not good polymer hosts. Specifically for complexation, PEO has the right monomeric length. Capability to complex many salts will be reduced by the addition or removal of another -CH₂- group to or from the repeat unit. Though amorphous polymer will be formed by the introduction of CH₃ group on carbon of PEO, it forces the polymer to adopt a more open helical structure which is less favourable for complexing cations. But, practically PEO is not an ideal electrolyte by itself. In order to obtain the elastomeric phase by preventing the crystalline nature several manipulations are required. By bringing the PEO into elastomeric phase helps in achieving extraordinary ionic conductivity. Generally PEs possesses long organic molecular chains and dissolved salts. When a changed polymer chain is divided into small pieces, it transforms into an ionic liquid, becomes an insulator glass or super ionic conductor glass by being frozen into glassy states. PEs generally
consists of two main components: one is the polymerized network of organic monomer units as given in Table 1.1 along with their glass transition temperature \(T_g\) and ionic conductive substances.

### Table 1.1 Polymer hosts for PEs

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Polymer name</th>
<th>Monomer unit</th>
<th>(T_g) (°C)</th>
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<td>1</td>
<td>Polyethylene oxide (PEO)</td>
<td>((-\text{CH}_2\text{-CH}_2\text{-O})_n) -</td>
<td>-60</td>
</tr>
<tr>
<td>2</td>
<td>Poly vinylidene fluoride (PVdf)</td>
<td>((-\text{CHCF}_2))(_n) -</td>
<td>-40</td>
</tr>
<tr>
<td>3</td>
<td>Poly propylene oxide (PPO)</td>
<td>((-\text{CH}(-\text{CH}_3\text{-CH}_2\text{O})_n) -</td>
<td>-60</td>
</tr>
<tr>
<td>4</td>
<td>Poly acrylonitrile (PAN)</td>
<td>((-\text{CH}_2\text{-CH(-CN)})(_n) -</td>
<td>125</td>
</tr>
<tr>
<td>5</td>
<td>Polymetha methacrylate (PMMA)</td>
<td>((-\text{CH}_2\text{C(-CH}_3\text{-COOCH}_3))(_n) -</td>
<td>108</td>
</tr>
<tr>
<td>6</td>
<td>Poly vinyl chloride (PVC)</td>
<td>((-\text{CH}_2\text{-CHCl}))(_n) -</td>
<td>82</td>
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</table>

### 1.3 Characteristics of metal salts

For polymer salt complex formation, a metal salt needs to possess the following characteristics.

- Low lattice energy or high salvation energy.
- Smaller cationic radii and bigger anionic size
- The charge density of anion should be low to reduce the number of ion pairs with cation.

### 1.4. Classifications of polymer electrolytes

The main aim has been to prepare PEs with high ionic conductivity at room temperature (RT) which is close to liquid/gel polymer electrolytes. Based on the synthesis methods and physical properties of polymer thin films, the PEs can be divided into five categories. Fig 1.1 shows the broad classification of electrolytes for Lithium batteries.

#### 1.4.1. Solid polymer electrolytes (SPE)

Complexation of polar polymers like PEO and ionic salts with low lattice energy gives rise to PEs, where cations/anions are mobile. When compared to solid electrolytes, PEs have high mechanical integrity, good electrode-electrolyte contacts, mouldability etc., PEs can be prepared by sol-gel method, hot-press technique, electro deposition method and solution casting method.
Fig. 1.1 Classification of electrolytes

PEO – AgNO₃, PEO-LiCF₃SO₃, PEO-LiClO₄ and PPO - LiClO₄ etc., are some of the PEs. Above glass transition temperature, polymers exhibit fast ion conduction behaviour. Ionic conductivity is very low and it is less than glass transition temperature because, in the polymer segments chain motion does not take place. Free volume model and percolation model explains the conduction mechanism in PEs. For all practical applications, SPEs are better than other solid electrolytes due to the following reasons

- Formation of thin films of larger area is quite easy. This in turn will reduce the internal resistance and improve the current density.
- Stability is high and compatible with electrode systems.
- Production on mass scale is possible as the PE is not going to vary with temperature, pressure and atmosphere.

These electrolytes are synthesized by dissolving ionic salts into polymer hosts. Generally the ionic salts like LiClO₄, LiCF₃SO₃, LiBF₄ and polymer hosts like PEO and PPO are used in the Lithium ion polymer battery applications. The polymer films are synthesized by using solution casting technique or by hot-pressed method. In the present research work, the PEs were synthesized by solution casting method. The first report on the discovery of SPE by using potassium and sodium salts with PEO polymer was released in 1973. Armand and co-workers extensively investigated the
PEO with Li$^+$ ion PEs in 1979. They prepared thin and flexible films of SPE. A tremendous development in this field has been observed since three decades. SPE films prepared till this date were based on polymers of high molecular weight such as PEO and PPO complexed with lithium ion salts. PEO/PPO was mainly used because of their higher ionic conductivity as compared to solvating polymers. The ability to dissolve ionic salts is due to the presences of macromolecules CH$_2$-CH$_2$-O and polar groups –O–, –H– and –C=H– in the polymer chain [11]. Polymer salt complex: (PEO)$_n$ salt formation was restrained by manipulating the energy distribution between the polymer and inorganic salts by the processes of solvating and lattice energies. The stability and flexibility of SPE is due to the low lattice energy between polymer host and inorganic salt used. Generally conductivity and Li$^+$ ion transference no. varies inversely with Li$^+$ salt concentration. However, the decrease in conductivity is due to obstructing the movement of polymer chain in turn blocks the transportation of ion. Further, the formation of ion-pair results in decrease of the number of free lithium ions which are available for conduction [12].

From NMR studies, at higher concentrations and temperatures, the formation of ion triplets of both positively and negatively charged ions were observed. F.M Gray reported that, when cation distribution: either by the setting of oxygen to ion pair ratio which exceeds 1:8; and the ratio of 1:4 for the formation of ion aggregates in PEO/salt complex [13]. This limitation of salt concentration in the polymer host restricts the maximum ionic conductivity obtainable in PEO/salt complex. SPE films can be obtained by complexing PEO with a variation of lithium salts LiX where X= ClO$_4$, Cl, Br, BF$_4$, I, AsF$_3$, CF$_3$SO$_3$, etc. The structure of SPE membrane consists of Li$^+$ ions helixed with PEO chain separating them from their counter anions [14]. This supports the suspension of LiX salt in the PEO host leading to a shifting mechanism similar to that in liquid electrolytes. However the local relaxation and branched motion of charge carriers in the polymer chains takes place in the high degree of amorphousity in the host polymer. The Li$^+$ ion transport takes place easily in amorphous phase Li$^+$ ion of the host polymer. PEO is semi crystalline in nature and melting temperature($T_m$) is around 70$^\circ$C and above this $T_m$, it exhibits amorphous nature. Hence an empirical valuable conductivity of $\sim 10^{-4}$ S/cm in PEO/LiX complex is simply obtained in between 70 to 90$^\circ$C. Many researchers have been working to achieve high degree of
amorphous phase at ambient temperature. There is a possibility that, inside the PEs the anions also migrate, which is not desirable feature because the device performance would be deteriorated due to self-discharge and electrode surface degradation takes place. To reduce the migration of anions in PEO can be achieved by complexing with salts containing huge organic anions viz lithium bis(trifloromethy sulfonyl) methide (LiTFSM) and lithium bis (trifloromethylsulfonyl ) imide (LiTFSI). Here salts act as plasticizers because of delocalization of electrons in the anions leading to extra flexible polymer chains in PEs. Due to these plasticizers, an extraordinary degree of amorphousity with high cation transport leading to a higher conductivity values with minimum migration of anions can be achieved.

1.4.2 Plasticizer Polymer electrolytes

The plasticized PEs are achieved by the addition of high dielectric constant liquid organic solvents such as low molecular weight polyethylene glycol (PEG), ethylene carbonate (EC) and propylene carbonate (PC) into SPEs. The characteristics of the plasticizer are low volatile, solvating power of a salt is high, and mobility of ionic conduction is adequate and increases the amorphous phase of the polymer matrix. The conductivity of SPE is increased by addition of these plasticizers at ambient temperature. Flexibility and simple processing procedures can be achieved by the addition of non-volatile and low molecular weight substances as plasticisers. The size of plasticizer molecules must be smaller when compared to the polymer host molecules such that the plasticizer molecules can be penetrated into the host polymer and forms attractive forces between plasticizer molecule and chain segments. By reducing the cohesive force between polymer chains and by increasing the branched mobility result to reduce the glass transition \( (T_g) \) temperature of the polymer [15]. It establishes conducting path ways to enhance the conductivity in the polymer-in-salt complex system. At low temperature, by increasing the concentration of plasticizer, the transition from glassy state to rubbery state can be observed. In addition, it can be observed over a wide range of temperature instead of unplasticizer polymer. Adding plasticizers like PEG into the SPE system results in the decrease of degree of crystallinity and enhanced branched motion of charge carriers across the polymer chain. It also favours ion dissociation so that more number of ions will be available for the charge transport. However, it has certain limitations. [16].
a. Deterioration of mechanical integrity of SPE system.
b. Enhance the relation between electrolyte and metal anode.
c. Decrease in thermal, electrical and electrochemical stabilities.
d. Less interfacial stability with lithium electrode.

Hence addition of plasticizers will result in the loss of most intrinsic characteristics of the PEs. Therefore the usage of this plasticizer in the electrochemical devices is very limited.

1.4.3 Gel polymer electrolytes

One of the latest developments in the field of electrolytes is gel PEs. They possess higher ambient ionic conductivity than the SPE. These electrolytes are also called as polymers of “hybrids and gelionics” prepared by adding high amount of organic solvents to the SPE. It is an amalgam of cohesive properties of solid and diffusive transport properties of liquid. This twofold nature of gel electrolytes is exfoliated in the applications of electrochemical devices like electrical supercapacitors, actuators, light emitting electrochemical cells and dye sensitive solar cells. The major drawback with these electrolytes is reduced mechanical strength which can be improved by cross-linking components like DEC-diethyl carbonate, EMITF with gel electrolytes [17]. The idea of plasticizing polymers using solution containing an alkali metal salts has been demonstrated by Fenullade et al., in 1975 [18].

The high ionic conductivity of these materials is of the order which is similar to liquid electrolytes is due to the trapping of organic solution of alkali metal salts in the polymer matrix. Hence by using number of polymer hosts like PEO, PVdF, PAN, PMMA etc. [19], polymer gel electrolytes are synthesized with conductivities in the range \(10^{-4}\) to \(10^{-3}\) S/cm at RT. The amorphousity in the host can be increased by the addition of plasticizer leading to a single \(T_g\) as small as -40 °C. The increased ionic mobility in gel electrolytes leads to growth in the ionic conductivity due to diffusive conductivity property in the liquid phase. Generally PEO-based gel electrolytes are formed with the addition of plasticizers such as EC and PC into the PEO/LiX SPE system. Though the ionic conductivity is very high \((10^{-3} \text{ S/cm})\) at ambient temperature, due to the solubility of PEO in the solvent, mechanical strength will be minimized by cross-linking of PEO.
Cross-linking of polymer host is possible by exposing radiations like UV, thermal, photo and electron beam [20], resulting in the trapping of liquid electrolyte in the polymer host.

1.4.4 Rubbery polymer electrolytes

The Angell and co-workers introduced a new PEs system called rubbery electrolytes in 1993[21]. This electrolyte was prepared by complexing a high proportion of salt with low proportion of high molecular weight polymer like PEO and PPO, also called as polymer-in-salt system where as in salt-in-polymer system like SPE, salt concentrations will be very low. In a high molecular weight polymer which are soluble in salt mixture exhibits a rubbery character due to decoupled cation motion. For the mixture of polymer with salt like AlCl$_3$-LiBr-LiClO$_4$-PPO [22], the conductivity obtained at ambient temperature is $2 \times 10^{-4}$ S/cm. Rubbery materials possessing low $T_g$ are obtained by adding small amount of polymer to the salt mixture. Even though it gives very high conductivity, the crystallization of salt takes place at lower temperature. As a consequence of this electrochemical stability gets affected leading to very limited uses in potential electrochemical devices. The mechanism of ion transport is due to the transportation of high degree of ion clusters through the bulk materials in polymer-in-salt electrolyte. The role of PAN polymer matrix on the transport of ion species has been studied by Ferry et al. [23] in terms of salt stabilization and hence reducing crystallization.

1.4.5 Composite solid polymer electrolytes

Composite solid polymer electrolytes (CSPE) are obtained by dispersion of inorganic inert micro/nano fillers like ceramic particles and metal oxide into the CSPE. Instead of conventional/gel/plasticized PEs, CSPE are used to overcome some of the drawbacks associated with Lithium battery like reactivity at the electrode-electrolyte interface. Increase in the internal resistance due to the growth of a passivation layer at the lithium metal surface. Morphological, structural, electrochemical and mechanical properties exhibited by SPE membrane will be improved by the dispersion of micro/nano ceramic fillers [24]. Skaarup et al. [25] studied physical and electrolytic properties of CSPE by incorporating insulating ceramic materials like Al$_2$O$_3$, SiO$_2$, TiO$_2$ and also the effect of dispersing filler particle of high conducting zeolites etc. They observed that the physical nature and particle size of dispersed filler particles
play a major role in enhancing the electrical and mechanical properties of PEs. Therefore the physical, electrochemical and mechanical properties can be improved due to the dispersion of nano sized filler particles. Hence these materials are also called as Nanocomposite polymer electrolytes (NCPE) [26]. Advantages due to dispersion of nano sized ceramic filler particles in the conventional SPE are

- Mechanical integrity of the electrolyte membrane will be improved.
- Improvement in electrolyte-electrode interface.

Local PEO chain reorganization has been prevented by the nano sized ceramic filler because of its surface area resulting in freezing at ambient temperature. Increase in conductivity of PEO-LiI/ Al₂O₃ CPE when the size of the filler particles is < 4 μm has been demonstrated by Weiczorek et al. [27] According to them, surface clusters of ceramic elements played an important role in the promotion of native structural variations. Ionic conductivity of CPE complexed with alkali-metal salts and its structure has been analyzed by Wieczorek et al. [28] By applying Lewis acid-base theory. The filler particles with dissimilar appeals like Lewis acid centres (AlCl₃), Lewis base centres (N, N dimethyleacrylamide) and amphoteric Lewis acid-base has been incorporated in the PEO:LiClO₄ system. As PEO possess Lewis base and Li⁺ cation possess Lewis acid character, the method employed in the composite electrolyte was due to the equilibrium between various acid-base reactions. By inserting inert sub μm particles of SiO₂ and TiO₂, substantial improvement in the temperature and mechanical reliability of PEO-LiClO₄ has been reported by Scrosati et al. [29] According to them when PEO was annealed at ~70°C, filler particles act like solid plasticizers reducing the formation of crystallization of PEO chain thereby increasing its amorphous nature which in turn reduces the temperature at which amorphous phase gets stabilized in the CSPE increasing its range of applications. There is possibility for ceramic filler particles to have path ways for Li⁺ migration, which is the consequence of Lewis acid-base interaction happening at the surface (PEO: LiClO₄) and interfaces [30]. This hypothesis has been confirmed by Croce et al [31] by dispersing a functionalized filler super acid sulfated zirconia into the PEO-LiBF₄ electrolyte system. An enormous increase in lithium conversion can be achieved due to the dispersion of this filler. By dispersing solid super acid zirconia into PEO-LiClO₄, increase in ionic conductivity and electrochemical properties has been observed. On
dispersing sub micrometre size particles of ferroelectric materials like PbTiO$_3$, BaTiO$_3$, LiNBO$_3$ into PE system based on PEO/ lithium salts like LiClO$_4$, LiBFO$_4$, LiPF$_6$ and LiCF$_3$SO$_3$, it was observed that conductivity enhancement takes place at RT [32]. Kumar and Scanlon [33] presented a wide review on alterations in ion conductivity, charge transfer quantity and electrode-electrolyte interfacial activity of CSPE systems. According to them, electrode-electrolyte compatibility can be increased by dispersing nano sized particle when compared with micrometer sized particles. DSC studies on PEO-LiClO$_4$ dispersed with high dielectric constant nano sized particles like TiO$_2$, ZrO$_3$ was carried out by Kumar and co-workers [34]. It was observed that augmentation in ionic conductivity was due to the interaction between polymer chain and high dielectric constant organic filler which were influenced by the size and mass of the particles. When inorganic filler LiN$_2$O$_3$ was dispersed in PEO-grafted (polymethacrylate) complexed with lithium salt, enhancement in conductivity and ionic mobility was observed by Morita et al [35].

**1.5 Lithium batteries**

Battery or an electrochemical cell is a device which converts the exothermic energy obtained during chemical reaction into electricity. Electrochemical cell had been introduced to mankind at the end of 18th century by Luigi Galvani and Alessandro Volta. 19th century has witnessed a series of discoveries of electrochemical systems. In 1866 Georges-Lionel Leclanche discovered a battery (Leclanche battery) with zinc rod as anode and manganese oxide- carbon mixture as cathode immersed in an aqueous ammonium chloride solution [36]. Later in 1859 by French scientist Gaston Plante by inventing lead-acid rechargeable battery and a rechargeable Ni-Cd battery (Swedish engineer Waldmar Tungner) which are finding place in today’s commercial batteries used in power supply for car ignition and other portable tools. The low energy density associated with electrode combination had limited the usage of commercial batteries to serve the evolving technology. Very soon it was found that lithium- based battery has high energy density because of very high specific capacity of Li than Zinc. The success of Li-iodine battery highlighted the potentiality of Li and it paved the way for the development of a series of new batteries which can be used for device applications. In 1970s Lithium battery was fabricated using Manganese dioxide as cathode resulted in the reduction of volume and size of the battery. One capable of accepting Li ions
acting as anode (Li sink) and other releasing lithium ions as cathode (Li source). Finally the electrochemical process involves the transfer of Li ions between two insertion electrodes during charging and the entire process is reused during discharge and cycle repeats.

In order to provide the battery life and safety, Armand in 1978 used a solvent free polymer which led to the fabrication of PEO based electrolyte of large-size and laminated battery module.

1.5.1 Working of Lithium-ion polymer batteries

Lithium ion secondary battery works on intercalation mechanism. According to this mechanism, Li ions are inserted into the crystalline lattice of the host electrode without changing its crystal structure. In batteries, the motion of electrons from one electrode to other electrode leads to the phenomenon of storing and releasing of energy. Structure of lithium-ion battery is shown in Fig 1.2.

![Fig 1.2 Structure of Lithium-ion battery](image)

During charging, positive electrode (Li-Cobalt oxide) releases Li ions which move to the negative electrode (Graphite) through the electrolyte (mixture of Li salts). At the negative electrode, electrons and ions combine and deposit lithium. When the movement of ions ceases, the battery is said to be fully charged. Now energy will be stored in the battery during this process.
While discharging, Li ions move back to the positive electrode through the electrolyte and also electrons flow from negative to positive electrode in the outer circuit. Again electrons and ions combine at positive electrode and deposits lithium there. After all the ions have moved back, the battery is said to be fully discharged. During the charging and discharging, movement of electrons around the outer circuit and ions through the electrolyte will be in mutually opposite directions and it is an interconnected process. That is, if either the movement of ions stops, electrons can’t move through the outer circuit if movement of electrons stop then ions cannot move.

1.6. Applications of polymer electrolytes

PEs play a vital role in a wide variety of applications since their invention in 1970s. Fuel cells, sensors, actuators, supercapacitors, electrochromic displays and dye-sensitized solar cells are some of the fields that have fascinated the scientific community. In the applications mentioned above the role of PEs are

1. to allow selective and a fast transport of required ions.
2. to provide good electrical insulation and
3. to separate two electrodes.
4. to be suitable for usage in a device

For all these requirements, PE must have important requirements such as “performance, durability and cost”.

In order for its adoption in a specific application, PE must show-case an especially high performance. Generally “performance level” is expressed in terms of ionic conductivity of the material. If the PE is in the form of thin film with the high conductance, this requirement may be relaxed. Generally in electrochemical device, electrolyte sets the upper limit of the output power. Hence, a higher output power may be achieved if the electrolyte conductivity is higher [37]. A wide electrochemical stability window used for energy storage devices like supercapacitors is another important requirement. PE should only transport the selected ion in case of sensors and actuators in order to get response from the material. Related performance for a long time interval of that particular application must be maintained by the PE used as device component. As a result the PE can withstand the operating temperature, electrochemical potential and the presence of contaminate. Mostly, the PE must be
compatible with other components like electrodes. In order to have a wide spread applications the cost of a device with PE should not be so high. Usually relatively high cost is due to limited abundance of materials like Li, Pb etc., and an intricate preparation procedure using hazardous intermediates like perfluorinated ionomers. A complex device assembly method needs to be performed in stable atmosphere in order to utilize the potential of the materials.

a. Secondary battery
In secondary battery the PE will allow the transport of alkali, alkali-earth metal ions from anode to cathode during discharge and cathode to anode during charging the battery. PEs being capable of carrying Li$^+$ ions, enormous research has been focussed on transporting other ions like Na$^+$, K$^+$, Mg$^{2+}$ etc. For the applications in secondary batteries, SPE and gel PEs are used. PEs used in modern secondary batteries can with stand nearly 1000 charge-discharge cycles, possess a power density of $10^3$ W/kg and energy density of 150 W/kg.

b. Fuel cells
In the fuel cells the role of PE is to carry H$^+$ ions from anode to cathode procured by fuel oxidation. Perchlorinated ionomers such as Nafion and Aquivion designed to operate at less than 120 °C are the modern membranes for the fuel cells [38].

c. Sensors and actuators
Some PEs upon exposure to external stimulus has an ability to undergo reversible change. Hence induced in the broad group of “stimuli: responsive” materials. In the case of PEs used in sensors, diffusion will control the transport of stimuli and slows the kinetic response. PEs has attracted more interest because of its reversible changes when placed between two electrodes, acting as an actuator [39]. When a field is applied the response time will significantly accelerate because the entire active materials experience the stimulus at the same time because of the improved ionic conductivity in GPEs and SPEs. They have found applications in the field of actuators. Ionic liquids are also introduced recently in this group [40]. Excellent durability has been exhibited by the resulting polymer matrix system with an immobilized ionic-liquid.
d. Supercapacitors

Supercapacitors have high electrochemical stability and wide surface area. The SPE, GPEs, hybrid PEs are used to improve the electrochemical stability and conductivity of super capacitors. The conductivity of super capacitor is significantly improved by using PEs at RT ($10^{-3}$ S/cm), durability is also as high as $10^5 - 10^6$ charge-discharge cycles [41].

e. Electrochromic display

These are multi-layer systems which undergoes a colour change when electric field is applied. Generally when an electric field is applied, the active component undergoes reversible colour change upon oxidation or reduction in its unperturbed state. Either positive or negative ions must be introduced into the active component to counter balance the electrical charge. PEs with ionic conductivity of $10^{-4}$ S/cm at RT finds applications in the electrchromic displays due to the ease of processing into thin films with small ohmic losses [42].

f. Dye-sensitized solar cells (DSSC)

The liquids such as methanol, acetonitrile are used as electrolytes, which deteriorates the life of the DSSC due to leakage. Assembly of DSSC consists of SPE, gel and hybrid PEs, conductance of electrolyte layers can be enhanced by processing these electrolytes as thin films. Utilizing ionic-liquid based PEs in DSSC improves the conductivity and durability; however the ionic conductivity of polymer electrolyte used in DSSC should be greater than $10^{-3}$ S/cm.

### 1.7 Nano science and nanotechnology

The term nano has been derived from the Greek word “nanos” meaning dwarf i.e., very small. At this size, i.e., $10^{-9}$ m, specific properties get differ from their bulk counterparts. At this scale, materials having atomic and molecular dimensions will be considered. At the beginning of fourth century A.D, humans have been known to take advantage of the peculiar properties of nanoparticles when Roman glass makers were fabricating glasses containing nano sized metals. In 1960, a famous physicist Richard Feynman presented a visionary and prophetic lecture at the meeting of the American Physical society entitled “there is plenty of room at the bottom” where he speculated on the possibility and potential of nanosized materials. This began the advent of nanotechnology and sets systematic study in the modern times. The research work on
Nanosized materials gained momentum in the latter half of the twentieth century. Nano science has been identified as one of the most critical technologies that would shape the future of the human race with its varied applications in the diverse areas and holds the key to extreme miniaturization of devices.

Nanotechnology was coined in 1974 by Norio Taniguchi is the area of science and technology for the materials size from 0.1nm to around 100nm (which is 0.00000001cm to 0.00001cm). DNA molecule is wide of about one nanometer. The area of nano science and nanotechnology has become increasingly important in recent years. Many researchers all over the world are now involved in the preparation, characterization and evaluation of a wide range of nanostructured materials occurring at the scale between 1nm and 100nm. This is the range that encompasses both the smallest artificial structures and ubiquitous molecules of the natural world and a wide variety of applications of these materials are expected in various branches of Science and Technology comprising Physics, Chemistry, Biology, Materials Science, Medicine, Environmental etc. and thus providing a profound impact in our daily lives. Nanoscience can be seen in nature - peacock feathers and butterfly wings contain nano-scale features which provide iridescent colors. Nanotechnology has found a place in consumer products, medical treatment, the food industry and so much more.

1.7.1 Significance of nanoscale

Many of the properties of solids depend on the size of the solid. Microscopic details become averaged out in bulk materials. In case of bulk materials, the properties such as density, elastic modulus, resistivity, dielectric constant etc. are averaged properties. Many properties of materials change in the micrometre or nano meter range. As materials become smaller and smaller and reaches to a stage where the properties are different from its bulk. Such properties were exhibited by the nanoscale materials due to the following reasons:

1. Nanomaterials have a relatively larger surface area when compared to their bulk counterpart. This can make material more chemically reactive (in some cases materials there will be an exceptional case) and affect their strength or electrical properties.
2. Quantum effects dominate the behaviour of matter at the nanoscale which affects the optical, electrical and magnetic behaviour of materials.
3. Physical properties of the materials are generally characterized by critical lengths. If the size or one of the dimensions of nanomaterial is smaller than the critical length, the nanomaterial exhibits properties that are different from the corresponding bulk material.

4. Further, the bulk properties of materials often change dramatically with nano ingredients. Composites made from particles of nano-size ceramics or metals smaller than 100 nanometers can suddenly become much stronger than predicted by existing materials-science models. The size variations of different materials are shown in Fig. 1.3

![Fig. 1.3 Size variations of different substances at nanoscale level](image)

### 1.7.2 Nanostructures

Nanostructures are classified based on the number of dimensions. They are zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D).

zero-dimensional nanomaterials: Materials which are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm). The most common representation of zero-dimensional nanomaterials is nanoparticles.
One-dimensional nanomaterials: Nanostructures between 1 - 100 nm in one direction are called one-dimensional nanomaterials. This leads to needle-shaped nanomaterials like nanotubes, nanorods, and nanowires.

Two-dimensional nanomaterials: Dimensions are not confined to the nanoscale. 2-D nanomaterials exhibit plate-like shapes. Examples are nanofilms, nanolayers, and nanocoatings.

### 1.7.3 Applications of nanotechnology in various fields

All-solid-state electrochemical device applications demand the following properties from the PE materials. These properties are (i) ionic conductivity \( \geq 10^{-4} \text{ S cm}^{-1} \) at RT (ii) PE should preferably a single ion (cations) conducting system (iii) high chemical, thermal and electrochemical stabilities and (iv) the materials must be higher stability domain in the voltage range of 0 - 5 V.

PEs must be compatible with the variety of electrode materials. Presently more effort has been diverted to explore in identifying the suitable PE and the electrode materials which would improve the performance level of electrochemical devices. The nanosized filler particles lead to better electrode/electrolyte compatibility as compared with micrometer sized particles. Vinyl-functionalized SiO\(_2\) nanoparticles were used as cross-linking sites as well as inorganic filler in the preparation of a CPE. In this SiO\(_2\) particles helped in adhering the PAN membrane to electrodes, providing favorable interfacial charge transport between the electrolyte and electrodes during cycling which helped in high discharge capacity and good cycling stability. The PEO chains and SiO\(_2\) interact through mechanical wrapping and chemical binding. [43]

Kumar et al [33] explained as the effect of size of particles on the crystalline-amorphous transition of polymer electrolyte (PEO: LiBF\(_4\)) dispersed with inorganic fillers (Al\(_2\)O\(_3\), SiO\(_2\) etc). Further, by dispersing PEs with nano-sized ceramic filler particles with high dielectric constant such as TiO\(_2\), ZrO\(_2\); interaction between polymer chain and high dielectric constant inorganic fillers must be dipole-dipole type driven by dielectric constant gradient. The nanoparticles associated with PE cation enhance the conductivity and also participate in the segmental motion of polymer chains due to weakening of polymer-cation association. Using these composites, the flexible batteries with high specific power and high ionic conductivity can be created which suits to the electronic products.
Recently, the ionic conductivity at RT could be achievable in SPEs only when the polymer host contains a large glass transition temperature (Tg). The amorphous phase of polymeric host supports high ion transport in SPEs. Ion conduction in SPEs is a complex process and it must lead to higher longitudinal conduction than orthogonal conductivity. PE with TiO$_2$ nanoparticles of 30 – 40 nm composites were used for the effective design of dye sensitized solar cells (DSSC). Kim et al [44] CPE prepared using PEO, fumed silica, iodide salt and iodine improved the conversion efficiency (4.5 % at 100 mWcm$^{-2}$) of DSSC.

In the microbial fuel cell (MFCs), the anode supports have been coated with carbon nanotubes (CNT) and graphene (GN) showed higher performance than that of the cells with uncoated anodes. This was mainly due to the high surface area and conductivity of these materials. Composites of metal-carbon, metal-polymer, polymer-carbon, polymer-polymer and carbon-carbon materials can also be used to enhance the performance of MFCs as electrodes and membranes [45]. Methanol alkaline fuel cells were reported using nanocomposites of chitosan nanoparticles with quasi polyvinyl alcohol matrix. The permeability was enhanced by using cross linked glutaraldehyde with nanocomposites membranes [46]. Overall the blend of polymer electrolytes with the various types of nanoparticles used in nanotechnology showed the route map to the new generation energy production, conversion and storage devices such as batteries, supercapacitors, actuators, fuel cells, DSSCs etc. There is still lot of research avenues in studying the effect of PE morphology on the electrochemical performance of the devices, understanding the physicochemical properties of self-assembled PEs and their applications in energy devices.

1.8 Objective of present work

SPEs are most promising materials in the area of material science and engineering. The SPEs are the most suitable materials for the compact design of the solid state electrochemical devices. Among the polymer hosts, polyethylene oxide (PEO) based composites have been intensively studied. PEO contain ether oxygen atoms which act as a Lewis base to coordinate the cations, and thus the dissolution of inorganic salt such as LiSCN, LiI, LiCF$_3$SO$_3$, LiClO$_4$, LiBF$_4$ and LiAsF$_6$, etc [47].
To enhance the ionic conductivity of SPE, various modifications have been proposed to modify the polymer matrix such as addition of plasticizers, addition of ionic liquids, copolymer, blending, addition of nano clay, dispersion of inorganic oxides, and ceramic powders [48].

CPE have been receiving technological importance in the field of electrochemical cells and high energy density lithium batteries since last two decades. CPE are more advantageous than liquid and gel electrolytes in terms of flexibility, shape, leak proof nature, good interfacial contact with electrodes, high mechanical strength and prevent the corrosive problems with the electrodes [49]. CPE are obtained by the dispersion of micro/nano inert inorganic fillers such as ceramic and metal oxide fillers in the SPE. PEO-based composite PEs gained technological importance because of their commercial availability in various molecular weights, low cost and high solvating power [50]. In enhancing ionic conductivity of PEO/lithium salt SPE system, the dielectric properties and thermal treatment of fillers played an important role. The loaded fillers influence the PEO dipole orientation to align polarized dipolar moments. The thermal treatment determines the flexibility of the polymer chains for Li⁺ ion migration.

The dispersion of micro/nano sized ceramic particles like SiO₂, MgO, Al₂O₃, TiO₂, Fe₂O₃, SnO₂, ZrO₂, Sm₂O₃, SiC etc., enhance the ionic conductivity and also improves the mechanical strength of the PE [51]. The enhanced ionic conductivity and ion transference number of CPE can be explained on the basis of Lewis acid-base theory. Lewis acid-base interaction centres possess ionic species in the electrolyte, low ionic coupling in resulting the promotion of salt dissociation via ‘ion-ceramic complex’ formation.

In this present work, Lithium ion conducting SPEs are prepared. PEO is used as polymer host with lithium perchlorate (LiClO₄) as added metal salt and various fillers like CoO, graphite and CuO are dispersed in the [85%PEO+ 15%LiClO₄] SPE system. The systematic study of present research work is described below:

1. PE system-1: In this system, SPE films are prepared according to:

\[(1-x)\% \text{PEO} + (x)\% \text{LiClO}_4, \text{where } x=0, 5, 7.5, 10, 12.5 \text{ and } 15\]

2. PE system-2: In this system, CPE films are prepared according to:

\[85\% \text{PEO} + 15 \% \text{LiClO}_4 + x\% \text{CoO}, \text{where } x=0, 1, 2, 3, 4 \text{ and } 5\]
3. PE system-3: In this system, graphite (GP) is dispersed in the SPE system.

\[85\text{PEO} + 15 \text{LiClO}_4 + x\% \text{GP}, \text{ where } x=0, 1, 2, 3, 4 \text{ and } 5\]

4. PE system-4: In this system, the CuO nanoparticles are dispersed in the SPE system.

\[85\text{PEO} + 15 \text{LiClO}_4 + x\% \text{CuO}, \text{ where } x=0, 1, 2, 3, 4 \text{ and } 5\]

5. PE system-5: In this system, the effect of Ethylene carbonate (EC) as plasticizer studied in the following composite electrolyte system:

\[85\text{PEO} + 15 \text{LiClO}_4 + 25\text{mole}\% \text{ EC} \] and \[85\text{PEO} + 15 \text{LiClO}_4 + 25\text{mole}\% \text{ C+2\%CuO}\]

For above mentioned systems synthesis, characterization techniques and electrical properties are elaborately discussed in the forthcoming chapters.