CHAPTER-1

Solid State Ionics: An Overview

This chapter contains a brief introduction to different types of electrolyte materials and detailed discussion on various solid polymer electrolytes.

INTRODUCTION

Solid State Ionics is a very prominent and interesting branch of material science. It mainly concerns fast ion transport through the bulk exhibited by solid electrolytes. The ionic conductivity of these solids is exceptionally high (10^{-4} – 10^{-1} Scm^{-1}) and comparable to those of liquid / aqueous electrolytes and are much safer in terms of storage and transport. Research in the field of solid state ionics circumscribes investigations of physical and chemical properties of solids with fast ion transport and their technological applications. Such materials better known as Super Ionic Solids (SICs) or Solid Electrolytes (SEs) or fast Ion conductors (FICs) pose as potential candidates in development of all-solid-state electrochemical devices such as batteries, super-capacitors, fuel cells, sensors, electro-chromic displays, photo-electrochemical solar cells and so on. Fig. 1.1(a) shows energy density versus power density diagram for these devices and (b) shows construction of a typical sodium-ion battery.

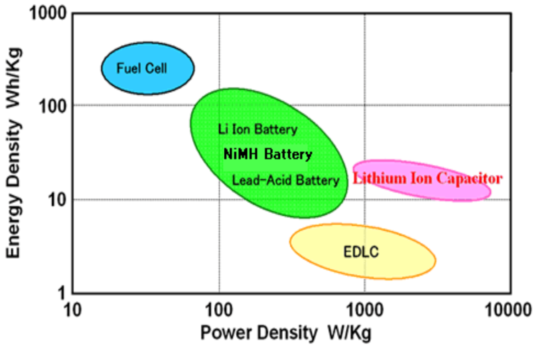

Fig. 1.1(a) *Energy density vs power density of electrochemical devices.*
https://energyeducation.ca/encyclopedia/Energy_density_vs_power_density

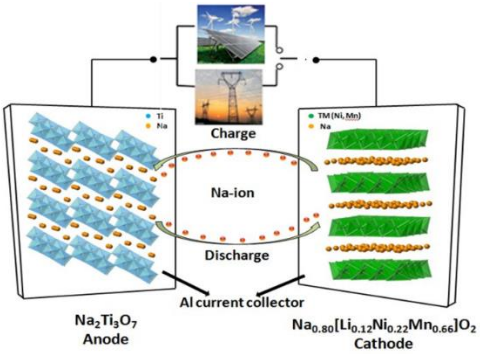

Fig. 1.1(b) *Typical Sodium Battery.*
http://smeng.ucsd.edu/supercapacitors/

A super ionic solid can be represented by following necessary and sufficient properties

- High conductivity (10^{-4} – 10^{-1} Scm^{-1})
- Low Energy of Activation (< l ev)
- Ions as majority charge carriers (t_{ion} ~ 1) with negligible contribution from electrons.

The earlier known forms of ionic solids, like alkali halides and silver halides etc., exhibit very low room temperature conductivity (10^{-7} – 10^{-16} Scm^{-1}) and are chiefly governed by theories of thermally generated point defects (Schottky and Frenkel). Attempts were made by the means of aliovalent doping to increase the conductivity of such solids ***(Chandra, 1981)*** but with a limited success. The year 1976 marked epoch making event of discovery of sodium ion conduction in β-alumina by Yao and Kummer ***(Yao and Kummer, 1967)*** and silver ion conduction in MAg_4I_5 (M = K, Rb, NH_4) ***(Owens and Argue, 1967)***. Subsequently, a large number of solid electrolytes have been investigated till date with some of them having extremely promising chemistry for applications in various electrochemical devices. Over the years, research was not only directed towards discovery of fast ion conductors, but also focussed on various methods of enhancing their electrochemical properties. Those techniques include blending (mixing) of two polymers ***(Marinov et al., 2017; Sharma et al., 2013)*** addition of high dielectric constant plasticizers like EC, PC, DEC, DMC, PEC ***(Isa et al., 2014; Monti et al., 2016; Das and Ghosh 2015; Saikia and Kumar, 2005)***, dispersion of inert nano-fillers like Al_2O_3, SiO_2, TiO_2 ***(Pitawala et al.,2007; Vignarooban et al.,2014; Ketabi and Lian, 2015)***, incorporation of ionic liquids ***(Zhai et al., 2014; Kumar and Hashmi, 2010)*** and irradiation with swift heavy ion beam ***(Kumar et al., 2006; Abdul-Kader et al., 2012; Kumar et al., 2011; Kumar et al., 2010)***, x-rays, γ-rays and electron beams ***(Raghu et al., 2014; Nanda et al., 2010; Aggour, 2001)***. These techniques have proved to be very reliable, tech savvy and cost effective. In this chapter, we have briefly discussed various types of solid-state ionic materials and techniques of modifications employed for enhancing their electrochemical properties. The work reported in present thesis is focussed on the role of ion-beam irradiation on sodium salt-based blend electrolyte system for fabrication of all-solid-state battery hence relatively more discussion has been done about the same.

1.1 Classification of Solid State Ionic Materials

On the basis of their properties, structural morphology and synthesizing techniques, solid state ionic materials have been divided into following categories.

- Framework crystalline / polycrystalline solid electrolytes
- Glassy / Amorphous solid electrolytes
- Composite solid electrolytes
- Polymer Electrolytes

1.1.1 Framework Crystalline / Polycrystalline solid electrolytes

These superionic solids are usually prepared by solid state reaction technique invariably containing a rigid cage like skeletal structure within which majority of the ions find an easy conduction passage. Most of the superionic materials discovered in the initial stages of development of field of solid state ionics are grouped under this category. Framework solids are further classified as below.

Soft-Framework Materials: Generally described as materials having pure ionic bonding, highly polarisable ions (Ag^+, Cu^+, etc), exhibiting low Debye temperature and low melting points. Also have a sharp order-disorder phase transistors existing between high and low conducting phases. These materials take the form ($MX : xNY$), where NY is the host salt such as AgI, CuI and M is the doping salt, M = K, Rb, NH_4 etc. X = I, Br, Cl, S, P_2O_7 etc.

Hard-Framework Materials: In contrast to soft-framework solids, the hard-framework materials are characterized by high Debye temperature, low polarizability of mobile ions and less sharp or complete absence of order-disorder phase transitions.

Ion transport phenomenon in this class of solid electrolytes is governed by jump/hop mechanism. Certain well-known theories and models proposed to explain the conduction process of this category are phenomenological model ***(Huberman, 1974a)*** Lattice gas model ***(Sato and Kikuchi, 1971)***, free ion model ***(Rice et al., 1972)***, jump diffusion model ***(Huberman and Sen, 1974)***, Jump-relaxation model ***(Funke, 1993)***, coupling model ***(Ngai and Rendell, 1993)*** and counter ion model ***(Dieterich et al., 1980)***.

1.1.2 Glassy / Amorphous Solid Electrolytes

Study of fast ion conduction in glassy / amorphous solid electrolytes gathered impetus in late 1970s. These systems exhibited important advantageous material properties over crystalline / polycrystalline counter parts which include high isotropic ionic conduction, absence of grain boundary conduction, wide range of compositional variability, ease of fabrication into desirable geometries etc. **Kunze et al. (1973)** for the first time reported fast ion conduction in AgI – Ag_2SeO_4 system. This glassy electrolyte exhibited exceptionally high conductivity of ~ 10^{-2} Scm^{-1} at room temperature. Their compositional formula can be generated as $MX : M_2O : A_xO_y$ where MX is the dopant salt (Ag1, PbI_2, CdI_2, etc) , M_2O is glass modifier (B_2O_3, MoO_3, P_2O_5, SiO_2, As_2O_5 etc) Preparation of these solid electrolytes is done by splat quenching or ball-milling or liquid N_2 method ***(Sharma, 2013)***. Some examples of such materials are AgI – Ag_2SeO_4, AgI-A_2O, B_2O_3, AgI-Ag_2O-V_2O_5, CdI_2-Ag_2O-V_2O_5-B_2O_3 and PbI_2-Ag_2O-V_2O_5-B_2O_3 ***(Licheri et al, 1986; Padmashree et al., 2006; Jayswal et al., 2011; Malugani et al., 1979; Minami et al., 1992; Kawamura 1990)***. Different theories proposed to explain ion conduction in glassy / amorphous solid electrolytes are Anderson Stuart (A-S) model, weak electrolyte model, Random site model, The Cluster By-pass model and Ion-Association model ***(Anderson et al., 1954; Ravaine et al., 1977; Ravaine et al., 1978; Glass et al., 1980; Minami et al., 1982; Ingram et al., 1988)***.

1.1.3 Composite Solid Electrolytes

Composite solid electrolytes, also referred to as dispersed solid electrolytes are high ion conducting multiphase solid systems. They are a two-phase mixture, containing a moderately conducting ionic solid such as AgI, CuI etc as I-phase host salt and II-phase material which is either an inert insulating compound such as Al_2O_3, SiO_2, ZrO_2, Fe_2O_3 etc ***(Kumar, 2014)*** or another low conducting ionic solid such as AgBr, AgCl, KCl etc. On the basis of physical and chemical mature of the constitute phases, these two-phase composite electrolyte systems have been sub-grouped as:

Inorganic Composite Electrolytes: These are either composite electrolytes like moderately ion conducting alkali / silver halide salts dispersed with insulating / inert materials such as Al_2O_3, SiO_2, ZaO_2, fly-ash etc or crystal-glass composite electrolytes like ion conducting glass dispensed with above mentioned insulating / inert materials. Examples of this type of electrolytes are Gallium-doped LiLaZrO garnet-type electrolytes ***(Wu et al., 2017)***, (NASICON)-type $Na_{1-x}Zr_2P_{3-x}Si_xO_{12}$ ***(Gao et al., 2018)***

Organic Composite Polymer Electrolytes: They are either polymer electrolyte composites i.e. conventional solid polymer electrolytes (SPEs) dispersed with filler particles or organic / inorganic materials such as: Polymers like PS, PMMA, PAA, PVA or inorganic compounds like Al_2O_3, SiO_2, β-alumina, NASICONS, $LiAlO_2$, Li_3N etc or glass-polymer composite electrolytes viz. conventional solid polymer electrolytes dispersed with ion conducting glasses like $Li_2O : B_2O_3$, $LiBF_4$, $Na_2O: B_2O_3$, $Li1 : B_2S_3$, $Li1 : Li_2S : B_2S_3$ etc.

Models proposed to explain conduction process occurring in such systems are space-charge model ***(Jow and Wagner, 1979)***, Adsorption / Desorption model ***(Maier, 1984)***, Percolation model ***(Bunde et al., 1985)*** and Mobility enhancement model ***(Shaju et al., 1995)***.

1.1.4 Polymer Electrolytes

Polymer Electrolytes are those which possess number of competent material properties over other solid electrolyte systems which include high mechanical integrity, mouldability, flexible thin-film formation ensuring intimate electrode – electrolyte contact during the fabrication of all-solid-state electrochemical devices. As mentioned earlier, since present thesis work is focussed on solid polymer electrolyte systems, an extensive and detailed discussion has been made for these materials.

1.1.4.1 Polymer Electrolytes: A Brief Overview

Fenton in 1973 ***(Fenton et al., 1973)***, synthesized polymer electrolyte (PE) membrane by complexing alkali ion salts in a high molecular weight polar polymer poly (ethylene oxide) (PEO). Later a practical thin film battery based on poly (ethylene oxide) PEO-Li^+ salt complex solid polymer electrolyte (SPE) was demonstrated for the first time by Armand and co-workers in 1979. This discovery attracted a wide spread attention from both academic and industrial sectors. As a consequence of this, since past more than four decades, a large number of polymer electrolytes with a variety of mobile ions like H^+, Li^+, Na^+, Cu^+, K^+, Ag^+, Mg^+ etc as principle charge carriers have been investigated for their possible application as electrolytes in a variety of all-solid-state electrochemical power sources, namely high power density rechargeable batteries, fuel cells, super capacitors etc has been widely explored. Number of books, research papers and monographs have been published which describe designing of these materials and the techniques employed to study the structural, thermal and ion-transport properties of these materials and their device characterizations ***(Hema et al., 2016; Tarascon and Armand, 2001; Osman et al., 2005)***. Fig. 1.2 shows amorphous and crystalline regions inside a polymer matrix. In order to act as host matrix for applications in all-solid-state electrochemical devices, polymer electrolytes require to possess the following characteristic properties

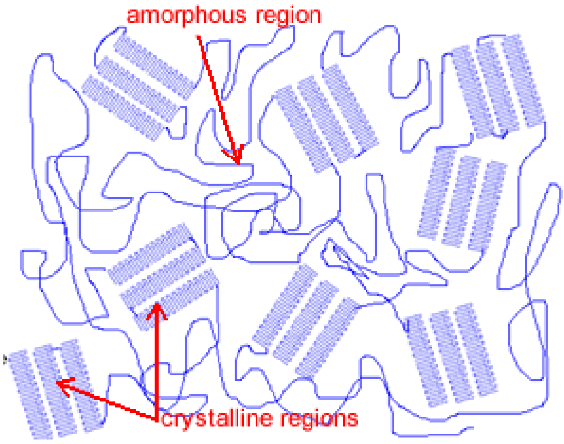

Fig. 1.2 *Amorphous and crystalline regions in a polymer.*

http://www.dynamicscience.com.au/tester/solutions1/chemistry/crystallinestructures.html

Ionic conductivity $\sigma \geq 10^{-4}$ Scm^{-1} at room temperature

Majority of polymer electrolyte membranes reported so far in the form of free-standing films exhibit conductivities of the order of 10^{-4} Scm^{-1}, yet efforts are on to further increase the conductivity value at room temperature.

A variety of host polymers viz. PEO (Polyethylene Oxide), PPO (Polypropylene Oxide), PEG (Polyethyleneglycol), PVdF (Poly Vinylidene fluoride), PVA (Poly Vinyl Alcohol), PAM (Polyacrylamide) PMMA (Polymethylmetha-acrylate) etc. complexed with a variety of salts like $LiClO_4$, $LiCF_3SO_3$, $LiBF_4$, $NaClO_4$, $NaCF_3SO_3$, $NaPF_6$, NaBr, Nal, NH_4l, NH_4ClO_4, KCl, KI, $AgNO_3$, AgI, $MgCiO_4$, $MgCF_3SO_3$, ***(Gondaliya et al., 2011; Kumar and Hashmi, 2010; Sharma and Hashmi, 2013; Tripathi et al., 2012)*** have been investigated. Ionic conductivity and mechanical integrity of polymer electrolyte membranes can be improved by (i) blending (mixing) of two polymers ***(Marinov et al., 2017; Sharma et al., 2013)*** (ii) by plasticization i.e. adding low molecular weight solvents with high dielectric constants like EC, PE, DEC etc ***(Isa et al., 2014; Monti et al., 2016; Das and Ghosh 2015; Saikia and Kumar, 2005)*** (iii) by incorporation of inert nano fillers like Al_2O_3, SiO_2 etc ***(Pitawala et al., 2007; Vignarooban et al., 2014; Ketabi and Lian, 2015)***.

Ionic Transference number (t_{ion}) should be close to unity (t_{ion}~ 1): This is one of the most important requirements for a useful electrochemical device performance. The polymer electrolytes must be single-ion (preferably cation) conducting systems and should act as perfect ion conducting and electron separator medium. Specifically, for battery applications, as the values of t_{ion} approach unity, polarization effect decreases and hence the power density increases.

High thermal/ mechanical/ chemical/ electrochemical stability: In order to ensure a reliable performance of the electrochemical devices based on the polymer electrolyte films sandwiched between appropriate cathode and anode materials, these stability criteria should be fulfilled. Thermal stability provides broad temperature range of operation whereas a good electrochemical stability means a wider working voltage range as high as 3-5 V. The chemical stability ensures prevention from chemical degradation and the mechanical integrity favours large scale manufacturing of the polymer electrolyte membranes.

Electrode-Electrolyte Compatibility: The chemicals employed as anode / cathode materials in fabrication of all-solid-state polymer electrolyte batteries should be chemically compatible with electrolyte materials so that an intimate contact at electrode-electrolyte surface can be maintained for optimum performance of the device.

1.1.4.2 Fundamentals of Polymer-Salt Complexation

The strength of interaction between polymer co-ordinating group and cation and the electrostatic interaction between cations and anions of the dissolving salt, including lattice energy etc decide the solvation enthalpy of salt in a polymer host matrix. Poly-ethers, polyesters, poly-imines and poly-thioethers have strong co-ordinating groups along the chain and can dissolve a wide variety of salts. The molecular weight of the host polymer also plays a vital role in the salt complexations. In low molecular weight solvents, solvation of the cation mainly depends upon the number of molecules that pack around it. In high molecular weight polymers, the chain must wrap around the cation without excessive strains PEO has been largely identified as an ideal solvent for alkali metals, alkaline earth metals, transition metals, lanthanides and rare earth metal cations. Its solvating properties are comparable to water, since water and ether have very similar donicity and polarizability. However, unlike water, ethers are unable to dissolve the anions. Salts of singly charged polyatomic anions such as $NaCF_3SO_3$, $NaClO_4$ will dissolve readily in poly-ethers. Salts containing monatomic anions are soluble in poly-ethers provided they are large enough and polarisable e.g. I^-, Br^-. Theoretically some anions suitable for formation of polymer electrolytes are ClO_4^-,

$CF_3SO_3^-$, $(CF_3SO_2)_2\ N^-$, BF_4^-, AsF_6^-, PF_6^- etc. Based on these observations, **Ratner (1987)** summarized the important criteria that favour the formation of polymer-salt complexes as follows.

1. Polymer should have large number of polar groups (e.g. O, N or S) in the chain for coordination of cations.
2. The polymer chain should be flexible i.e. the value of glass transition temperature (T_g) should be low for effective solvation.
3. The lattice energy of the salt and cohesive energy of the polymer should be low to facilitate salt dissociation.

1.2 Classification of Polymer Electrolytes

Considering the difference in preparation methods adopted during the casting of polymer electrolyte membranes and considering the physical parameters, polymer electrolytes can be further classified as follows.

1.2.1 Conventional Polymer salt complexes / solid polymer electrolytes (SPEs)

Conventional solid polymer electrolytes (SPEs) are prepared by complexing / dissolving ionic salts into coordinating polar polymer hosts of high molecular weight such as PEO, PPO etc. The electrolyte films are formed by traditional solution casting technique. However, a novel hot-press method has been recently developed and used to cast the films. This method is a completely dry / solution free process of film casting with number of merits such as low cost, rapid and with minimum loss of chemicals etc. PEO remains to be the most investigated polymer host matrix till date ever-since its first use in 1970s. PEO forms stable dry complexes as compared to other polymers. The sequential oxyethylene group –CH_2-CH_2O-O and polar groups -O-, -H-, -C-H- in the polymer chains have the ability to dissolve different ionic salts ***(Gray, 1991)***. Large variety of sodium salts: NaX, X = 1, Cl, Br, ClO_4, CF_3SO_3, BF_4, PF_6 etc can be complexed with PEO to form SPE membranes. Basic structure of SPE membrane involves PEO chains coiled around Na^+ - ions separating them from X-counter anions. The ion (Na^+) transport in polymer electrolytes as a consequence of local relaxation as well as segmental motion of the polymer chains is more favourable in presence of high degree of amorphocity in the host matrix. PEO is generally in crystalline phase below 70°C which approximately corresponds to its melting temperature. Above this temperature, PEO predominantly exists in amorphous phase. Hence a practically useful conductivity value ($\geq 10^{-4}$ Scm^{-1}) in PEO- Na^+ polymer-salt complexes is easily achievable in the temperature range 70 °C - 90 °C. Intensive efforts are employed to create higher degree of amorphous phase in polymer hosts at room temperature. Examples of such conventional electrolytes are PEO-$NaCF_3SO_3$ ***(Joshi et al., 2015)***, PEO-$NaPF_6$ ***(Hashmi and Chandra, 1995)***, PVdF-CO-HFP-$NaCF_3SO_3$ ***(Kumar and Hashmi, 2010)*** and PEO-$AgNO_3$ ***(Gondaliya et al., 2011)***.

1.2.2 Plasticized / Solvent swollen Polymer salt complexes

Plasticized polymer-salt complexes are prepared by adding liquid plasticizers in conventional solid polymer electrolytes which lead to a substantial enhancement in room temperature conductivity. As mentioned earlier, practically useful conductivity value ($\geq 10^{-4}$ Scm^{-1}) in PEO-based dry SPEs could be achievable only beyond $T_m \sim 70$ °C. One of the common approaches adopted to increases the degree of amorphosity in PEO below T_m is addition of liquid plasticizers. Plasticizers are high dielectric constant, low viscosity aprotic organic solvents such as Ethylene Carbonate (EC), Propylene Carbonate (PC), Poly ethylene Glycol (PEG) DEC (Diethyl Carbonate), DMC (Dimethyl Carbonate) etc. Apart from increasing the flexibility and processability of polymer, plasticizers also support ion dissociation which results in a greater number of migrating ions available for charge transport. Some examples of such plasticized polymer electrolytes are PAN – EC/PC – $LiClO_4$ ***(Abraham et al., 1990)***, PMMA-$NaCF_3SO_3$-EC/BC ***(Othman et al., 2017)***.

Although addition of plasticizers generally results in conductivity enhancements in SPEs, it adversely affects mechanical integrity of polymer electrolyte membrane. During battery applications, reactivity of the electrolytes towards metal anode increases ***(Croce et al., 1993)*** and thus the gain in conductivity is simultaneously accompanied by loss of solid-state configuration and lack of compatibility with the electrode.

1.2.3 Gel Polymer Electrolytes (GPE)

Gel Polymer electrolytes are prepared by incorporating large amount of organic liquid solvent or liquid plasticizer. i.e. ionic liquid into the polymer matrix which forms a stable gel polymer host ***(Agrawal et al., 2008)***. Gel electrolytes possess both solid-like rigid structure as well as liquid like diffusive transport properties. Due to these dual characteristics, GPEs have their own importance in a variety of electrochemical device applications but suffer from disadvantages like those mentioned for plasticized polymer electrolytes. Examples are PVdF-PMMA-(PC + DEC)-$LiClO_4$ ***(Gohel et al., 2018)***, EC-PC-$NaClO_4$-PMMA-SiO_2 ***(Kumar and Hashmi, 2010)***.

1.2.4 Composite Polymer Electrolytes

These polymer electrolytes are formed by dispersing inorganic inert micro / nano sized particles in conventional polymer electrolytes. Zeolites, ionites, solid superacid sulphated- zirconia, insulating ceramic materials like Al_2O_3, SiO_2 and TiO_2 are some examples of such micro/nano filler materials. Dispersion of fillers in polymer electrolyte improves its physical morphological, electrochemical and mechanical properties ***(Croce et al., 1998)***. Particle size plays an important role in such a system and hence the dispersal of nano-sized fillers has been reported to be more useful for the formation of composite polymer electrolyte systems. Examples are PEO-$LiClO_4$-SiO_2 ***(Ahn et al., 2006)***, PVdF-LiTFSIi-SiO_2 ***(Shanthi et al., 2018)***.

1.2.5 Plasticized-nano Composite Polymer Electrolytes

This class of polymer electrolytes is obtained by dispersing inert nano sized fillers in plasticized polymer electrolytes. Examples are EC-PC-$NaClO_4$-PMMA-SiO_2 ***(Kumar and Hashmi, 2010)***. Main motive behind the dispersal of nano-fillers in a plasticized system is to achieve improved mechanical properties. Addition of nano-fillers ruptures the crystallinity of the polymer matrix and hence contributes in achieving a better conductivity of the system.

In PEO based polymer electrolytes, incorporation of nano-fillers deteriorates crystallization kinetics of PEO giving rise to a larger amorphous volume which is favourable for ionic transport. Ceramic fillers produce conducting pathways inside the network structure of the polymer host and thus lead to enhanced conductivities. However, addition of more than a permissible amount of nano-fillers creates a hindrance in the way of ions and hence conductivity decreases.

1.2.6 Rubbery Electrolytes

Rubbery electrolytes are also referred to as ‘polymer-in-salt’ systems. These electrolytes are prepared by adding small amount of high molecular weight polymers viz. PEO, PPO in large amounts of salt ***(Angell and Sanchez, 1993)***. These solid electrolytes are in complete contrast to the above mentioned ‘*salt-in-polymer*’ electrolytes. Glass transition temperature (T_g) of rubbery electrolytes is usually low enough to maintain a rubbery state. Room temperature conductivities of these electrolytes is very high but the nature of the salts to crystallize at lower temperatures adversely affect electrochemical stability of such systems. Hence only a few rubbery electrolyte systems have been reported so far. **Angell and Sanchez (1993)** reported conductivity value as high as ~ 2 x 10^{-2} Scm^{-1} at room temperature for $AlCl_3$-LiBr-$LiClO_4$- PPO polymer-in-salt electrolyte system.

1.3 Polymer Blending

During 1940s – 1960s, many polymers were developed, each with unique properties and specific applications. Despite this, the polymer industry and academia realized the need for more and more new polymer materials. The idea of bringing an entirely new polymer in the market seemed quite unfeasible and very expensive as well. Hence the industry and academia focussed their attention and efforts towards modifying the already existing polymers which opened an exciting and interesting branch popularly known as “Polymer blending”. The first known polymer blend was a mixture of natural rubber with Gutta-percha developed by the founder of British Rubber industry, Thomas Hancock in 1843. Polymer blending is a physical mixture of two or more polymers which may/may not have chemical interactions. The properties of polymer blends are largely governed by physical and chemical properties of component polymers and on the state of phase i.e. whether it is in homogeneous or heterogeneous phase. If two different polymers dissolve in a common solvent, the blend will be formed very quickly due to establishment of thermodynamic equilibrium. Polymer blends have been reported to display superior properties as compared to their parent polymers. Fig. 1.3 shows schematic figure of a blend system made up of two polymers.

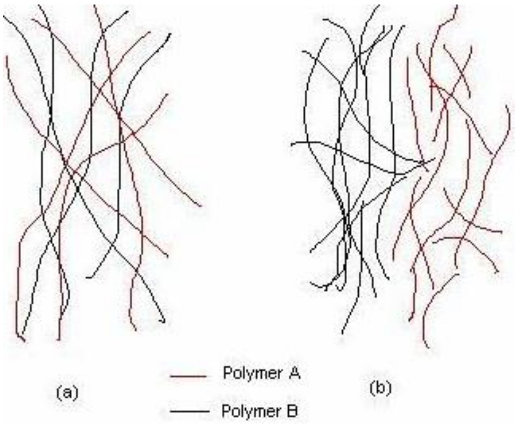

Fig. 1.3 *Polymer blend system.*

http://www.kazuli.com/UW/4A/ME534/asgn2.htm

1.3.1 Blend Polymer Electrolytes (BPE)

Highly competitive and constantly rising demands for improved properties and better performance of polymer electrolytes cannot be satisfied single-handedly by conventional PES. Hence, as discussed before various approaches have been undertaken to improve the applicability of PES. Polymer Blending has emerged as the most promising, cost-effective and green technology. Large number of BPEs have been investigated till date and have exhibited higher ionic conductivities and better electrode – electrolyte interfacial performance as compared to traditional PEO based polymer electrolytes ***(Ngai et al., 2016)***. Examples of BPEs include PEO-PAM-$NaCF_3SO_3$ ***(Dave et al., 2018)***, PEO-PMMA-$AgNO_3$ ***(Sharma et al., 2013)***, PVdF-PMMA-$LiClO_4$ ***(Gohel et al., 2018)***.

1.4 Irradiation of Polymer Electrolytes

Irradiation by swift heavy ion (SHI) beam is another favourable and green method of achieving better electrochemical properties in polymer electrolytes. Irradiation of polymer electrolytes by other sources such as γ-rays ***(Raghu et al., 2014)***, electron beam ***(Nanda et al., 2010)*** and *x*-rays ***(Aggour, 2001)*** have also been reported.

Irradiation by SHI beam has been known to bring about radical changes in physical, chemical, electrical, structural and optical properties of the polymers ***(Kumar et al., 2012)***. When an energetic ion-beam interacts with material, its effect on the material is governed by the energy of the ion, ion species and the fluence. In its passage through a material, ion beam majority loses its energy by two autonomous processes (i) by elastic collisions, wherein the energy of the ion beam is used up in displacing the atoms of the sample. This process is popularly known as nuclear stopping and the energy lost in this process is referred to as nuclear energy loss. Nuclear stopping is dominant at lower energies of the ion beam. (ii) The other form of energy loss is exciting the atoms of the samples by in-elastic collisions. This process is referred to as electronic stopping and the energy lost is teamed as electronic energy loss. Electronic stopping prevails at higher energies of the ion beam ***(Avasthi, 2000)***. Heavy ions carrying extremely high energies which lead to electronic losses are termed as swift heavy ions (SHIs) ***(Avasthi, 2000)***. SHIs travel a straight-line path in the polymer materials creating cylindrical damage zones on their way. The trajectory of such damaged zones is termed as Latent Ion Tracks ***(Fink et al., 2005)***. Because of their large range, SHI are not embedded into the material. Information regarding the processes occurring in the material during irradiation is stored in the resulting alterations developed in physical and chemical geometry of the materials ***(Kanjilal, 2001)***. Irradiation by SHI beam has reported to show better ionic conductivity as compared to their un-irradiated counterparts ***(Kumar et al., 2006)***. Fluence, of irradiation plays a vital role in the enhancement of ionic conductivity. Every new additive complexed in the polymer electrolyte to increase its conductivity has a critical value above which it hinders the motion of the ions and hence leads to a decrease in the conductivity. Similarly, there is a critical value of fluence after which it adversely affects the conductivity of the electrolyte. Critical fluence has different values for different materials i.e. critical fluence is dependent on the system of electrolyte material. It is a general observation that at lower fluencies, bonds of the polymer are broken and it undergoes chain scissioning process. This leads to faster ionic transport through the polymer matrix assisted by large segmental motion of the polymer backbone ***(Raghu et al., 2016)***. Chain-scissioning and cross-linking effects on a polymer due to irradiation are depicted schematically in Fig. 1.4. During irradiation, nuclear collisions cause atomic displacements which lead to chain scission or discharge of pendant atoms. Polymers have a large free volume and hence the probability of displacing two atoms simultaneously from neighbouring chains and creating two radical pairs for cross – linking via nuclear collision is small. On the other hand, electronic excitations occur as a result of electromagnetic interactions between the positively charged ion and target nuclear. Hence it produces a large number of free radicals, chemically active species, cations, anions and electrons along the ion track. Coulomb interactions among these active species cause rigorous bond stretching and segmental motion of the polymer chains which lead to cross-linking and bond-breaking. Hence both nuclear and electronic energy transfer contribute to cross-linking and chain-scissioning process. Nonetheless, nuclear stopping causes more chain-scissioning because of its nature of independent damage whereas in electronic stopping a collective excitation takes place which produces an excited volume within which coercive interactions among ions and the radicals occur, leading to cross-linking of the polymer chains ***(Lee, 1999)***. Thus at low fluence, chain scission predominates and at higher fluence, cross-linking mechanism takes the charge. Activation energy required for cross-linking is provided by the critical fluence ***(Kumar et al., 2010)***.

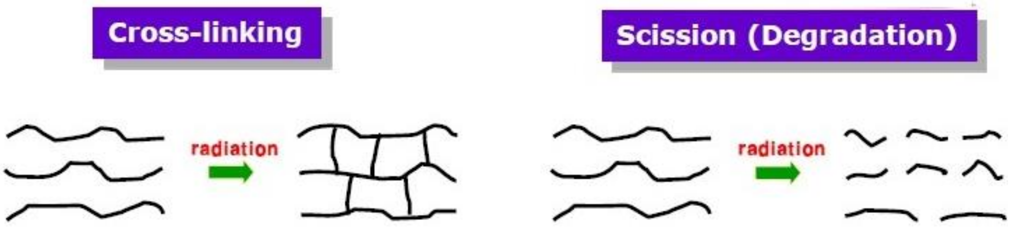

Fig. 1.4 *Irradiation effects on Polymer.*

https://aeb.gov.lk/web/index.php?option=com_content&view=article&id=293&Itemid=243&lang=si&limitstart=1

1.5 Applications of Polymer Electrolytes

Polymer electrolytes have found potential applications in various electrochemical devices such as secondary batteries, sensors, fuel cells, super-capacitors, memory devices, actuators, ultracapacitors, dye-sensitized solar cells and thermoelectric generators ***(Pope et al., 2005)***.

1.6 Present Work

Present thesis is aimed at understanding basic mechanism lying behind the electrochemical response of blend polymer electrolyte systems irradiated with SHI beam. As discussed in the above presented overview, it is mandatory to develop a system with better electrochemical performance to sustain the present demands of energy and also for the future of electrochemical devices. Safety issues present in the Li^+-ion electrolytes and limited resources of lithium metal have made it mandatory to investigate potential applications of an alternative system. Literature survey of electrolyte systems based on different metal salts apart from lithium, point out that sodium (Na^+) ion can be a competent alternative to Li^+ - ion electrolytes. Sodium has certain very important advantages which makes it stand next to lithium. These include its material abundance, low cost and environment friendly nature.

Keeping in mind all these aspects we report the following systems

1. First system **(PPS – system)** Blend electrolytes are prepared as
   1: 1 (*w/w*) (PEO – PAM) + x wt% $NaCF_3SO_3$
   x = 5 wt% - 17.5 wt% in steps of 2.5
2. Second system **(PPSP – system)** plasticized blend electrolytes are prepared as
   1: 1 (*w/w*) (PEO – PAM) – 12.5 wt% $NaCF_3SO_3$ + x wt% 1: 1 (*w/w*) (EC-PC)
   x = 5 wt% - 25 wt% in steps of 5
3. Third system **(PPSPN – system)** plasticized nano-composite blend electrolytes are prepared as
   1: 1 (*w/w*) (PEO – PAM) – 12.5 wt% $NaCF_3SO_3$ – 20 wt% (EC – PC) + x wt% SiO_2
   x = 5 wt% -15 wt% in steps of 2.5

These systems will be known as PPS, PPSP and PPSPN in succeeding chapters.

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