Ch. 1: Introduction

****

The initial part of this chapter mainly mentions the field of *'Solid State Ionics'* followed by an outline on electrolytes and their types. The later part of the chapter includes a brief discussion on various types of polymer electrolytes and their complexation with salt, plasticizer and nano-filler. The concluding part of the chapter consists of the applications of these polymer electrolytes in various solid state electrochemical devices and a brief discussion about the present research work.

****

1.1 Solid State Ionics

A highly exciting and challenging interdisciplinary branch of science and technology has become a major thrust area of research in the recent years. This new emerging field of materials science and technology was termed as *'Solid State Ionics'* in 1960 by **Prof. Takehiko Takahashi** of Japan and his co-worker **Prof. Osamu Yamamoto** [1]. Interestingly, Solid State Ionics is totally analogous to the term *'Solid State Electronics'*. Solid State Ionics majorly deals with the areas of physics & chemistry of defects, ionic thermodynamics, material science, chemical engineering, ion exchange phenomena, science of solid state interfacial properties amongst electrodes and electrolytes, intercalation science, solid state electrochemistry, science of structures, ionic transport in mixed conductors, etc. Since long Solid State Ionics is used extensively to study the phenomena of ions in solids which have exceptionally high ionic conductivity of the order of 10^{-6} to 10^{-1} S/cm at room temperature or at fairly low temperatures, usually less than their melting temperatures. Owing to such a high ionic conductivity comparable to liquid electrolytes, these ionic conductors are also termed as *'Solid Electrolytes'* wherein principle charge carriers are either cations or anions or both [2(a)-5]. Later, this field of Solid State Ionics flourished rapidly and put forward various newly designed materials and explored their potentialities for various electrochemical and optical applications viz. in electrolyzers, microbatteries, fuel cells, gas and microion sensors, solid state batteries and various other energy storage devices [2(b),6,7].

1.2 Electrolytes

Generally, *'Electrolytes'* are those substances which contain salts, acids, bases and also gases in a few cases. These electrolytes when dissolved in polar solvents such as water produce ions and form an electrically conducting solution i.e.

$$\text{Electrolyte} + \text{Polar Solvent} = \text{Electrolytic Solution}$$

An electrolyte in a solution is dilute one if it contains low concentration of ions whereas; it is concentrated if the concentration of ions therein, is high. Moreover, if the electrolytes are able to ionize completely upon dissolution and no neutral molecules are present in the solution then such electrolytes are termed as *'Strong Electrolytes'*. On the contrary, if only small fractions of electrolyte molecules are ionized when dissolved in the solvent and if some neutral molecules are still present in their solutions then such electrolytes are termed as *'Weak Electrolytes'*.

Basically, this electrolytic solution is electrically neutral. But when the electrodes are placed in such a solution and when the electrical potential (voltage) is applied to it, then electrolyte dissolved in the solution gets separated into cations and anions. These ions then get uniformly dispersed through the solvent and move towards the opposite directions within the solution to produce current. Here, the anions (negative ions) of the solution move towards the electrode that has a deficit of electrons whereas; the cations (positive ions) are drawn to the electrode that has an abundance of electrons. In this way the electrolyte dissociates into ions in the solution and conducts electricity. However, in terms of solid state ionics, electrolyte can be defined as an *'Ionic Conductor'* where; ions are dissolved in the host substance which is the one that conducts electricity through the movement of these ions. Hence, this electrolyte acts as a *'Medium'* for the transfer of charges (ions) between the electrodes [8].

1.3 Liquid Electrolytes

Traditional studies mainly dealt with *'Liquid Electrolytes'* which are basically the liquid solution of the electrolytes prepared in low molecular weight polar solvents, especially water. Basically, these electrolytes are conventional electrolyte materials formed by dissolution of the polymer electrolyte in a suitable solvent and are liquid at room temperature. These electrolytes comprise entirely of ions and hence, conduct ionically [9]. As these electrolytes were capable of yielding very high conductivity values (an essential requirement of the electrolyte for the application purposes) and possessed low vapour pressure, greater thermal and electrochemical stability, excellent contact area with high capacity electrodes as well as the accommodation capability of size changes of electrodes during charge and discharge cycles, they were given a major attention. On the contrary, these liquid electrolytes suffer from certain practically disadvantageous properties viz. strong reactivities of the battery with conventional liquid electrolytes in battery applications. Moreover, organic solvents of liquid electrolytes are highly inflammable in nature. All these factors may lead to the electrolytic leakage from the device and hence can cause highly hazardous accidents in a few cases. In addition to this, the devices in which the liquid electrolytes are employed are highly bulky. This makes the transport and carriage of such devices quite difficult. Hence, a need arose to prepare the electrolytes which not only provide the conductivity comparable to that shown by the liquid electrolytes but also hardly possess limiting properties as depicted by the liquid electrolytes. One such successful alternative towards liquid electrolyte is *'Solid Electrolyte'*.

1.4 Solid Electrolytes

Solid electrolytes also known as *'Superionic Conductors'* or *'Fast Ionic Conductors'* are those substances wherein, ions carry the current [10]. These solid electrolytes are usually divided into two types viz. inorganic solid electrolytes and polymer electrolytes and hence, are quite different from the organic liquid electrolytes. But as the inorganic solid electrolytes possess poor processability and difficulty to adjust with the change in volume of the battery electrode during the process of charging and discharging, polymer electrolytes are highly preferred over these electrolytes. In solid electrolytes, the single ion species generally (cations or anions) migrate into the solid lattice as charge carriers whereas; in liquid electrolytes, both anions and cations are simultaneously conducted. These reasons make solid electrolytes quite different from liquid electrolytes [11,12]. Also, these solid electrolytes possess various other advantageous properties which include excellent chemical and physical stability, appreciable performance as thin films of nearly 1 μm, conduction ability of majorly ions i.e. negligible contribution of electronic conduction, high conducting ability even in high temperature systems, stability under higher voltage which allow the use of electrode active materials with higher electric potential, easy handling and safety, high mechanical performance, low toxicity and wide potential window [13-17]. Moreover, the reduced packaging demands not only enhance the gravimetric energy density but also the volumetric energy density [18]. But to be the potential materials, these solid electrolytes should possess the requisite properties which include high ionic conductivity over the operating temperature range and a negligible electronic conductivity, good chemical stability with the electrodes over the working temperature range of the battery and good electrochemical stability within the operating potentials of the cell [19,20]. The general characteristics of the solid electrolyte for their use in various applications, especially in solid state batteries are as follows [3]:

- In order to undergo successful movement of large number of available mobile ions through the lattice, sufficient number of empty sites must be accessible.
- As miniaturization of the devices requires thin film structures, the processability of the electrolyte is highly essential.
- Transference (transport) number for ionic conduction should be appreciably close to unity with negligible or very less electronic transference (transport) number.
- Potential energies of empty and occupied sites should be similar with low activation energy barrier so that the ions can successfully jump between the neighbouring sites.
- Decomposition potential of the solid electrolyte must be lower than the Gibbs Free Energy of the anode as well as cathode which constitutes the open circuit voltage.
- Structure should possess solid (preferably 3D) framework, permeated by open channels.

- Solid electrolyte must depict high ionic conductivity in order to reduce the resistance polarization effects when applied to a solid state battery.
- Solid electrolyte should not only be thermodynamically stable and workable in wide range of temperatures but should also be physically and chemically compatible with anode and cathode.
- Framework ions which are usually anions should be highly polarizable.

These solid electrolytes are further classified into the following types.

1.4.1 Glass Electrolytes

Glass electrolytes are one of the integral components of all-solid-state devices and used generally for the conversion and storage of energy. These glasses are basically the fast ion or superionic conducting materials, usually formed by (i) melt cooling of mixtures of network formers which establish a non-periodic structure accommodating the cations and facilitate their movement via a system of interconnected sites that are most commonly furnished by negatively charged sulfide, oxide and fluoride ions and (ii) network modifiers that are the sources of highly mobile cations for electric transport. Here, the network formers are polyvalent main group element oxides or sulfides whereas; the network modifiers are usually alkaline oxides or sulphides [21]. The advantageous properties viz. high ionic conductivity, easy preparation technique, wide selection of composition and glass forming region, miniaturization in the form of thin films, absence of grain boundaries, isotropic properties, negligibly small electronic conductivity, inert to atmosphere, high stability, etc., of glass electrolytes, make them highly efficient for application purposes. The ionic conductivity of these glass electrolytes can be improved by considering two measures i.e. (i) addition of salt to enhance the number of mobile charge carriers (ions) and (ii) using mix glass formers in order to increase the free volume of the glass matrix. These glass formers can be bifurcated into two types i.e. typical glass formers e.g. SiO_2, P_2O_5, and B_2O_3 which form the glassy state naturally and conditional glass formers which are usually transition metal based oxide e.g. V_2O_5 and MoO_3 which can form a glassy state only in the presence of other compounds [22]. Some of the examples of glass electrolyte systems which are studied extensively include chalcogenide and borate, phosphate, vanadate, germanate and tellurite glass systems. Further, irradiation progresses the rate of formation and accumulation of induced defects in the glasses [23,24].

1.4.2 Ceramic Electrolytes

Another type of solid electrolytes is the *'Inorganic Ceramic Solid Electrolyte'*. Till date, several studies which included ionic conductivity, thermal characteristics, electrochemical stability and viscosity of these ceramic electrolytes are carried out at room temperature to test their applicability in various devices. Large electrochemical stability window, good thermal stability, absence of leakage, high energy density and high resistance to shocks and vibrations make these ceramic electrolytes an important class of materials for their applications in electrochemical devices such as batteries [25,26]. Basically, ionic conduction in some of these compounds is appreciably high even at relatively low temperatures which make them highly suitable to be used in battery applications viz. in Li^+ batteries working at low temperatures, in electrochemical cells having gaseous/liquid reactants and in separators between solid-reactant/liquid-electrolyte composite electrodes where different liquid electrolytes are needed at each electrode [27]. However, some of these concepts are hardly tested.

1.4.3 Polymer Electrolytes

Polymer electrolytes are another class of electrolytes after glass and ceramic electrolytes which are ionically conducting in nature [28]. These electrolytes are considered to be one of the most efficient classes of electrolytes owing to their advantageous properties which include leak-proof and shock-proof tendency, versatility in shape, lightness, good adherence to electrodes, high compliance, ability of fabricating into thin films owing to their flexible nature, easy processing, etc. [29,30]. Amorphous and semicrystalline polymers are majorly used in the preparation of these polymer electrolytes.

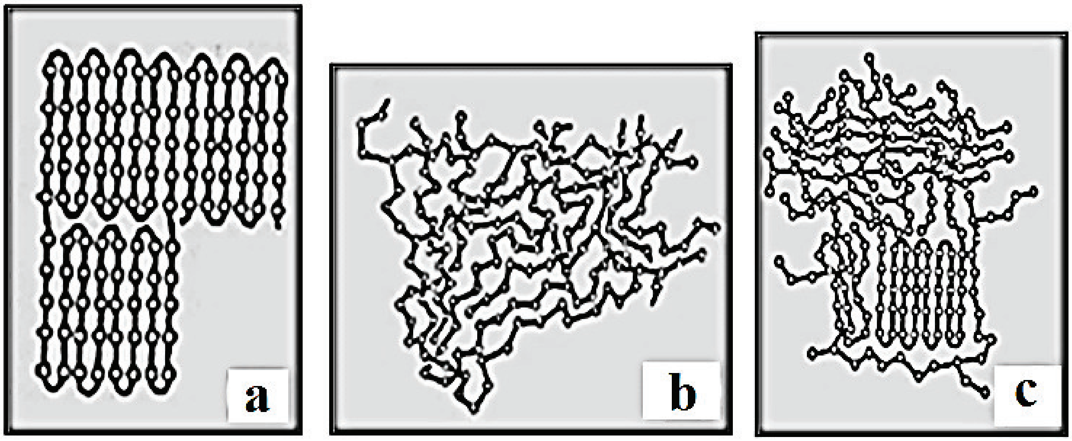

Fig. 1.1 (a) Crystalline polymer, (b) Amorphous polymer and (c) Semi-Crystalline polymer

Hence, certain polymer electrolytes are made up of two phases where one is the amorphous phase and the other is the crystalline phase. Here, the crystalline phase of the polymer acts as the mechanical support for the polymer electrolyte whereas; the amorphous phase assists higher conduction of ions [31]. **Berthier et al.** [32] also supports this concept that the ionic conductivity in polymer electrolytes is associated with amorphous phases of the polymeric specimens. The first ionically conducting polymer electrolyte was invented by Sheffield Polymer Chemist **P. V. Wright** in 1975 [33,34] wherein complexation of polyethylene oxide (PEO) polymer with sodium and potassium salts was studied. But this concept was firstly initiated by **Fenton et al.** [35,36] in 1973. These polymer electrolytes are divided into three major categories where the first is the one based on the combination of lithium salts and high molecular weight PEO, the second one is based on modified PEO and the new polymers and the third one with considerable dimensional stability as well as enhanced room temperature conductivity [37]. Usually, the ionic conductivity of the polymer electrolytes are influenced by two major factors which include (i) ion-pair formation and (ii) simultaneous motion of anions and cations [38,39]. But the host polymer participating in the preparation of the polymer electrolytes should satisfy the following requisites [40-43]:

- Host polymer should be capable of providing a connected polar domain as the path of conduction.
- Interactions of the host polymer with the cations should not be very strong in order to avoid the ion trapping.
- The barriers for the bond rotation should be low for the easy segmental motion of polymer chain.
- Components should possess the polar domains.
- Compatibility amongst the host polymer as well as the salt doped must be strong.
- The distance between the coordinating centres should be suitable as the formation of multiple intra polymer ion bonds seem to be quite important.
- Host polymers must contain a Lewis base or donor group (an atom with at least one lone pair of electron) to coordinate a bond with cations and hence, promote dissolution of salt.
- Lewis base of the polymer and the cation must be liable to allow the mobility of ion.

1.4.3.1 ***Polyelectrolytes***

A *'Polyelectrolyte Molecule'* is a macromolecule wherein, substantial portion of the constitutional units have ionic groups and/or wherein, the ionisable groups are present. Based on this concept, *'Polyelectrolytes'* can be defined as the group of polymers that carry either negatively or positively charged ionisable functional groups on their backbones which can dissociate into ions in a solution. The polyelectrolytes can be said to be those polymer chains whose every repeat unit consists of electrolyte group. These polyelectrolytes are also at times known as *'Polysalts'* as their properties are similar to both salt based electrolytes and high molecular weight polymers. The solutions of these polyelectrolytes are electrically conductive like salts and often viscous like polymers. Some of such polyelectrolytes are made up of polymers that can be soluble in water. However, almost all the polyelectrolytes are able to dissolve in polar solvents [44-46]. When the polymers are allowed to dissolve in the polar solvents such as water, these ionisable functional groups (small counter-ions) can dissociate in the solvents and leave charges or charged macro-ions on the polymer chains thus, making the polymer chains charged and releasing counter-ions in the solution. However, all the counter-ions do not get dissociated from the electrolyte which makes this polyelectrolyte quite different from the simple electrolytes. These counter-ions which are solvated by the solvent media (usually water) possessing high dielectric constant, are free to move or migrate within the matrix formed by chain foldings. However, the removal of the next ion gets difficult with the increasing magnitude of the charge on the chain. This phenomenon is called *'Counter-Ion Condensation'* owing to which the polyelectrolyte differs from the uncharged polymer.

1.4.3.2 ***Rubbery Polymer Electrolytes***

Rubbery polymer electrolytes were firstly discovered by **Angell & co-workers** [47] in 1993. These materials are ionically conducting materials wherein, large quantities of lithium salts are mixed with the small quantities of polymers such as polypropylene oxide (PPO) and polyethylene oxide (PEO). By considering this idea, many rubbery polymer electrolytes were then prepared by dissolving large amount of salt in a relatively small amount of high molecular weight polymer. As these polymer electrolytes contain large content of salt with a small amount of polymers the thus, formed system can be named as *'Polymer-in-Salt'* system. Matrix of such a rubbery polymer electrolyte is shown in Fig. 1.2. In order to remain rubbery polymer electrolytes at room temperatures, these materials need to have low glass transition temperature (T_g) which in turn preserves appreciably high ionic conductivities and electrochemical stability. Hence, 'T_g' values must be below ambient temperatures in order to provide and maintain the rubbery state of a polymer electrolyte. Generally, the rubbery materials show low 'T_g' values in their optimal form. However, the salt concentrations as well as temperatures can affect these ‘T_g’ values. In these types of solid state electrolyte materials, the movement of ions takes place in a fashion quite different from that taking place in common polymer electrolytes.

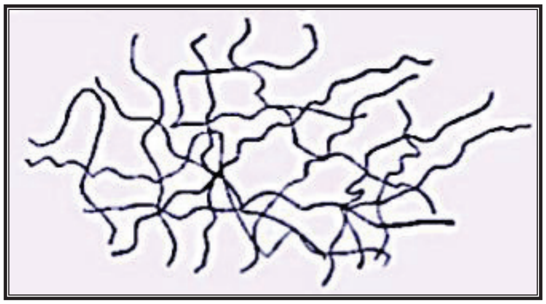

Fig. 1.2 Diagram of rubbery network structure model

These solvent free rubbery electrolyte materials are successfully applied in the solid state lithium ion secondary batteries as thin film separators as they can depict quite high conductivity at ambient temperatures [47-50].

1.4.3.3 ***Gel Polymer Electrolytes***

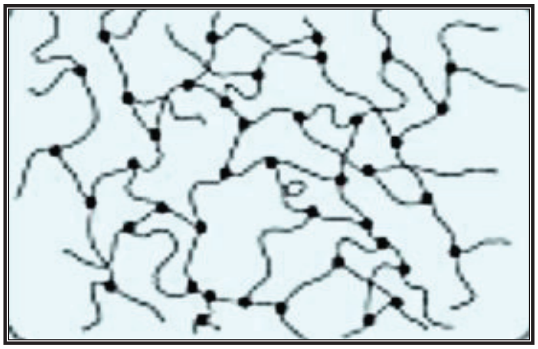

Fig. 1.3 Diagram of conventional gel network structure model

Gel polymer electrolytes (GPEs) are usually said to be a class of proton conducting materials that are basically the polymer matrices swollen with a solution that contains the conducting species which are dissolved in an appropriate solvent having ions. These GPEs which work successfully as an alternative to liquid electrolytes are neither perfectly liquid nor perfectly solid. Rather, they possess both, diffusive character of liquids and cohesive properties of solids, highly porous in nature and are filled with liquid electrolytes [51-56]. The Fig. 1.3 shows the diagram of conventional gel network structure model [57].

Basically, when salts and liquid plasticizers are added into a polymer matrix, a stable and porous gel is formed that possesses the structure of the polymer host [58,59]. Such a technique of preparation, based on which a GPE is formed is known as *'Gelation Theory'* [60]. Here, the polymer matrix of the GPEs retains the salt within itself and further provides the ions for the process of conduction. The pores which retain the liquid electrolyte should usually range from micrometer size to nanometer size [27,61]. But these GPEs offer low ionic motion as compared to the liquid electrolytes due to the intermolecular interactions between polymer chains and ions, which in turn increase the resistance to ionic conduction. Inspite of these limitations GPEs show considerably high conductivity. In addition to this, high mechanical stability, good interfacial compatibility, wide chemical and dimensional stability, electrochemical and thermal stability are also some of the favourable properties of these GPEs [51,62-68]. However, the most advantageous properties of these GPEs is that the liquid is trapped in the polymer host which suppresses the solvent volatilization. This in turn prevents the leakage of the liquid electrolyte [12,69]. Moreover, as suitable polymer hosts entrap the liquid, the polymer matrix favours the mechanical stability and the salt provides free-mobile ions which further take part in the conduction process. Here, the plasticizing solvent helps in solvating the salt [60].

1.4.3.4 ***Solid Polymer Electrolytes***

Solid polymer electrolytes (SPEs) are considered since long and applied successfully in various devices. These SPEs are basically polymeric thin films which consist of ionic salts dissolved in an appropriate solvent to yield appreciable ionic conductivity at room temperatures where the host polymer possesses a liquid like feature [70]. However, these SPEs are 'solvent-free' electrolytes consisting of both crystalline as well as amorphous phases as shown in Fig. 1.4 [71,72].

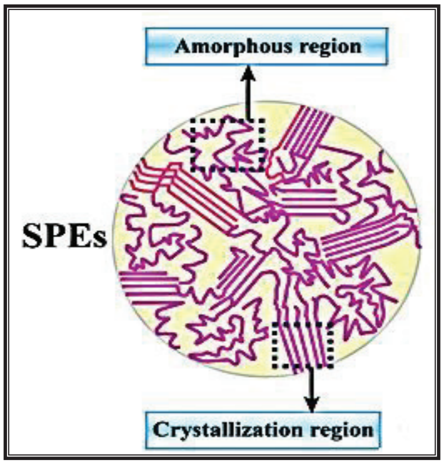

Fig. 1.4 Diagram of solid polymer electrolyte (SPE) network structure model

These SPEs are polymer ion-conducting single phase based polymer-salt complexes which not only depict high ionic conductivity but also possess appreciable mechanical strength [73,74]. The major advantage of these electrolytes is that they mainly serve as a medium for conduction of ions between the electrodes in the battery application and also act as a separator to prevent the electrodes by making a physical contact [70,75].

1.4.3.5 ***Plasticized Polymer Electrolytes***

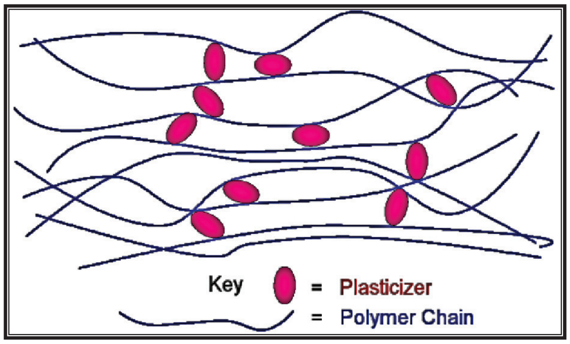

Fig. 1.5 Interaction of plasticizer with host polymeric chains in plasticized polymer electrolyte

The addition of non-volatile and aprotic liquids of low molecular weight, low vapour pressure and high dielectric constant termed as *'Plasticizers'* in the polymer electrolytes lead to the formation of a new class of polymer electrolytes termed as *'Plasticized Polymer Electrolyte'*. Plasticizers are mainly used to lower the glass transition temperature and degree of crystallinity of the polymers as well as to decrease the ion association process by enhancing the relative permittivity of the polymeric system. All these factors in turn improve the salt solvating power, enhance flexibility of the polymeric chains and increase the chain mobility. Such a method of addition of plasticizer in polymer electrolytes is termed as *'Plasticization'*.

1.4.3.6 ***Composite/Nano-Composite Polymer Electrolytes***

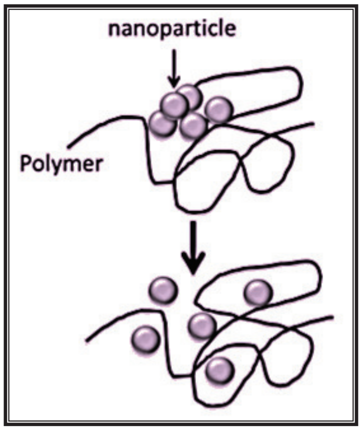

Fig. 1.6 Dispersion of filler particles in the polymer matrix

Solid blends usually consist of 2-phases wherein the first phase is an ion conducting host matrix of a conventional solid electrolyte or ion conducting solids such as salts and the second phase is composed of chemically inert insoluble materials also called as *'Fillers' or 'Extenders'*. These class of electrolytes are termed as *'Composite Electrolytes'* or *'Heterogeneously Doped Materials'* or *'Dispersed Solid Electrolytes'*. In case, the first phase is of polymer host matrix, then the electrolytes are termed as '*Composite Polymer Electrolytes (CPEs)*'. In this case, filler particles are usually of microsize. On the other hand, if the second phase dispersoid has fine size of particles, especially of nano-size (dimensions ~ 1-100 nm), then the 2-phase solid electrolytes are known as *'Nanocomposite Electrolytes'*. But these electrolytes are termed as '*Nanocomposite Polymer Electrolytes'* if first phase is of polymer host matrix [44,76]. This class of polymer electrolytes wherein; the ceramic/inorganic or high molecular weight/organic filler particles are dispersed in polymer matrix to enhance the electrical conductivity and to improve mechanical, thermal and electrochemical stability of the polymer film is diagrammatically shown in Fig. 1.6 [77-80].

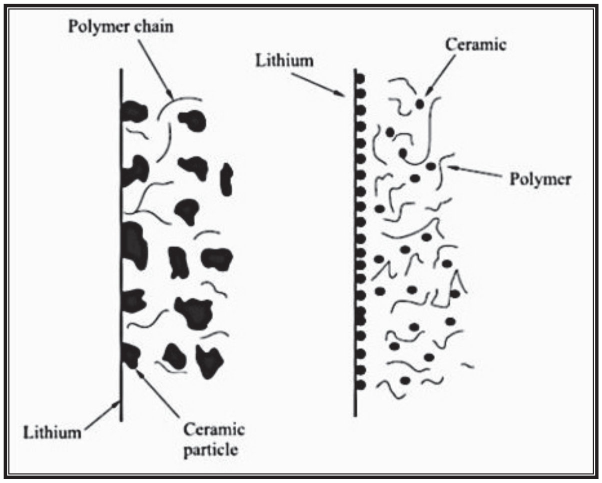

Fig. 1.7 Incorporation of bigger and smaller sized inert filler particles in a polymer host

Usually, the fillers with smaller particle size, generally of nano-size are incorporated in the polymer host(s) as such filler particles with smaller size reduce crystallinity of the polymer matrix, decrease the internal resistance and hence, improve ionic transport number as well as ionic conductivity of the host polymer as visible from Fig. 1.7 [70]. Usually, the dispersoids or nano-fillers used in the preparation of such nanocomposites include graphite powder, zeolites, flyash, mica, clay, ZnO, TiO_2, $CaCO_3$, SiO_2, Fe_2O_3, Al_2O_3, carbon black, etc. Basically, these filler particles also reduce glass transition temperature of the host polymer(s) thus, promoting segmental motion of the polymeric backbone and generating free volume in polymeric matrix which facilitates easy migration of ions through voids hence, created as seen from the Fig. 1.7 [27,70,77-83].

1.4.3.7 ***Plasticized Composite/Nano-Composite Polymer Electrolytes***

Addition of either the plasticizer or nano-filler, at times leads to some deterioration in various electrolytic properties of the polymer electrolytes. Hence, there is a need to prepare such a polymer electrolyte system which not only possesses the beneficial properties of the plasticizers and fillers to enhance the electrolytic properties, but also filters out all their individual limiting properties. Such a system can be successfully prepared by incorporating filler/nano-filler along with plasticizer therein. This system thus, formed can be termed as *'Plasticized Composite Polymer Electrolyte'* or *'Plasticized Nano-Composite Polymer Electrolyte'* depending upon the particle size of the incorporated fillers.

1.4.3.8 ***Blend Polymer Electrolytes***

Blending or mixing of two or more polymers is a method to obtain a new electrolyte system which contains the desired properties of each of the host polymers. In this way, the structural and physical properties of the individual host polymers can be modified to obtain a blend polymer electrolyte system having the properties which are more suitable than the individual polymers. Hence, this process of blending of polymers easily prepares a new polymeric material which not only controls but alters the structural and physical properties within the compositional regime as per requirement.

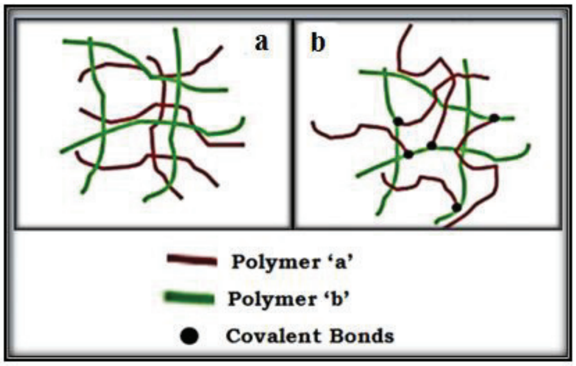

Fig. 1.8 (a) Physical interaction amongst two polymers in a blend polymer electrolyte
(b) Chemical interaction amongst two polymers in a blend polymer electrolyte

1.5 Applications of Polymer Electrolytes

As an electrolyte enables fast ionic movement in solid state, they play highly important role in the development of solid state devices [79]. Out of various solid state electrolytes which show tremendous technological scopes over wide spectrum of non-battery and battery applications, polymer electrolytes are often chosen to be employed in the fabrication of miniaturized electrochemical devices as they can be easily moulded into flexible thin films with low area.

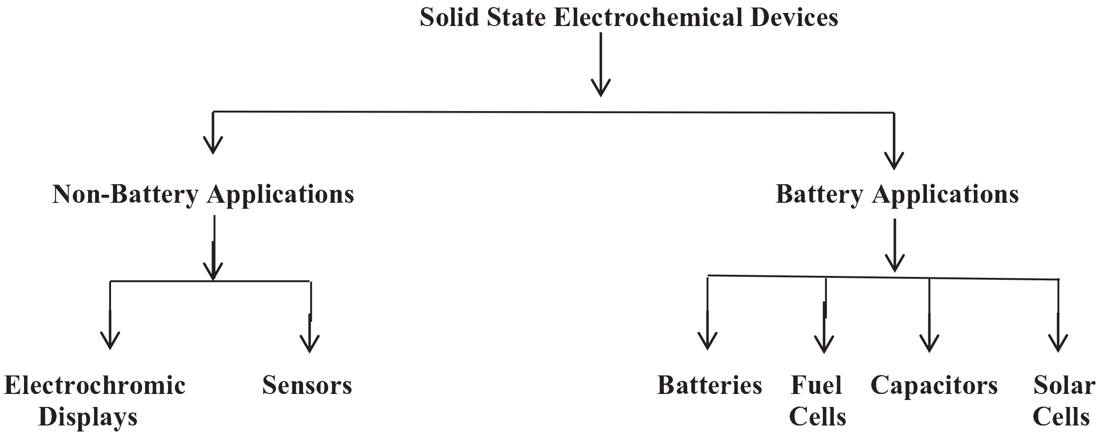

Fig. 1.9 Flow chart showing the subdivision of solid state electrochemical devices in various non-battery and battery applications

Basically, these electrochemical devices are those which are capable of storing and/or converting energy from one form to another and are mainly composed of two major components which include electrolyte and electrodes. The performance of each of these components decides the overall performance of these devices [84]. Some of these solid state electrochemical devices are subdivided into various non-battery and battery applications as seen from the flow chart depicted in Fig. 1.9 and explained briefly as follows.

1.5.1 Non-Battery Applications

Polymer electrolytes are highly applicable in certain non-battery applications especially, in sensors and electrochromic display devices. Brief information about these devices is presented as follows.

1.5.1.1 Sensors

Sensors are basically fast ion conductors used as sensing devices in industrial sectors. These sensors which work on the electrochemical principle, firstly sense the changes taking place in the chemical or physical quantities of a material under consideration and later convert these changes into electrical signals. These sensors majorly sense humidity, various ions and gases such as CO_x, NO_x, SO_x, etc., concentration levels of various hazardous and toxic gases, pollutants and chemicals present in different systems as well as physical changes such as strain, pressure, temperature, humidity, etc. Polymer electrolytes such as gel polymer electrolytes, polyelectrolytes as well as the solvent free solid polymer electrolytes have gained considerable importance to be used in sensors as they not only possess high ionic conductivity but are also able to undergo reversible changes when they are exposed to an external stimulus such as ionic or chemical gradient, temperature, etc.

1.5.1.2 Electrochromic Display Devices

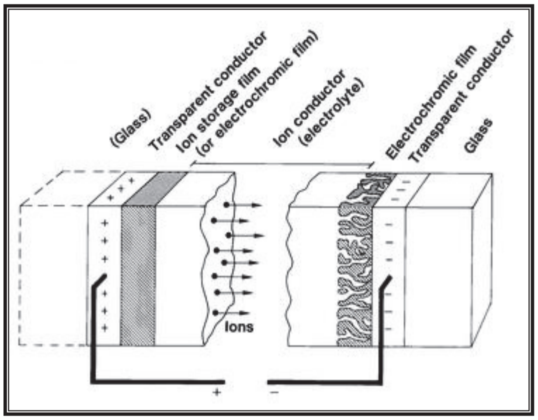

Fig. 1.10 Electrochromic display device: a multilayer system

Electrochromic display devices (ECDs) are multilayered systems as shown in Fig. 1.10. Such electrochromic display devices consist of three basic layers viz. electrochromic material (ECM), conducting glass plate usually made up of indium tin oxide (ITO) and ion conducting polymer electrolyte, which play a major role in construction of these devices. When electric field is applied, at least one these components undergoes colour change [85,86]. Basically, here, the active component is transparent in its unperturbed state. But when electric field is applied, it undergoes a reversible colour change upon oxidation or reduction. Thus, in order to counterbalance the electrical charge, either positive or negative ions originating from the 'ion storage layer' of the device must be introduced into the active component. These ions usually migrate through the electrolyte viz. polymer electrolyte such as gel polymer electrolyte, hybrid polymer electrolyte and solid polymer electrolyte. The major purpose of selecting polymer electrolytes for the application in electrochromic display devices is the easy processability into low thickness films having low Ohmic losses [87]. Thus, the basic principle on which these devices run is the capability of changing the optical properties (usually colour) of the electrochromic material upon application of the electric field.

Basically, when a small dc voltage or current is applied to the assembly; a small shifting of absorption and emission spectra of certain dyes takes place by hundreds of angstroms giving rise to *'Electrochromism'* which is closely related to the electronic structure of oxides. This phenomenon was firstly discussed for tungsten oxide. Some of the transition metal oxides which are extensively used in the electrochromic display devices are WO_3, MO_3 and IrO_3 along with the organic materials such as porphine compounds (tetraphenyl prophine vanadium oxide) and polymer systems such as $LiClO_4$ + (oxypropylene + oxyethylene) copolymer. Films based on these materials proved to be highly viable for electrochromic display devices [88-90].

1.5.2 Battery Applications

Polymer electrolytes are also used in various battery applications such as in fuel cells, solar cells, electrochemical capacitors & supercapacitors and most importantly in solid state batteries. All these devices are described briefly in the following section.

1.5.2.1 Fuel Cells

In the fabrication of a fuel cell, cathode and anode sandwiches the solid or liquid electrolyte that is capable of conducting ions from one electrode to other. The anodic and cathodic catalyst layer facilitates and speeds up the electrochemical redox reaction. These anode and cathode consist of porous gas diffusion layers that are usually made of materials such as porous graphite thin layers having high electron conductivity. For low temperature fuel cell the most common catalyst used is platinum whereas; for high temperature fuel cell nickel is the catalyst which is commonly used. The devices ultimately combine the fuel and air (mainly oxygen) or oxidant and allow them to react electrochemically when they come into contact through an ion conducting material or a porous membrane (electrolyte) which separates them.

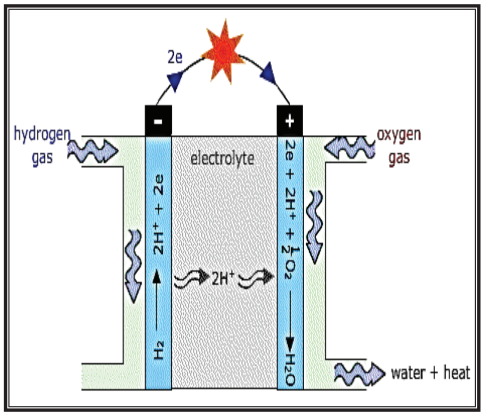

Fig. 1.11 H_2/O_2 fuel cell configuration

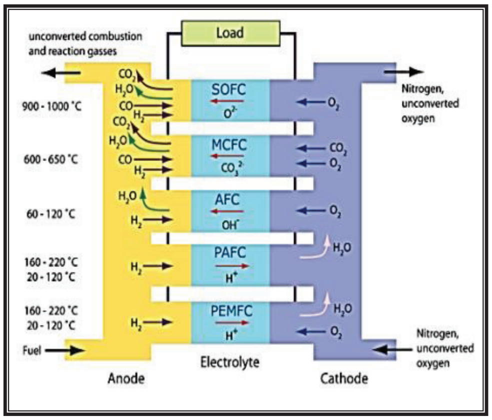

Fig. 1.12 SOFC, MCFC, AFC, PAFC & PEMFC configurations

In this way, transfer of electrons and ions takes place across the electrolyte from anode to cathode. In case, an external load is attached to this arrangement, a complete circuit is formed and a voltage is generated from the flow of electric current. Hence, these devices are capable of supplying continuous electrical voltage and current. However, for doing so a fuel cell needs to continuously supply fuel and air from outside to the electrodes/electrolyte. Hence, as long as active materials such as fuel and oxidants are supplied to the electrodes/electrolyte these fuel cells ought to keep on generating electric energy and power.

1.5.2.2 __Solar Cells__

One of the mostly used solar cells is *'Photoelectrochemical Solar Cell (PESC)'* as shown in Fig. 1.13. In case of this solar cell, the light energy is harnessed and converted into electrical or chemical energy by the means of electrochemical reactions occurring at the interface. The compositions of most of these PESCs include the semiconductor-electrolyte interface with an appropriate redox couple in a solution. In case of n-type semiconductor, the photons are absorbed and the electron-hole pairs are created when light of the energy > band gap strikes the interface. However, the recombination of some of these electron-hole pairs takes place in the bulk which emits the photons and dissipates their energy thermally thus, creating phonons. This electron can now flow in the external circuit. But when it is dark (absence of light), the concentration of holes is very low. Hence, hardly any reaction in the species is possible to occur in the solution owing to which negligible or at times no photocurrent is produced [91].

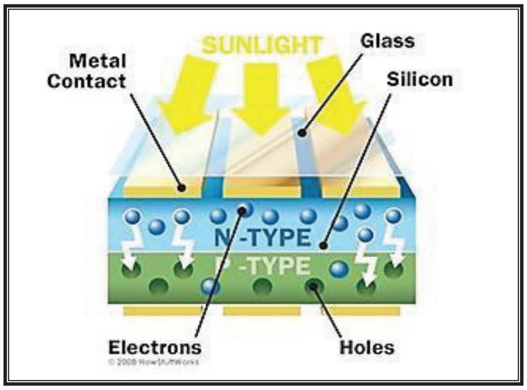

Fig. 1.13 Photoelectrochemical solar cell

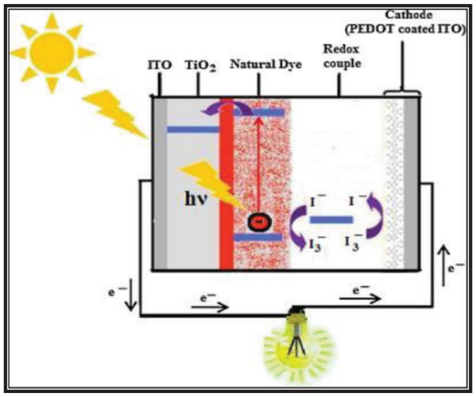

Fig. 1.14 Dye sensitized solar cell

Another most commonly used solar cell is the *'Dye Sensitized Solar Cell (DSSC)'* as shown in Fig. 1.14 which came into existence as a result of efforts done to understand the process of photosynthesis [92-97]. The generation of electricity by illuminating an organic dye was recognized for the first time in 1968 [98]. In this assembly of DSSC, TiO_2 nanoparticles are coated with a dye to absorb the sunlight. The assembly is then covered by a conducting glass, an electrolyte solution usually acetonitrile that carries I^-/I_3^- redox couple and a secondary platinum electrode. This assembly generates the ground state of dye after photoexcitation. Basically, the dye absorbs the photo energy and results in the excitation of electrons present in it. These excited electrons firstly get injected into the TiO_2 nanoparticles, then diffuse towards the glass electrodes and finally flow to the external circuit. After passing through external circuit, these electrons are firstly received by the platinum electrode and then by the iodine molecules present in the electrolyte [99].

1.5.2.3 ***Electrochemical Capacitors & Supercapacitors***

'Capacitors' are basically active circuit elements which are used to store electrical energy in the electrical circuits. Hence, these capacitors can be used as the power sources similar to the fuel cells. Various components forming basic capacitor are shown in Fig. 1.15. Usually, capacitors with aqueous electrolytes have low break-down voltage as well as very low resistance whereas; it is reverse for the capacitors with organic electrolytes. Although capacitors can store very little energy, they can produce high power output but for very short periods and have exceptionally long cycle-lives. However, these capacitors are highly emerging energy storage devices wherein; polymer electrolytes are applied successfully.

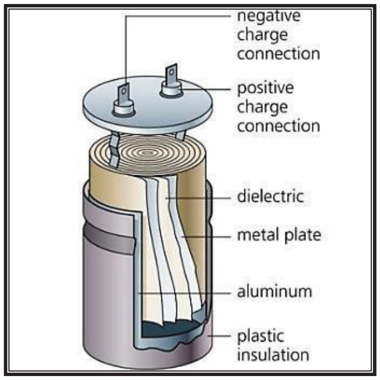

Fig. 1.15 Diagram of a basic capacitor

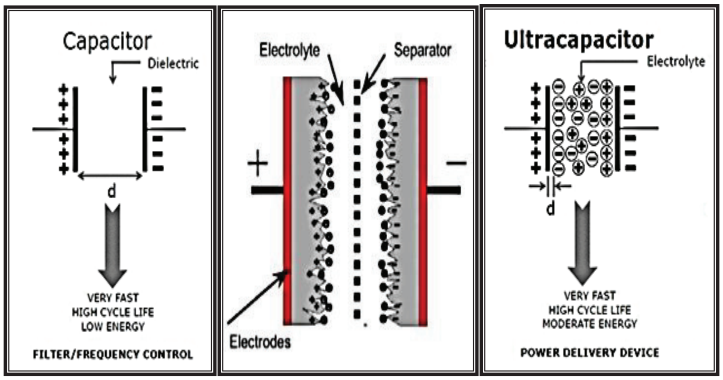

Fig. 1.16 Diagrams showing conventional capacitor, supercapacitor and ultracapacitor

♣ **Conventional Capacitor**

The conventional 'electrostatic' capacitor as shown in Fig. 1.16 is the one wherein, an insulator (traditional dielectric) separates the two conductors (plates). The device firstly separates the positive and negative electrostatic charges. These equal but opposite charges are further carried by the plates and lead to the storage of energy [51,100]. However, this conventional capacitor depicts a very low value of capacitance say of ~ μF to pF. Hence, in order to store high amount of energy it became highly essential to prepare capacitors that possessed high capacitance value. The new versions of such enhanced capacitors include supercapacitors and ultracapacitors.

♣ Supercapacitor

The electrochemical devices that are able to store charge electrostatically by exploiting the reversible adsorption of ions carried by the electrolyte onto the electrode materials that are characterized by a high electrochemical stability and a wide specific surface area are termed as *'Supercapacitors'* [87,100,101] or as *'Electric Double-Layer Capacitors (ELDCs)'* as seen from Fig. 1.16 [102]. These supercapacitors physically store charge by forming an electric double-layer at the interfaces between the electrode and the electrolyte [103,104] and possess 10^3 to 10^5 times higher capacity and also high power than that of traditional capacitors. Hence, these supercapacitors show great technological importance as the alternate/auxiliary power sources for operating the electronic circuits, medical equipments, load levelling, peak power sharing etc. The power density of these supercapacitors is 10 to 100 times higher than the conventional batteries however; the energy density is only 10% approximately.

♣ Ultracapacitor

In case of ultracapacitor as shown in Fig. 1.16, the energy is stored by ionic capacitance as well as by the surface (near-surface) redox processes occurring during the charging and discharging. The amount of stored energy is enhanced by the latter Faradaic reactions. But they are completely reversible for a long cycle-life as they are confined to the surface layers. Both supercapacitors as well as ultracapacitors ideally meet sudden transient power demands. All these devices are evaluated for various applications which include electric/hybrid electric vehicles and in the situations where transient, high power pulses are required. This requirement was already satisfied at around 1990 by applying solid state ionic materials.

These capacitors are further subdivided into three categories based on the electrodes which act as controlling elements for the storage capacity and they are Hybrid capacitor, Pseudo capacitor and Double Layer capacitor.

1.5.2.4 ***Solid State Batteries***

The term *'Battery'*, defined as an electrochemical device which stores electricity by converting chemical energy to electrical energy, is basically a multi-cell array particularly of primary cells. It usually also encompasses to *'Single Cell'*, in a special case of primary systems. However, this device is unable to store electricity directly as is possible in electrolytic capacitors and superconducting coils. The usual configuration of such a battery is *'Anode //Electrolyte //Cathode'* where the electrolyte separates the two electrodes i.e. anode and cathode [105]. There are typically two types of batteries out of which one is the conventional battery consisting of electrolyte in the solution form and the other one is the solid state battery wherein the electrolyte is in the solid form as shown in Fig. 1.17.

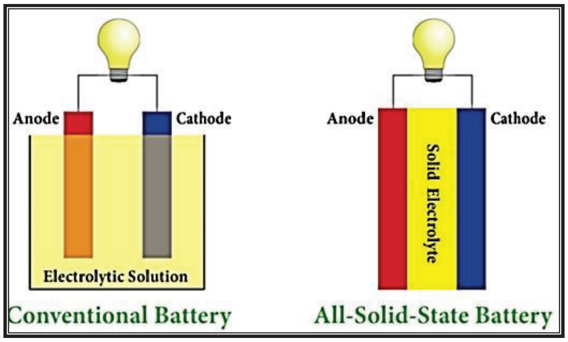

Fig. 1.17 Figure showing conventional battery with electrolytic solution and solid state battery with solid electrolyte

The use of polymer electrolytes, especially solid polymer electrolytes became highly prominent since **Armand** [106,107] applied it in the lithium ion battery fabrication in 1978. Here, the electrolytes are basically the electronic insulators which act as separators between two active electrodes and conduct ions between these electrodes. Such solid state batteries are usually applied in electronic watches, automatic exposure cameras, pacemakers, etc. These practical solid state batteries are used as energy sources and power sources and can be widely classified as *'Primary'* and *'Secondary'* batteries depending upon their single-use or multiple-use, respectively. Both these battery types are explained briefly as follows:

♣ Primary Battery

Primary battery is the one which undergoes a single discharge by utilizing chemical energy only once. Owing to this reason, the primary batteries are also termed as *'Non-Rechargeable'* batteries. The life of a primary battery can be usually defined by the end-point voltage on the steep part of the discharge curve. As the battery is primary, it can be discarded once it is discharged completely.

♣ Secondary Battery

Secondary battery is the one which can be recharged and used again and again as in this case, the charging process involves the uptake of electricity and conversion of the chemicals back to their original forms. Hence, these chemicals are available again for the next discharge even if they are once used. This phenomenon makes the secondary battery to be also termed as *'Rechargeable'* battery.

1.6 Present Research Work

Polyvinyl alcohol (PVA) which is the first artificial polymer used worldwide during the first half of the 20th century, is basically made from polyvinyl acetate via the process of hydrolysis. PVA is a semicrystalline, biodegradable material possessing excellent oxygen barrier and mechanical properties, high chemical resistance, water and aqueous solubility, thermal stability upto a large temperature variation and biocompatibility [108-114]. One of the most important properties of PVA is the presence of a large number of pendant hydroxyl (-OH) groups which, along with carbon chain backbone, are attached to the methane carbons and provide the structural formula as '$—(CH_2–CH–OH)_n—$' [95,115,116]. Thus, the presence of these (-OH) groups can act as a source of intermolecular and intramolecular hydrogen bonds. These (-OH) groups make PVA highly compatible in interacting with organic and inorganic materials. PVA also possesses high polarity and hydrophilic properties which enhance the mechanical properties of the polymeric film. Moreover, it is widely blended with various compounds such as biopolymers, natural polymers and other polymers possessing hydrophilic properties thus, aiding in the formation of the polymeric blends [95,108,111,116-119]. Owing to all these properties, PVA is selected as a host polymer in the present work. However, as it is highly crystalline, rigid and viscous in nature, possessing a high melting point (219 °C) and stiff chained structure, it is not very compatible for electrolyte formation. Hence, PVA based electrolytes usually show very low ionic conductivity of 2.5×10^{-10} S cm^{-1} [120]. In order to enhance such electrolytic properties, PVA polymer has to be blended with such a polymer which possesses flexible chains, low melting points and low glass transition temperatures [121-124]. One such a suitable polymer possessing all these requisite properties is polyethylene oxide (PEO) and hence, is chosen to be blended with PVA in the present work. Moreover, (-OH) groups of PVA polymer makes it a good source of hydrogen bonding and hence, assists in the formation of polymeric blends with PEO polymer [204].

PEO is basically highly polar polymer possessing linear chains of ethylene oxide with general formula '$—(CH_2–CH_2–O)_n—$', where a series of polar group '— O —' exists in a sequential oxy-ethylene group i.e. $—(CH_2–CH_2–O)—$ in the chemical structure. These ether coordination sites make PEO a highly polar polymer [125,126]. PEO chains adopt the helical conformation consisting of C-O, C-C and C-H bonds where, all the C-O bonds are in trans and the C-C bonds are either in gauche or gauche-minus configuration. Basically, each seven $—(CH_2–CH_2–O)—$ groups get repeated in two turns of the helix thus, making the structure of PEO polymeric chains helical in nature. When salt is added in the PEO based salt complexes, the PEO chains get wrapped around the cation, where each cation viz. lithium ion gets coordinated with three ether oxygen atoms from the polymer chain. In this geometry, cations are able to be located in each turn of the helix or tunnels where these cations are coordinated with three ether oxygen atoms. However, the basic structure of the host remains intact for all the sizes of anions. PEO is capable of complexing with various salts even at higher salt concentrations as its chemical structure can easily associate with the metal structure. Owing to this reason, PEO is able to play as a host to various metal-salt systems for wide range of salt concentrations where the salts constitute different mobile species such as H^+, Ag^+, Li^+, Na^+, K^+, Mg^+, etc. and hence, PEO is used as one of the most appropriate base material or host polymer. Further, owing to the presence of C-O, C-C and C-H bonds, PEO possesses good chemical and electrochemical stability and hence, its reactivity slows down. In this way, PEO is not only able to efficiently coordinate with the metal ions owing to the finest distance and alignments of ether oxygen atoms in the polymer chains but also facilitates the segmental motion of polymeric chains owing to the presence of the ether linkages with oxygen atoms at a favourable inter-atomic separation in the structure of PEO. In the PEO based polymer electrolytes, the transient crosslinks between cation and ether oxygen of PEO facilitates the salt dissociation thus, promoting facile ion conduction [41,61,127-136]. Also, low lattice energy, low glass transition temperature, low melting temperature, high solvating power for alkali metal salts, ease of forming flexible polymeric films and good chemical and electrochemical stability make PEO as a suitable host polymer for blending with PVA in the present study.

In the present work, one of the salts used as a dopant in the preparation of the PVA-PEO blend electrolyte films is silver nitrate ($AgNO_3$) as this transition metal ion conducting salt possesses several advantageous factors which include its non-toxic and environment friendly nature, non-flammability and capability of forming good coordination amongst polar groups [3]. But these Ag^+ conducting PVA-PEO blends often get oxidized with passing time, owing to the presence of ‘silver’ component in them. This limitation is overcome by replacing $AgNO_3$ salt by one of the most preferred super-acid $LiCF_3SO_3$ salt also known as lithium trifluoromethansulfonate or lithium triflate, therein. This is one of the most common salts used in the preparation of the polymer electrolytes [42]. To further enhance electrolytic properties of the present blend specimens, these specimens are plasticized using selective polyethylene glycol (PEG) and ethylene carbonate (EC) plasticizers. Here, PEG is a low molecular weight plasticizer which contains hydroxyl end groups and hence, leads to increase in free volume of blend matrix thus, reducing the degree of crystallinity therein [31,137,138]. Another plasticizer, EC is a highly polar plasticizer with low vapour pressure and high dielectric constant of 89.8 and hence, is quite compatible with various host polymers. Moreover, owing to appreciable polarity and high dielectric constant, EC can easily ionize the salts especially, lithium salt. This leads to the enhancement in the amorphous phases in the polymer matrix thus, increasing its flexibility and also the release of the mobile charge carriers due to ion dissolution effect. These EC based electrolytes can be successfully employed in the batteries specially lithium ion batteries owing to their large stability windows over wide operating potentials [139-143]. However, use of plasticizer tends to reduce the mechanical strength of the electrolytes. Hence, to overcome such a difficulty, the nano-fillers are incorporated in the polymer electrolytes which not only improve the mechanical strength of electrolytic films but also enhance the ionic conductivity therein.

In the present work, the inert and insulating nano-filler particles of aluminium oxide, also known as alumina (Al_2O_3) are chosen and uniformly dispersed in the blend polymer electrolyte specimens. These nano-particles are basically hydrophilic in nature due to the presence of hydroxyl groups on their surface. One of the most important advantageous properties of these nano particles is that they are highly cost effective which makes them a widely used material in materials science [129]. Moreover, high dielectric constant of Al_2O_3

ceramic filler aid in capturing anions in the electrolytes, especially in the liquid electrolytes and transfer the cations without coordinating with the anions [144]. However, instead of micron sized, the nano sized Al_2O_3 filler particles are added in the electrolytic specimens as these nano-sized Al_2O_3 filler particles not only reduces the crystallinity of polymer host(s) but also reduces its internal resistance thus, improving the ionic transport number and ionic conductivity of the host polymer [70]. Al_2O_3 filler particles also enhance the mechanical properties as well as interfacial stability of the electrolytes. In addition to excellent size and shape gaining capability and fine grain particles, Al_2O_3 also possesses significant strength, purity in the range from 94 % and easy metallizable composition which makes it highly demanding in high temperature applications. Basically, strong ionic/interatomic bonding gives rise to the desirable material characteristics and existence of several crystalline phases which revert the most stable hexagonal alpha phase at elevated temperatures. Al_2O_3 nano-filler can also provide large surface contact area along with its branched primary structure which in turn enhances the volume fraction of amorphous proportion in the polymeric systems thus, enhancing ionic conductivity. This filler further forms the native surface and gives rise to flaw by reducing the fracture strength in the polymer chains which makes it capable of tailoring the surface functionalities [34,129]. Considering all this discussion, in the present work, the novel PVA-PEO blend series are prepared using respective $AgNO_3$ and $LiCF_3SO_3$ salts as dopants, PEG and EC as plasticizers and Al_2O_3 as nano-filler and listed as follows.

1) ***PPAP Series:*** $[PVA_{(100-x)} : PEO_{(x)}]$ – 5 wt% $AgNO_3$ – 10 wt% PEG
where, x = 10 % to 50 % in the steps of 10

2) ***PPAPA Series:*** $[PVA_{(50)} : PEO_{(50)}]$ – 5 wt% $AgNO_3$ – 10 wt% PEG – x wt% Al_2O_3
where, x = 2 wt% to 10 wt% in the steps of 2

3) ***PPLE Series:*** $[PVA_{(50)} : PEO_{(50)}]$ – 5 wt% $LiCF_3SO_3$ – x wt% EC
where, x = 2 wt% to 10 wt% in the steps of 2

4) ***PPEL Series:*** $[PVA_{(50)} : PEO_{(50)}]$ – 6 wt% EC – x wt% $LiCF_3SO_3$
where, x = 3 wt% to 11 wt% in the steps of 2

5) ***PPELA Series:*** $[PVA_{(50)} : PEO_{(50)}]$ – 6 wt% EC – 9 wt% $LiCF_3SO_3$ – x wt% Al_2O_3
where, x = 2 wt% to 10 wt% in the steps of 2

In the present research work, a systematic study on PVA-PEO blend polymer electrolyte specimens is undertaken. The major interest of the present study is to investigate the transport properties as well as the electrical properties viz. conductivity, dielectric and relaxation properties of the as prepared PVA-PEO blend specimens of the above mentioned series. Transport properties of the blend specimens of each blend series are investigated by measuring their ionic transport number using dc polarization technique whereas; the electrical properties are examined using impedance spectroscopy. The supportive characterization studies of these specimens are carried out using various techniques viz. X-ray diffraction (XRD), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) which predict the respective physical, thermal, structural, microstructural and morphological properties of the PVA-PEO blend specimens. Based on the experimental results, the specimen depicting optimum ionic transport number and ionic conductivity is identified from each step and brought to the next step. The blend specimens depicting optimum transport and electrical properties of the respective Ag^+ and Li^+ conducting series are considered as electrolytes in the assembly of the respective Ag^+ and Li^+ primary polymer batteries. The lab-made Ag_2O and $LiMn_2O_4$ cathodes are further employed to fabricate the Ag^+ and Li^+ primary polymer battery assemblies respectively, using suitable anodes. Discharge characteristics and various battery parameters including plateau voltage, discharge capacity, specific capacity, electrical energy, specific power and specific energy of both these Ag^+ and Li^+ primary polymer batteries are thoroughly investigated at five different suitable loads of 330 Ω, 1 kΩ, 2.2 kΩ, 3.3 kΩ and 4.7 kΩ to gain insight regarding the electrochemical properties of the as chosen cathode materials and optimized PVA-PEO blend polymer electrolytes.

References

[1] B.B. Owens, *Journal of Power Sources* 90 (2000) 2.

[2] T. Sakuma, K. Basar, T. Shimoyama, D. Hosaka, Xianglian, M. Arai, in: T. Sakuma, H. Takahashi (eds.), *Physics of Solid State Ionics*, India, 2006, (a) pp. 323, (b) pp. 324.

[3] P. Sharma, *Ph.D. Thesis*, Department of Physics, The M.S. University of Baroda, Vadodara, 2013.

[4] C. Tubant, E. Lorentz, *Z. Physik. Chem.* 86 (1913) 513.

[5] B.J. Goodenough, *Pure and Appl. Chem.* 67 (6) (1995) 931.

[6] S. Furusawa, in: T. Sakuma, H. Takahashi (eds.), *Physics of Solid State Ionics,* India, 2006, pp. 272.

[7] C. Julien, in: P.J. Gellings. H.J.M. Bouwmeester, *The CRC Handbook of Solid State Electrochemistry,* CRC Press, Inc., USA, 1997, pp. 372.

[8] A. Shahzada, T.K. Saxena, A. Sharif, S.A.A. Agnihotry, *Journal of Power Sources* 159 (2006) 205.

[9] Z.L. Wang, Z.Y. Tang, *Electrochimica Acta* 49 (2004) 1063.

[10] A.V. Chadwick, *Ionics* 5 (1999) 321.

[11] S. Tamura, M. Yamane, Y. Hoshino, N. Imanaka, *Journal of Solid State Chemistry* 235 (2016) 7.

[12] Q. Lu, Y. Gao, Q. Zhao, J. Li, X. Wang, F. Wang, *Journal of Power Sources* 242 (2013) 677.

[13] T. Kawaguchi, H. Nakamura, S. Watano, *Powder Technology* xxx (2016) xxx.

[14] T. Matsuyama, R. Takano, K. Tadanaga, A. Hayashi, M. Tatsumisago, *Solid State Ionics* 285 (2016) 122.

[15] H. Inaba, H. Tagawa, *Solid State Ionics* 83 (1996) 1.

[16] Y.X. Gao, X.P. Wang, H. Lu, L.C. Zhang, L. Ma, Q.F. Fang, *Solid State Ionics* 291 (2016) 1.

[17] M. Sakuma, K. Suzuki, M. Hirayama, R. Kanno, *Solid State Ionics* 285 (2016) 101.

[18] C. Yu, L.V. Eijck, S. Ganapathy, M. Wagemaker, *Electrochimica Acta* 215 (2016) 93.

[19] D.P. Sveinbjornsson, *Ph.D. Thesis,* Department of Energy Conversion and Storage, Technical University of Denmark, Denmark, 2013.

[20] J. Zhang, C. Zhang, J. Xia, Q. Li, D. Jiang, X. Zheng, *Sensors and Actuators* B 249 (2017) 76.

[21] H. Ecker, *Diffusion Foundations* 6 (2016) 144.

[22] M. Rathore, A. Dalvi, *Solid State Ionics* 263 (2014) 119.

[23] A.S. Hassanien, A.A. Ak, *Journal of Non-Crystalline Solids* 432 (2016) 471.

[24] A.M. Abdelghany, F.H. ElBatal, H.A. ElBatal, F.M. EzzElDin, *Journal of Molecular Structure* 1074 (2014) 503.

[25] K. Vignarooban, R. Kushagra, A. Elango, P. Badami, B.E. Mellander, X. Xu, T.G. Tucker, C. Nam, A.M. Kannan, *International Journal of Hydrogen Energy* 41 (2016) 2829.

[26] S.B.R.S. Adnan, N.S. Mohamed, *Ionics* 20 (2014) 1641.

[27] P. Yan, Z. Huang , Y. Lin, X. Wu, Y. Yang, D. Wang, F. Chen, C. Zhang, D. He, *Ionics* 21 (2015) 593.

[28] B. Scrosati, J. Garchesong, *Journal of Power Sources* 195 (2010) 2419.

[29] G.H. Kwak, Y. Tominaga, S. Asai, M. Sumita, *Electrochim. Acta* 48 (2003) 4069.

[30] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359.

[31] A.M. Stephan, K.S. Nahm, Y.P. Kumar, M.A. Kulandainathan, G. Ravi, J. Wilson, *Journal of Power Sources* 159 (2) (2006) 1316.

[32] C. Berthier, W. Gorecki, M. Minier, M.B. Armand, J.M. Chabagno, P. Rig, *Solid State Ionics* 36 (1989) 165.

[33] F. Croce, F. Gerace, G. Dautzemberg, S. Passerini, G.B. Appetecchi, B. Scrosati, *Electrochim. Acta* 39 (1993) 2187.

[34] R. Kumar, S. Sharma, D. Pathak, N. Dhiman, N. Arora, *Solid State Ionics* 305 (2017) 57.

[35] B.E. Fenton, J.M. Parker, P.W. Wright, *Polymer* 14 (11) (1973) 589.

[36] P. Meneghetti, S. Qutubuddin, A. Webber, *Electrochim. Acta* 49 (2004) 4923.

[37] M. Ulanganathan, S. Rajendran, *Ionics* 16 (2010) 515.

[38] T.J. Pinnavaia, G.W. Bell, *Polymer-Clay Nanocomposite,* Wiley, England, 2000.

[39] P. Aranda, E. Ruiz-Hitzky, *J. Chem. Mater.* 4 (1992) 1395.

[40] I.J. Singh, S.V. Bhat, *Journal of Power Sources* 129 (2004) 280.

[41] P. Prabakaran, R.P. Manimuthu, *Ionics* 22 (2016) 827.

[42] L.N. Sim, S.R. Majid, A.K. Arof, *Vibrational Spectroscopy* 58 (2012) 57.

[43] F.M. Gray, *Solid Polymer Electrolytes: Fundamental and Technological Applications,* VCH Publishers, New York, 1991.

[44] C.E. Carraher (Jr.), *Introduction to Polymer Chemistry,* second ed., CRC Press: Taylor & Francis Group, LLC, USA, 2010.

[45] P. Bahadur, N.V. Shastry, *Principles of Polymer Science,* second ed., Narosa Publishing House Pvt. Ltd., India, 2005.

[46] M. Nagasawa, M. Kurata, H. Morimoto, I. Noda, T.O. Oyama, *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems,* Elsevier Science Publishers B.V., The Netherlands, 1988.

[47] C.A. Angell, C. Liu, E. Sanchez, *Nature* 362 (1993) 137.

[48] F.L. Auger, J. Prudhomme, *Electrochimica Acta* 47 (2002) 4433.

[49] L. Feng, H. Cui, *Journal of Power Sources* 63 (1996) 145.

[50] F.L. Auger, J. Prudhomme, *Electrochimica Acta* 46 (2001) 1359.

[51] A.A. Latoszynska, G.Z. Zukowska, I.A. Rutkowska, P.L. Taberna, P. Simon, P.J. Kulesza, W. Wieczorek, *Journal of Power Sources* 274 (2015) 1147.

[52] W. Pu, X. He, L. Wang, Z. Tian, C. Jiang, C. Wan, *Ionics* 14 (2008) 27.

[53] J.P.T. Guisao, A.J.F. Romero, *Electrochimica Acta* 176 (2015) 1447.

[54] J. Tarascon, A. Gozdz, C. Schmutz, F. Shokoohi, P.C. Warren, *Solid State Ionics* 86-88 (1996) 49.

[55] W. Li, Y. Xing, Y. Wu, J. Wang, L. Chen, G. Yang, B. Tang, *Electrochimica Acta* 151 (2015) 289.

[56] Y.Q. Yang, Z. Chang, M.X. Li, X.W. Wang, Y.P. Wu, *Solid State Ionics* 269 (2015) 1.

[57] A.B. Imran, T. Seki, Y. Takeoka*, Polymer Journal* 42 (2010) 839.

[58] O. Mahendran, S. Rajendran, *Ionics* 9 (2003) 282.

[59] Z. Dong, Q. Zhang, C. Yu, J. Peng, J. Ma, X. Ju, M. Zhai, *Ionics* 19 (2013) 1587.

[60] I.V. Hekerle, J. Vondrak, *Polymer Gel Electrolytes*, Doctoral Degree Programme (1), Dept. of Electrical and Electronic Technology, FEEC, BUT.

[61] J.K. Kim, L. Niedzicki. J. Scheers, C.R. Shin, D.H. Lim, W. Wieczorek, P. Johansson, J.H. Ahn, A. Matic, P. Jacobsson, *Journal of Power Sources* 224 (2013) 93.

[62] Y. Huai, J. Gao, Z. Deng, J. Suo, *Ionics* 16 (2010) 603.

[63] A.A. Latoszynska, P.L. Taberna, P. Simon, W. Wieczorek, *Electrochimica Acta* 242 (2017) 31.

[64] J.F. Veleza, L.V. Alvarez, C.D. Rio, B. Herradon, E. Mann, E. Morales, *Electrochimica Acta* 241 (2017) 517.

[65] S.S. Zhang, D.T. Tran, *Electrochimica Acta* 114 (2013) 296.

[66] P.F.R. Ortega, J.P.C. Trigueiro, G.G. Silva, R.L. Lavall, *Electrochimica Acta* 188 (2016) 809.

[67] W. Kang, N. Deng, X. Ma, J. Ju, L. Li, X. Liu, B. Cheng, *Electrochimica Acta* 216 (2016) 276.

[68] X. Zhong, J. Tang, L. Cao, W. Kong, Z. Sun, H. Cheng, Z. Lu, H. Pan, B. Xu, *Electrochimica Acta* 244 (2017) 112.

[69] D.W. Kang, J.K. Kim, *Journal of Electroanalytical Chemistry* 775 (2016) 37.

[70] S. Ramesh, S.C. Lu, *Journal of Molecular Structure* 994 (2011) 403.

[71] N. Yadav, K. Mishra, S.A. Hashmi, *Electrochimica Acta* 235 (2017) 570.

[72] R. Chen, W. Qu, X. Guo, L. Li, F. Wu, *Mater. Horiz.* 3 (2016) 487.

[73] F.F. Hatta, M.Z.A. Yahya, A.M.M. Ali, R.H.Y. Subban, M.K. Harun, A.A. Mohamad, *Ionics* 11 (2005) 418.

[74] X. Zuo, X.M. Liu, F. Cai, et. al. *J. Mater. Chem.* 41 (2012) 22265.

[75] D.M. Correia, C.M. Costa, J.N. Pereira, M.M. Silva, G. Botelho, J.L.G. Ribelles, S.L. Mendez, *Solid State Ionics* 268 (2014) 54.

[76] A. Turkovic, P. Dubcek, K. Juraic, S. Bernstorff, M. Buljan, *American Journal of Nanoscience and Nanotechnology* 1 (2013) 6.

[77] H. Palza, *Int. J. Mol. Sci.* 16(1) (2015) 2099.

[78] J.E. Weston, B.C.H. Steele, *Solid State Ionics* 7 (1982) 75.

[79] S.K. Chaurasia, A. Chandra, *Solid State Ionics* 307 (2017) 35.

[80] J. Wilson, G. Ravi, *Polimeros: Ciencia e Tecnologia* 16 (2) (2006) 88.

[81] G. Choudalakis, A. Gotsis, H. Schut, S. Picken, *European Polymer Journal* 47 (2011) 264.

[82] Y.L. Nimah, M.Y. Cheng, J.H. Cheng, J. Rick, B.J. Hwang, *Journal of Power Sources* 278 (2015) 375.

[83] S.P. Low, A. Ahmad, M.Y.A. Rahman, *Ionics* 16 (2010) 821.

[84] D. Saikia, C.G. Wu, J. Fang, L.D. Tsai, H.M. Kao, *Journal of Power Sources* 269 (2014) 651.

[85] X. Fu, in: C. Sequeira, D. Santos (Eds.) *Polymer Electrolytes – Fundamentals and Applications,* Woodhead Publishing Limited, Oxford, 2010, pp. 471.

[86] G.A. Niklasson, C.G. Granqvist, *The Royal Society of Chemistry: J. Mater. Chem.* 17 (2007) 127.

[87] Editorial: Polymer Electrolytes: Present, Past and Future, *Electrochimica Acta* 57 (2011) 4.

[88] S.K. Deb, *Appl. Opt. Suppl.* 3 (1969) 192.

[89] C.A. Vincent, *Prog. Solid State Chem.* 17 (1987) 145.

[90] Z. Osman, Z.A. Ibrahim, A.K. Arof, *Carbohydrate Polymers* 44 (2) (2001) 167.

[91] N. Bonanos, B.C.H. Steele, E.P. Butler, W.B. Johnson, W.L. Worrell, D.D. Macdonald, M.C.H. McKubre, in: E. Barsoukov, J.R. Macdonald, *Impedance Spectroscopy Theory, Experiment and Applications,* second ed., A John Wiley & Sons, Inc. Publication, USA, 2005.

[92] M.A. Mingsukang, M.H. Buraidah, M.A. Careem, I. Albinsson, B.E. Mellander, A.K. Arof, *Electrochimica Acta* 241 (2017) 487.

[93] S.N.F. Yusuf, A.D. Azzahari, V. Selvanathan, R. Yahya, M.A. Careem, A.K. Arof, *Carbohydrate Polymers* 157 (2017) 938.

[94] N. Zebardastan, M.H. Khanmirzaei, S. Ramesh, K. Ramesh, *Electrochimica Acta* 220 (2016) 573.

[95] M.F. Aziz, M.H. Buraidah, M.A. Careem, A.K. Arof, *Electrochimica Acta* 182 (2015) 217.

[96] H.T. Chou, H.C. Hsu, C.H. Lien, S.T. Chen, *Microelectronics Reliability* 55 (2015) 2174.

[97] N. Tiautit, C. Puratane, S. Panpinit, S. Saengsuwan, *Energy Procedia* 56 (2014) 378.

[98] H. Gerischer, M.E.M. Beyerle, F. Rebentrost, H. Tribijxch, *Electrochim. Acta* 13 (1968) 1509.

[99] S.G.S Tadesse; A. Abebe, Y. Chebude, I.V. Garcia, T. Yohannes, *J. Photon. Energy*. 2 (1) (2012) 027001.

[100] A. Djire, J.Y. Ishimwe, S. Choi, L.T. Thompson, *Electrochemistry Communications* 77 (2017) 19.

[101] P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845.

[102] S. Wasterlain, A. Guven, H. Gualous, J.F. Fauvarque, R. Gallay. *Hybrid power source with batteries and supercapacitor for vehicle applications*. Available at http:// www.garmanage.com/ (accessed 16 June 2017).

[103] J. Zhong, L.Q. Fan, X. Wu, J.H. Wu, G.J. Liu, J.M. Lin, M.L. Huang, Y.L. Wei, *Electrochimica Acta* 166 (2015) 150.

[104] G.P. Pandey, T. Liu, C. Hancock, Y. Li, X.S. Sun, J. Li, *Journal of Power Sources* 328 (2016) 510.

[105] L. Meabe, N. Lago, L. Rubatat, C. Li, A.J. Muller, H. Sardon, M, Armand, D. Mecerreyes, *Electrochimica Acta* 237 (2017) 259.

[106] A. Perea, M. Dontigny, K. Zaghib, *Journal of Power Sources* 359 (2017) 182.

[107] M.B. Armand, *Solid State Ionics* 9-10 (1983) 745.

[108] T.S. Gaaz, A.B. Sulong, M.N. Akhtar, A.A.H. Kadhum, A.B. Mohamad, A.A. Al-Amiery, *Molecules* 20 (2015) 22833.

[109] H. Tian, J. Yan, A.V. Rajulu, A. Xiang, X. Luo, *International Journal of Biological Macromolecules* 96 (2017) 518.

[110] L.C.K. Liau, Y.H. Lin, *Journal of Luminescence* 181 (2017) 217.

[111] L.M. Marvdashti, A. Koocheki, M. Yavarmanesh, *Carbohydrate Polymers* 155 (2017) 280.

[112] W. Yang, J.S. Owczarek, E. Fortunati, M. Kozanecki, A. Mazzaglia, G.M. Balestra, J.M. Kenny, L. Torre, D. Puglia, *Industrial Crops and Products* 94 (2016) 800.

[113] N. Sanaeifar, M. Rabiee, M. Abdolrahim, M. Tahriri, D. Vashaee, L. Tayebi, *Analytical Biochemistry* 519 (2017) 19.

[114] Nurhayati, C.L. Cheng, D. Nagarajan, J.S. Changa, *Biochemical Engineering Journal* 114 (2016) 298.

[115] C.C. Demerlis, D.R. Schoneker, *Food Chem. Toxicol.* 41 (2003) 319.

[116] I. Yu. Prosanov, N.V. Bulina, *Physics of the Solid State* 56 (6) (2014) 1270.

[117] X. Ma, X. Huang, J. Gao, S. Zhang, Z. Deng, J. Suo, *Electrochimica Acta* 115 (2014) 216.

[118] A. Abraham, P.A. Soloman, V.O. Rejini, *Procedia Technology* 24 (2016) 741.

[119] S.B.R.S. Adnan, N.S. Mohamed, *Electrochimica Acta* 146 (2014) 598.

[120] V. Parameswaran, N. Nallamuthu, P. Devendran, E.R. Nagarajan, A. Manikandan, *Physica B* 515 (2017) 89.

[121] S.R. Sudhamani, M.S. Prasad, K.U. Sankar, *Food Hydrocolloids* 17 (2003) 245.

[122] Z.I. Ali, H.M. Said, H.E. Ali, *Radiation Physics and Chemistry* 75 (2006) 53.

[123] P. Joge, D.K. Kanchan, P. Sharma, N. Gondaliya, *Advanced Materials Research* 665 (2013) 227.

[124] P. Joge, D.K. Kanchan, P. Sharma, N. Gondaliya, *Indian Journal of Pure and Applied Physics* 51 (2013) 350.

[125] S. Jayanthi, B. Sundaresan, *Ionics* 21 (2015) 705.

[126] A.M. Stephan, *European Polymer Journal* 42 (2006) 21.

[127] N. Angulakhsmi, S. Thomas, J.R. Nair, R. Bongiovanni, C. Gerbaldi, A. Manuel Stephan, *Journal of Power Sources* 228 (2013) 294.

[128] N. Angulakshmi, D.J. Yoo, K.S. Nahm, C. Gerbaldi, A.M. Stephan, *Ionics* 20 (2014) 151.

[129] R. Prasanth, N. Shubha, H.H. Hng, M. Srinivasan, *Journal of Power Sources* 245 (2014) 283.

[130] R. Blanga, D. Golodnitsky, G. Ardel, K. Freedman, A. Gladkich, Y. Rosenberg, M. Nathan, E. Peled, *Electrochimica Acta* 114 (2013) 325.

[131] X. Yan, B. Peng, B. Hu, Q. Chen, *Polymer* 99 (2016) 44.

[132] P. Kesharwani, D.K. Sahu, Y.K. Mahipal, R.C. Agrawal, *Materials Chemistry and Physics* 193 (2017) 524.

[133] A.R. Polu, H.W. Rhee, *International Journal of Hydrogen Energy* 42 (2017) 7212.

[134] B. Jinisha, K.M. Anilkumar, M. Manoj, V.S. Pradeep, S. Jayalekshmi, *Electrochimica Acta* 235 (2017) 210.

[135] R. Nadimicherla, R. Kalla, R. Muchakayala, X. Guo, *Solid State Ionics* 278 (2015) 260.

[136] P.G. Bruce, C.A. Vincent, *Chem. Soc. Faraday Trans.* 89 (17) (1993) 3187.

[137] D.K. Pradhan, R.N.P. Choudhary, B.K. Samantaray, *Materials Chemistry and Physics* 115 (2009) 557.

[138] H.J. Oh, J. Park, S. Inceogl, I. Villalueng, J.L. Thelen, X. Jiang, J.E. McGrath, D.R. Paul, *Polymer* 109 (2017) 106.

[139] O. Mahendran, S.Y. Chen, Y.W. Chen-Yang, J.Y. Lee, S. Rajendran, *Ionics* 11 (2005) 251.

[140] R. Muchakayala, S. Song, S. Gao, X. Wang, Y. Fan, *Polymer Testing* 58 (2017) 116.

[141] J.E. Lim, M.S. Oh, J.H. Ahn, J.K. Kim, *Electrochimica Acta* 238 (2017) 107.

[142] S.A. Mohamed, A.A. Al-Ghamdi, G.D. Sharma, M.K.E Mansy, *Journal of Advanced Research* 5 (2014) 79.

[143] J.L. Tebbe, T.F. Fuerst, C.B. Musgrave, *Journal of Power Sources* 297 (2015) 427.

[144] K.W Kim, H.W. Kim, Y. Kim, J.K. Kim, *Electrochimica Acta* 236 (2017) 394.