CHAPTER 1

INTRODUCTION

This chapter gives a brief introduction to history and literature review on Solid State Ionics. The various classification of ion-conducting electrolytes is discussed as especially the classification of polymer electrolytes is elaborated in detail. The various applications of polymer electrolytes in electrochemical devices are discussed.

1.1 Introduction on Solid State Ionics

Having a look into the history of research on materials science, the researchers have been showing persistently interest in searching for new materials along with their application in the field of science and technology. Before 1960, the majority of devices were based on electronically conducting materials, namely semiconductors. In 1950, the invention of the transistor pioneered the field of semiconductors electronics with an emerging new branch of science, named solid-state electronics. Only a few devices were based on ion-conducting materials till the mid-1960s, many of them were liquid-aqueous based electrolytes named aqueous batteries. Owing to the limited working temperature range, corrosion of electrodes due to the liquid electrolyte, too bulky, etc., the need for replacement of this liquid electrolyte discovered a new kind of ion-conducting solid namely alkali metal halides [1,2]. Having a poor ionic conductivity, approximately 10^{-7} to 10^{-12} S cm^{-1} made it an unsatisfactory choice. By keeping in mind, above all shortcomings of developed materials, in 1967, a new kind of solid ion-conductors came into existence i.e. Ag^{+} and Na^{+} based ion-conducting materials such as MAg_4I_5 (where M = Rb, K, NH_4) [3] and Na-β-alumina [4]. Owing to the high ionic conductivity, later on, a wide range of ion-

conducting materials have been reported with ionic species i.e. H^+, K^+, Li^+, Na^+, F^-, O_2^- etc. Ultimately, in 1967, a new branch of science, termed Solid State Ionics emerged in the era of the material science field [5].

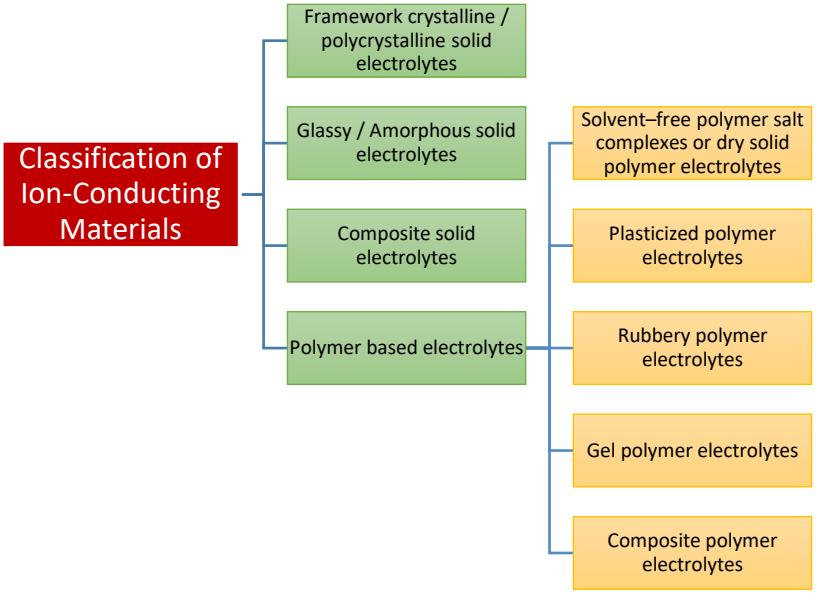
Solid State Ionics (SSI) is an interdisciplinary area of Science and Technology that deals with the study of ionic solid exhibiting a wide range of ionic conductivity from $10^{-13} – 10^{-1}$ S cm^{-1} [6,7]. The class of solid material having ionic conductivity of the order of $10^{-5} – 10^{-1}$ S cm^{-1} comparable to those liquid electrolytes are referred to as "Fast Ion Conductor" or "Superionic Solid". In 1970, T. Takahashi (Japan) referred: The study of these new emerging fields of material science as Solid State Ionics and development of Solid State Ionics materials such as glass, ceramic, and polymer electrolytes was initiated which established an upsurge of interest among researchers later [8]. The discovery of two new super ion-conducting materials, one is silver ion-conducting material [9] and Na ion-conducting material [4] created curiosity in the field of solid state ionics. Thereafter many superionic solids containing different species such as Li^+, K^+, Ag^+, H^+, F^-, O_2^- were studied and reported tremendous promises.

Nowadays, the active area of research study is on ion-conducting polymer electrolytes due to their interesting and wide variety of applications in electrochemical devices such as batteries, supercapacitors, fuel cells, sensors, electrochromic display devices, etc [10]. A Superionic Solid or Solid Electrolytes have the following properties:

- High ionic conductivity of the order of $10^{-5} – 10^{-1}$ S cm^{-1};
- Ions as principle charge carriers and ionic transport number are close to unity ($t_{ion} \approx 1$);
- Negligible electronic conductivity (Small electronic transference number ($t_e < 10^{-4}$);
- Low Activation Energy (0.1 ev – 1 ev).

The main key factor of these ionic conducting materials to be used in the application is high ionic conductivity which depends on many factors such as the structure of the crystal, degree of disordered in the lattice, mobile ion size, the interaction between ion-ion, number of the vacant site, the available path for the migration of ion [11,5]. Based on composition and microstructural properties, various ion-conducting were broadly classified into different categories [12,13].

1.2 Classification of Ion-Conducting Materials



Based on the microstructure and physical properties, the ion-conducting materials are classified as follows:

- Framework crystalline / polycrystalline solid electrolytes.
- Glassy / Amorphous solid electrolytes.
- Composite solid electrolytes.
- Polymer-based electrolytes.

1.2.1 Framework Crystalline / Polycrystalline Solid Electrolytes

The material having an ordered structure where a significant number of ions find an easy conduction pathway is defined as crystalline/polycrystalline solid electrolytes. Such a type of material contains a rigid skeleton structure and mobile ions. These materials can be classified into the following subcategories:

a) Soft framework crystalline materials e.g. AgI, CuI.
b) Hard framework crystalline materials e.g. β-Alumina, $LiAlSiO_4$, NASICON.

The soft framework crystalline materials have the following properties:

1) They have ionic bonding.
2) The mobile ions are highly polarisable (e.g. Ag, Cu) with low Debye temperatures.
3) Shows sharp order-disorder phase transition. Soft frameworks are generally prepared by using a solid solution of double type MX:X NY, where, MX is doping

salt with M = K, Rb, etc. X = I, Br, Cl, S etc. And NY is host salt such as CuI, LiI, AgI, etc. AgI is the most studied material [14].

The hard framework crystalline materials have the following properties:

1) They have a covalent bond.
2) The mobile ions have low polarizability with high Debye temperature.
3) There is less sharp order-disorder phase transition.

They are usually metal oxide. NASICON / LISICON [15] and β – Alumina [4] are two families of hard crystalline material. The ion transport phenomenon in these class of solid electrolytes are governed by the Lattice gas model, Free-ion model, Jump relaxation model, Coupling model, and Counter-ion model, etc. [16,17].

1.2.2 Glassy /Amorphous Solid Electrolytes

Glassy/Amorphous solid electrolytes have certain advantages over their crystalline counterparts or crystalline/polycrystalline materials such as high isotropic ionic conduction at room temperature, absence of grain boundaries, low activation energy, low electronic conductivity, higher thermal stability below glass transition temperature (T_g), the possibility of preparation into a desirable shape, size, thin films. They can be prepared over a wide range of compositions. Generally, glassy/amorphous materials can be prepared by melt quenching method which contains a mixture of glass former, a metal oxide as glass network modifier, and dopant salt. The compositional formula is $MX:M_2O:A_xO_y$, where MX = dopant salt (AgI, PbI_2, CdI_2, etc.), M_2O = glass modifier usually metal oxide Ag_2O, Cu_2O, Li_2O, Na_2O, etc.) and A_xO_y = glass former (SiO_2, B_2O_3, GeO_2, P_2O_5, MoO_2, etc.) [18-20]. The ion conduction mechanism in this class of material is governed by the Anderson Stuart model, Weak electrolyte model, Random site model, Cluster by-pass model, Ion association model [21,22].

1.2.3 Composite Solid Electrolyte

Composite solid electrolytes are known as multi-dispersed phase solid electrolytes (heterogeneous solid electrolytes) which may be obtained by mixing inert insulating materials i.e. AP_2O_3, SiO_2, Fe_2O_3, ZrO_2 in different ionic salt AgBr, Ag Cl, KCl. It has been observed that the addition of these nano-size particles in the host ionic conductor results in improvement of various properties such as ionic conductivity, physical, mechanical properties as well as improve electrode-electrolyte interfacial properties. In 1973, Liang had

observed an enhancement in conductivity (10^2-10^3 times) of Li^+ in LiI – Al_2O_3 system [23]. Then lots of studies in this field were done. Some examples are AgI –Al_2O_3, AgI – AgCl, AgI – SiO_2 fumed, AgI – AgCl - Al_2O_3, LiCl - Al_2O_3, and Li_2MnClO_4 – CeO_2 [24,25]. Conduction Mechanism can be explained in these types of materials by Space-charge model, Adsorption – desorption model, Percolation model, Mobility enhancement model [26,27].

1.3 Polymer Electrolytes

Polymer-based electrolytes have attracted the interest of scientists due to high ionic conductivity near to that of liquid electrolytes due to ease of fabrication in form of thin film, good electrode-electrolyte contact, free from leakage as compared to traditional liquid electrolytes. It has superior properties as compared to other solid electrolytes [28-30]. Polymers are large macromolecules composed of repeating structural units connected by covalent bonds. The polymer backbone generally consists of carbon atoms with various side groups like CH_2, CH_3 CH_2, Cl, N, Br, I, and the polymers with carbon atoms only in its backbone are known as organic polymers (Ex. PEO, PVA, etc.) and the inorganic do not contain any carbon atom in their backbone chain (Ex. Glass, Silicone rubber). Polymer solid electrolytes are formed by adding alkali metal salt MX (M = Li, Na, Ag, Cu, etc. and X = I, F, Cl, etc.) having low lattice energy and bulky anion [31] in host polar polymers like polyethylene oxide (PEO), polypropylene oxide (PPO), etc. These electrolytes can be prepared via various preparation techniques such as Solution-casting techniques, Electrodeposition method, Sol-gel method, Hotpress technique [32-34]. To explain the ion conduction mechanism in polymer electrolytes, free volume model and percolation model are applicable [35,36].

1.3.1 Polymer-Based Electrolytes: An Overview

The first polymer electrolyte was reported by Fenton et al. in 1973 [37] by complexing alkali metal salts in a high molecular weight polar polymer polyethylene oxide (PEO) and then P. V. Wright reported the electrical properties of these polymer salt complexes [38]. Later, Armand et al. in 1979 in their work, demonstrated the battery application by using PEO and lithium salt complex solid polymer electrolyte (i.e., PEO – Li^+ system) [13]. After then a wide range of polymer electrolytes has been investigated involving different kinds of mobile ion species like Li^+, Na^+, H^+, K^+, Ag^+, F^{-1}, O^{2-} as principle charge carriers [39] and

various kinds of the polymer are being used as host polymers like PEO, PMMA, PVA, PVC and PVDF [40]. These polymer electrolytes have shown tremendous applications in a wide variety of electrochemical devices such as Electrochemical batteries, Supercapacitor, Fuel-cells, Electrochemical displays, etc. [10].

Polymer electrolytes should possess the following properties to be used in the development of solid-state devices:

- High ionic conductivity $\sigma \geq 10^{-4}$ S cm^{-1} at room temperature close to liquid electrolytes.
- High ionic transference number $t_{ion} \approx 1$.
- Good mechanical, thermal, and chemical stability. High chemical stability is required to avoid chemical reactions at electrode-electrolyte interfaces. To operate at a wider temperature range, thermal stability is required.
- Wider electrochemical stability window as high as 4 to 5 V.
- Low activation energies for ion conduction.
- Low glass transition temperature (T_g) is required for high ionic conductivity.

Properties required for a polymer to be used as host polymer:

In polymer electrolytes, the fundamental mechanism of ion conduction is the covalent bonding between the polymer backbones with the ionizing groups. When lithium salt is added to the host polymer. It gets dissociated by interaction with the polar groups of polymer and ion moves through long polymer chains by hopping process [41]. The polymer should have the following properties:

- A polymer must have an electron donor group (an atom with at least one lone pair of electrons) such as O, N, and S for coordinating with ions (cations).
- Provide fast segmental motion of polymer chain with a low barrier to the bond rotation.
- Low glass transition temperature.
- High molecular weight.
- It should have the properties of more salt dissociation.

A large number of potential polymers have been explored [41]. Some of the polymers are listed along with their specification in Table 1.1.

Table 1.1 Properties of used polymers as polymer host in polymer electrolyte.

Sr. No.	Polymer	Repeat Unit	T_g (°C)	T_m (°C)
1	Poly(ethylene oxide) (PEO)	$-(CH_2 - CH_2O)_n-$	-64	65
2	Poly(propylene oxide) (PPO)	$-(CH(-CH_3)\ CH_2O)_n -$	-60	A
3	Poly (acrylonitrile) (PAN)	$-(CH_2 - CH\ (-\ CN))_n -$	125	317
4	Poly (methyl methacrylate) (PMMA)	$-(CH_2C(-CH3)\ (-COOCH_3))_n-$	105	A
5	Poly (vinyl chloride) (PVC)	$-(CH_2 - CH\ Cl)_n -$	85	A
6	Poly (vinyldene fluoride) (PVDF)	$-\ (CH_2 - CF_2)_n -$	- 40	171
7	Poly(vinylidene fluoride – hexafluoridepropylene) (PVDF-HFP)	$-\ (CH_2CF_2)_x\ (CF_2CF - CF_3)_Y -$	- 90	135

***** A = Amorphous

Properties of salt as conducting species

In polymer electrolytes, salt is a major component, which should have the following properties [42].

1. Smaller cationic radii and bigger anionic size.
2. It should have low lattice energy or high solvation energy.
3. High ionic conductivity.
4. The changing density of the anion should be low to reduce the number of ions – pairs with cations [43].
5. High thermal and chemical stability.
6. Anion and cation, both should be inert towards other components such as separator and electrode substrates.

The ionic conductivity for a given ionic species are as following:

$CH_3COO^- < F^- < Cl^- < Br^- < I^- < SCN^- < ClO_4^- < BF_4^- < CF_3SO_3^- < (CF_3SO_2)_2^-$. Among these, ClO_4^- or $CF_3SO_3^-$ have low lattice energy, so it can be easily dissociated when added to the polymer. So, it is the most suitable choice for polymer salt complexes.

Different kinds of cations are:

(i) Monovalent cations, such as Li^+, Na^+, K^+, Cs^+ and NH_4^+.

(ii) Divalent cations: Mg^{2+}, Ni^{2+}

(iii) Trivalent cations: La^{3+}, Nd^{3+}, Eu^{3+} have been utilized.

Some characteristics of salt are given below.

(1) Dissociation constant: LiTF < $LiBF_4$< $LiPF_6$ < LiTFSI < LiBOB.

(2) Average ion mobility: $LiBF_4$ > $LiClO_4$ > $LiAsF_6$ > LiTF > LiTFSI [41].

1.3.2 Classification of Polymer Electrolytes

Based on the preparation method, physical properties, and structural properties, the polymer electrolytes are classified into the following categories:

- Solvent-free polymer salt complexes or dry solid polymer electrolytes;
- Plasticized polymer electrolytes;
- Rubbery polymer electrolytes;
- Gel polymer electrolytes;
- Composite polymer electrolytes.

1.3.2.1 Solvent-Free Polymer Salt Complexes Or Dry Solid Polymer Electrolytes

Dry solid polymer electrolytes are prepared by dissolving ionic salt into high molecular weight polar polymer hosts where the organic liquid is not used. Usually, the polymer should have a high dielectric constant and salt with low lattice energy [44]. The ionic conductivity of these electrolytes is in the range of 10^{-7} to 10^{-5} cm^{-1}. In 1977, the first solvent-free or dry solid polymer electrolytes was invented which is a poly (ethylene oxide) (PEO) based system [45]. PEO is widely used due to the fact that it forms stable dry complexes because of the interaction of salt cation with polar polymer with polar groups (–O–, –H–, –C–H–) in polymer chain which has sufficient donor ability [45]. Ion transport in the polymer electrolyte, a consequence of local relaxation as well as segmental motion. Figure 1.1 depicts a schematic representation of ion conduction within the polymer electrolyte.

1.3.2.2 Plasticized Polymer Electrolytes

Plasticized polymer electrolytes are obtained by adding a small amount of low molecular weight polar organic solvent/plasticizer into dry solid polymer electrolytes. These small molecular plasticizers easily penetrate the polymer matrix and create attractive forces between themselves and polymer chain segments which reduces cohesive forces between polymer chain results in enhancement polymer segment motion, as a result, the glass transition temperature (T_g) value is reduced [40] and provide conduction channels. The

incorporation of plasticizers improves the flexibility of the polymer chain. The addition of plasticizers reduces the degree of crystallinity and enhances the segmental motion of the polymer chain. According to M. H. Buraidah, plasticizers and polymer do not interact chemically with one another but donor atoms of plasticizers might be placed in between coordinating sites in the polymer and present a network site for ions to reside [46]. So, the ion can hop from one coordinating site to another via donor atom sites contributed by the plasticizer hence hop requires low activation energy. Incorporation of low molecular weight plasticizer poly (ethylene glycol) (PEG), an organic solvent such as ethylene carbonate (EC), propylene carbonate (PC) diethyl carbonate (DEC), dimethylformamide (DMF) is a common approach. Such addition generally results in enhancements in solid polymer electrolytes which is accompanied by loss of dimensional stability and lack of compatibility with electrodes or poor interfacial stability with lithium electrodes which prevent them little use in all-solid-state electrochemical devices.

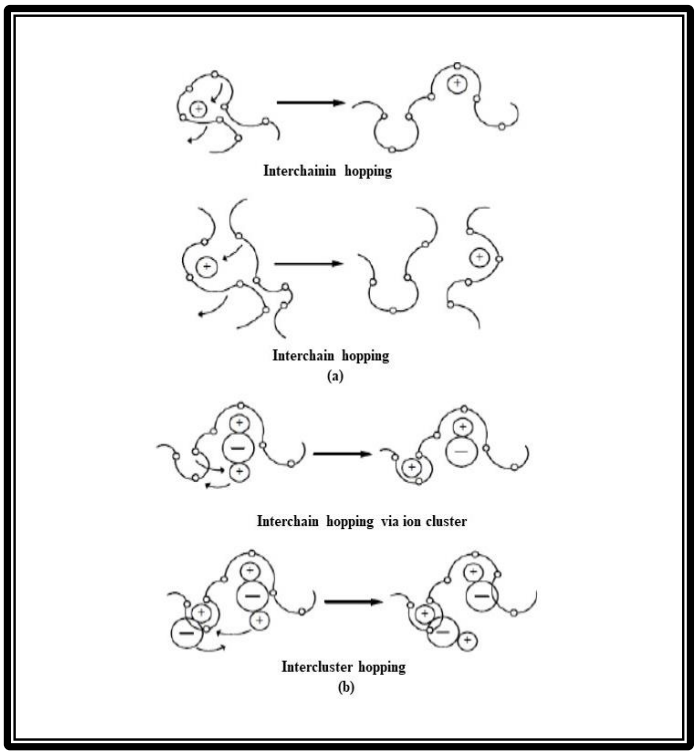


Figure 1.1 Pictorial view of hopping of cation through polymer chain motion and via ion clusters [43]

1.3.2.3 Rubbery Polymer Electrolytes OR Polymer-in-Salt Systems

Rubbery polymer electrolytes are prepared by dissolving a small amount of high molecular weight polymer like PEO, PPO in a relatively large amount of salt. This type is also referred

to as the 'Polymer-in-salt' system. The glass transition (T_g) of these polymer electrolytes is low enough to maintain a rubbery state. The highest room temperature conductivity of about ~ 2×10^{-2} S cm^{-1} has been reported for the polymer-in-salt system: $AlCl_3$ – LiBr – $LiClO_4$ – PPO [47]. The room temperature conductivity of rubbery electrolytes is quite high but the crystallization of salt at lower temperatures prevents its practical application in electrochemical devices.

1.3.2.4 Gel Polymer Electrolytes

Gel polymer electrolytes (GPEs) are usually obtained by incorporating a large amount of organic liquid solvents/ plasticizers into a polymer matrix. GPE is neither solid nor liquid [48]. The organic solvent /plasticizer remains trapped within the polymer matrix and gel is formed or polymer network swelled with organic plasticizers hence it possesses both the cohesive properties of solid and diffusive properties of the liquid. The ionic conductivity of these GPEs is comparable to liquid electrolytes. The idea of the plasticizing polymer was proposed by Feuillade and Perche in 1975 [49]. Since then, a large number of gel polymer electrolytes have been reported using various polymer hosts such as poly (ethylene oxide) PEO [50], poly (acrylonitrile) (PAN) [51], poly (methyl methacrylate) (PMMA) [52], poly (vinylidene fluoride) (PVDF), poly (vinylidene fluoride–co–hexafluoropropylene) (PVDF–co–HFP), etc. with high ionic conductivity ~ 10^{-4} – 10^{-3} S cm^{-1} at ambient temperature. The addition of plasticizers can result in greater ion dissociation which increases the number of charge carriers for ionic transport [40]. The commonly used plasticizers /organic solvents have been presented in Table 1.2.

Table 1.2 Properties of some organic solvent/ plasticizers [53,54].

Organic solvent/Plasticizers	Melting point (°C)	Boiling point (°C)	Density (g cm^{-3})	Dielectric constant (ε)	Molecular weight
ethylene carbonate (EC)	36.4	248	1.32	89.78	88.06
propylene carbonate (PC)	- 48.8	242	1.20	66.14	102.09
dimethyl carbonate (DMC)	2.4	90	1.06	3.12	90.08
diethyl carbonate (DEC)	- 43.0	126	0.98	2.82	118.13
Y–Btyrolactone (BL)	- 43.3	204	1.13	39.00	86.09

The plasticizers should possess specific properties such as [55,56]

1. It should have a high dielectric constant.
2. It must possess low viscosity.

3. It should have a high boiling point.
4. It must have a low melting point.
5. It should be non-toxic and non-volatile.
6. It should be non - reactive with electrodes.
7. It should have a higher donor number for more dissociation of ions.

The plasticizers with above said properties aid to form better gel electrolytes which ensure high ion concentration, better ion transport, prevent solvent evaporation, etc. The main drawback associated with these materials, mechanical properties detreat by applying a large amount of plasticizer. This problem was overcome by cross-linking of polymer, blending of two polymers. Cross-linking can be done by exposing radiation, UV, thermal, photo, electron beam, etc. which helps to trap the liquid electrolyte (plasticizers + salt) within the polymer matrix. Besides good ionic conductivity, compatibility with an electrode an essential parameter in electrochemical devices.

In the present work, PVDF-HFP has been chosen due to high anodically stable because of the strongly electron-withdrawing function group (–C–F–). In addition to this high dielectric constant ($\varepsilon \approx 8.4$) of PVDF-HFP assist in greater dissociation of lithium salt which provides a large concentration of charge carriers.

1.3.2.5 Composite Polymer Electrolytes

The composite polymer electrolytes are prepared by dispersion of nano-size filler particles in polymer electrolytes. These nano-size inert particles modify the mechanical, electrical, structural properties of polymer electrolytes. It has been observed, when nano/micron size inert particles are added to the polymer electrolyte system, the conductivity of the system enhances by some order. Fillers are basically oxides like TiO_2, SiO_2, Al_2O_3, $BaTiO_3$, $PbTiO_3$, ZrO_2, etc. This type of fillers are passive filler, when added to polymer electrolytes the system does not undergo any kind of chemical changes or chemical bonding and they do not involve in the ion transport process but with the addition of filler:

i) Increases amorphous region in the polymer.
ii) Provide a new path for charge carrier's transport.
iii) Behaves as a nucleation site for small crystallites formation.

Table 1.3 Examples of studied polymer electrolytes system along with conductivity values.

Sr. No.	Polymer electrolytes	Conductivity (S cm^{-1})	Ref.
1	PVA–PVDF–$LiClO_4$	3.03×10^{-5}	[59]
2	PVA–PVDF – $LiCF_3SO_3$	2.7×10^{-3}	[60]
3	PEO–$LiAsF_6$ – MMT	4×10^{-5}	[61]
4	PVA – $LiCF_3SO_3$	7.0×10^{-4}	[62]
5	PEO – $LiPF_6$	1.5×10^{-4}	[63]
6	PEO – $LiBF_4$	1×10^{-6}	[64]
7	PEO – $LiClO_4$ – PC	8×10^{-4}	[10]
8	PEO – $LiCF_3SO_3$ – EC	1.4×10^{-6}	[65]
9	PEO – $LiCF_3SO_3$ – PC	5.4×10^{-8}	[65]
10	PVC – PEMA – $LiClO_4$ – PC	3.45×10^{-3}	[66]
11	PAN – EC/PC/DMF – $LiClO_4$	4×10^{-4}	[67]
12	PMMA – EC/PC – $LiClO_4$	1×10^{-3}	[52]
13	PVDF/PMMA – EC/DMC – $LiPF_6$	1.21×10^{-3}	[68]
14	PVDF/PEMA – EC/PC – $LiC1O_4$	1.5×10^{-4}	[69]
15	PVC – EC/PC – $LiC1O_4$	4×10^{-3}	[70]
16	PAN – EC/PC – $LiClO_4$	4×10^{-3}	[70]
17	PVdF(HFP) – PC – DEC – $LiClO_4$	2.6×10^{-3}	[71]
18	PAN – PC – EC – $LiN(CF_3SO_2)_2$	2.0×10^{-3}	[72]
19	PMMA – DMA – $LiCF_3SO_3$	5.5×10^{-3}	[73]
20	PAN – PC-EC – $LiCF_4$	4.5×10^{-3}	[72]
21	PMMA – PC – DEC – $LiClO_4$ – MMT	1.3×10^{-3}	[74]
22	PMMA – $LiCF_3SO_3$ – SiO_2	7.30×10^{-5}	[75]
23	PEO – $LiBF_4$ – TiO_2	1×10^{-5}	[76]
24	PEO – $LiCF_3SO_3$ – Al_2O_3	9.78×10^{-5}	[77]
25	PEO – $LiClO_4$ – TiO_2	2×10^{-5}	[78]
26	PVDF – HFP – EC – DEC – $LiPF_6$ – Al_2O_3	1.95×10^{-3}	[79]
27	PVDF-HFP–PMMA–$LiCF_3SO_3$–(PC–DEC) – SiO_2	1×10^{-3}	[80]
28	PVDF-HFP – LiTFSI – SiO_2	1.3×10^{-3}	[81]
29	PVDF-HFP – EC – PC – $NaPF_6$ – TiO_2	1.3×10^{-3}	[82]
30	PVDF-HFP–PMMA–PEO –SiO_2@PMMA	8.54×10^{-5}	[83]

The nano-filler with Lewis-acid surface group interacts with host polymer and ion which reduces ion coupling between them gives rise to free charge carriers in the system. Additionally, the volume, size, and shape of the added filler particles have an impact on electrical properties. Li et al.[57] have investigated the effect of TiO_2 on the morphology of poly (vinylidene fluoride–co–hexafluoropropylene) (PVDF–co–HFP) complexed with $LiPF_6$. The incorporation of nanofillers to polymer electrolyte leads to better stability at the electrode-electrolyte interface compared to micron size filler as reported by Kumar et al. [58] and depicted in Figure 1.2.

Some of the different polymer electrolytes with their conductivity values are given in Table 1.3.

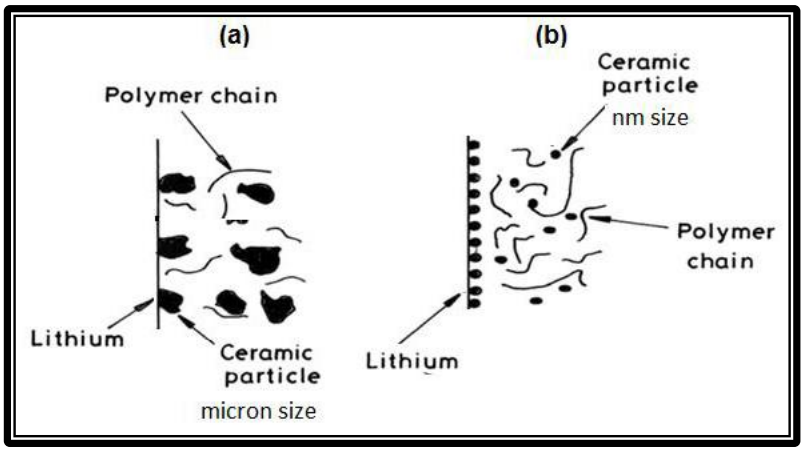
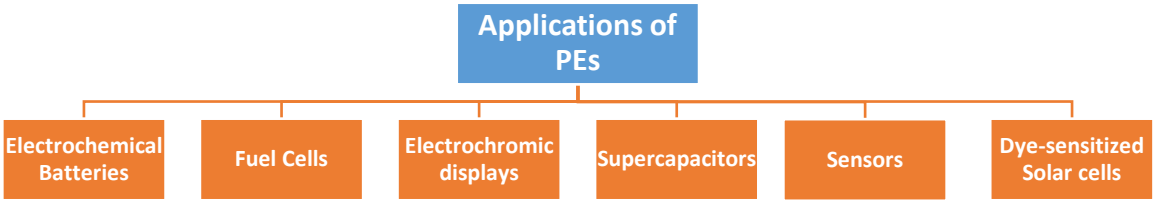


Figure 1.2 Schematic view of polymer host with inorganic nanofiller with the size of nanometre and (b) micron interfaced with electrodes [58]

1.4 Applications of Polymer Electrolytes

The polymer electrolytes have vast applications in different electrochemical devices due to their owing properties such as high ionic conductivity, wider electrochemical stability, ionic transport number close to unity.



1.4.1 Electrochemical Batteries

Batteries have become a need for everyone in everyday life. Batteries convert electrochemical energy into electrical energy and store it by means of oxidation-reduction reactions. EMF is developed across the electrodes due to the difference between the chemical potential of the anode and cathode, which is governed by Gibbs free energy (ΔG) involved in the chemical reactions at the electrode-electrolyte interfaces.

$$E = \frac{\Delta G}{nF} \tag{1.1}$$

where n is the valency of conducting species and F is faraday's constant.

The main role of polymer electrolytes in electrochemical batteries is to separate electrodes. i.e anode and cathode. The polymer electrolyte is an electron insulating material where migration of ions takes place from anode to cathode during the discharge process and the reverse process is done during recharging of batteries [84]. The battery generates power by means of the transfer of electrons via external circuits. Batteries consist mainly of three components. (1) The cathode as a positive electrode (2) Anode as a negative electrode (3) Electrolytes as a separator. Figure 1.3 depicts a schematic representation of the battery. Anode with low reduction potential undergoes an oxidation reaction at interface and electron transfers towards cathode via an external circuit. Cathode with high reduction potential undergoes a reduction reaction at the interface by accepting electrons which transferred from the anode via an external circuit.

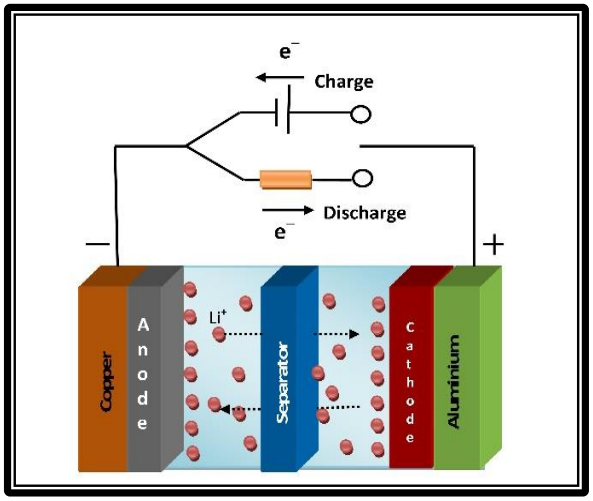


Figure 1.3 Schematic diagram of a typical battery

The energy of the battery depends on redox reactions that take place at electrodes. It is the difference between the standard electrode potential of anode and cathode.

$V = E_{cathode} - E_{anode}$

The chemical reactions involve the Gibbs free energy which leads to generates the emf across two electrodes. Generally, the batteries having gel polymer electrolyte compared to liquid electrolyte have many advantages such as leakage-proof, long life cycle, and safe. Till date, different types of electrochemical battery has been invented possess different energy density. Figure 1.4 depicts a comparison of different batteries with respect to their energy density.

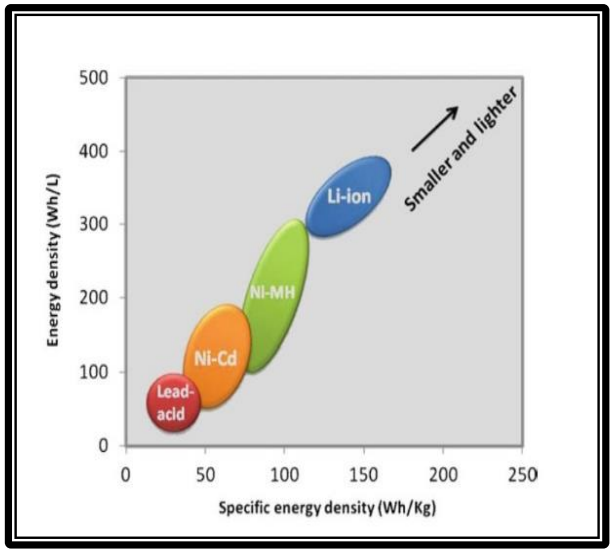


Figure 1.4 Comparison of all types of batteries in terms of energy density [85].

1.4.2 Electrochemical Capacitor or Supercapacitor

Supercapacitors are able to generate high power as compared to the battery but cannot store charges as the battery can. A supercapacitor is an energy storage device that possesses higher capacitance as compared to a conventional capacitor. Supercapacitor also consists of two electrodes and electrolyte material. A schematic diagram of the supercapacitor is given in Figure 1.5 [86]. A polymer electrolyte is sandwiched between two electrodes as shown in the diagram [87]. Supercapacitors are classified into three categories (Figure 1.6) depending on used electrode material and mechanism of charge storage.

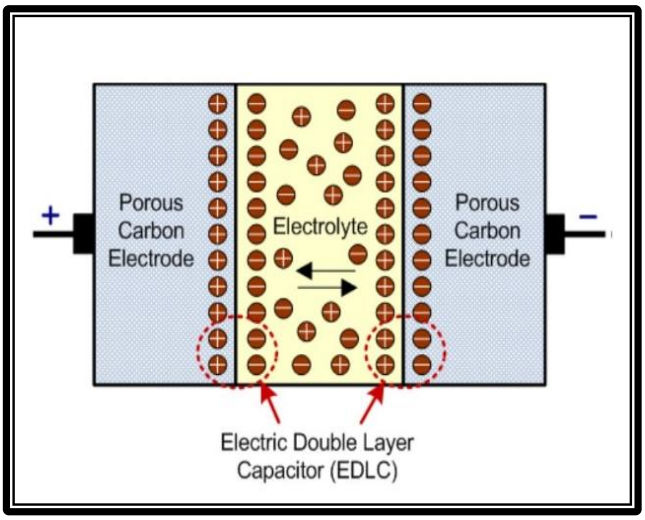


Figure 1.5 Schematic structure of Supercapacitor [89]

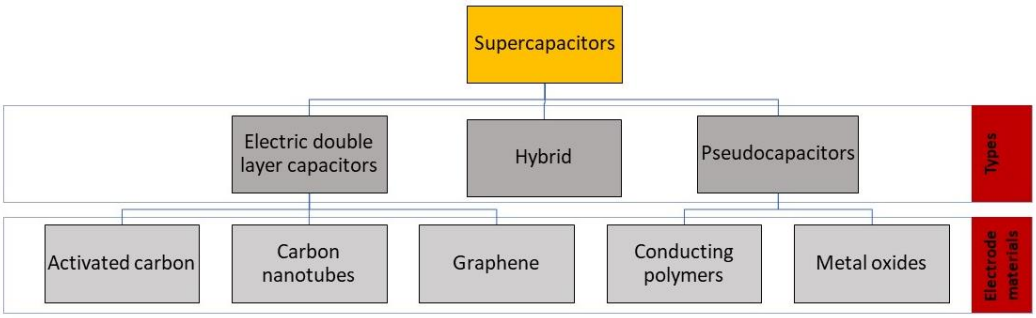


Figure 1.6 Classifications of Supercapacitor [88]

In the EDLCs capacitor, two identical electrodes are used which contain activated carbon graphene, carbon nanotube, aerogel, xerogel, etc. In Pseudo capacitor, noble metal oxides such as MnO_2, CoO_x, RuO_X, NiO_X or conducting polymers such as polyaniline, polypyrrole, polythiophene are used. In a hybrid supercapacitor, one electrode is of EDLC type and another electrode is of pseudo-capacitor type is used.

1.4.3 Fuel Cell

The Fuel cell is an electrochemical device that converts chemical energy into electrical energy. A schematic representation of the Fuel cell is depicted in Figure 1.7. Polymer electrolytes in the fuel cells are capable of carrying H^+ produced by fuel oxidation at the anode to cathode. Anode act as a reducing electrode and cathode act as an oxidizing electrode. The difference between fuel cell and battery, in which fuel should be continuously applied to it through external agencies, whereas reactants are stored in the case of battery.

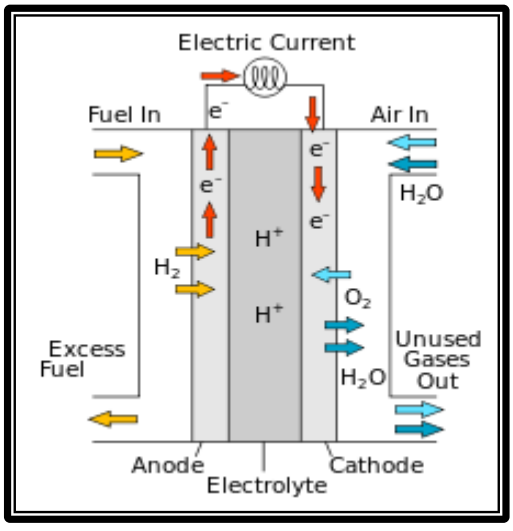


Figure 1.7 Schematic diagram of fuel cell

The fuel cell provides electrical energy as long as fuel is present whereas, in the case of a battery, it provides electrical energy depending on the charging-discharging cycle life of the battery. The fuel cell can be classified into different categories according to the type of electrolytes and electrode such as molten carbonate fuel cells (MCFC), alkaline electrolyte fuel cells (AFC), solid oxide fuel cells (SOFC), phosphoric acid fuel cells (PAFC), proton exchange membrane fuel cells (PEMFC) [90], direct methanol fuel cells (DMFC), etc [91].

1.4.4 Dye-Sensitized Solar Cell (DSSC)

A dye-sensitized solar cell (DSSC) is a photo-electrochemical device. The prediction of the generation of electricity by illuminating an organic dye was given in 1968 [92] and the first DSSC was constructed and shown in 1972 [93]. The design of a DSSC is shown schematically in Figure 1.8.

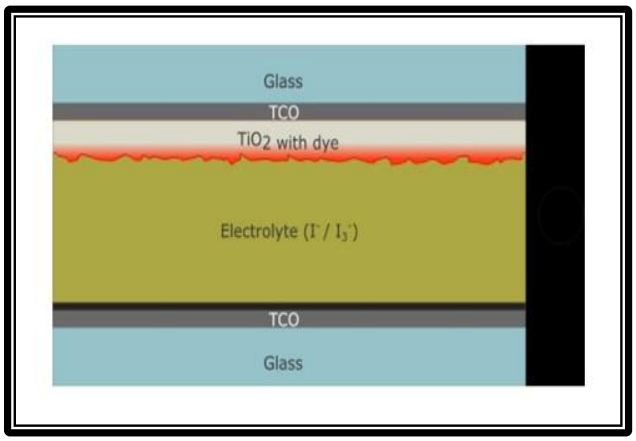


Figure 1.8 Schematic representation of Dye-sensitized Solar Cell

In traditional semiconductor solar cells, Si is used both for the generation of charge and as a transport medium but in DSSC photoelectrons are provided by the dye, and TiO_2 is used for their transport only. In DSSC, titanium oxide (TiO_2) nanoparticles are coated with a dye to absorb light from the sun and then covered by a conducting glass [94]. DSSC contains an electrolytic solution having I^-/I_3^- couple and platinum electrode. The electron gets excited after absorption of light energy in dye and injected electrons into TiO_2 nanoparticle diffuse towards glass electrode. These electrons pass through an external circuit and are received by the platinum electrode and then received by the iodine molecule within the electrolytic solution. Thereafter, the regeneration process takes place. The DSSC having liquid electrolyte has high efficiency compared to solid electrolyte but suffers from leakage and

corrosion problems. Nowadays, a wide range of solid, gel, and nanocomposite polymer electrolytes have been invented to fabricate solar cells [95,96].

1.4.5 Electrochromic Display Devices (ECDs)

It is an electrochemical display device in which color changes as a result of energy output. The phenomenon in which material changes their optical properties under the application of a small electric field called “Electrochromism” and the material is known as electrochromic materials. Because of the electrochemically induced oxidation and reduction process, it can reversibly change color with the response of the electric field [97]. This type of material has promising applications in various fields such as smart windows, color-changing displays, aircraft, sunglasses, sunroofs, etc [98].

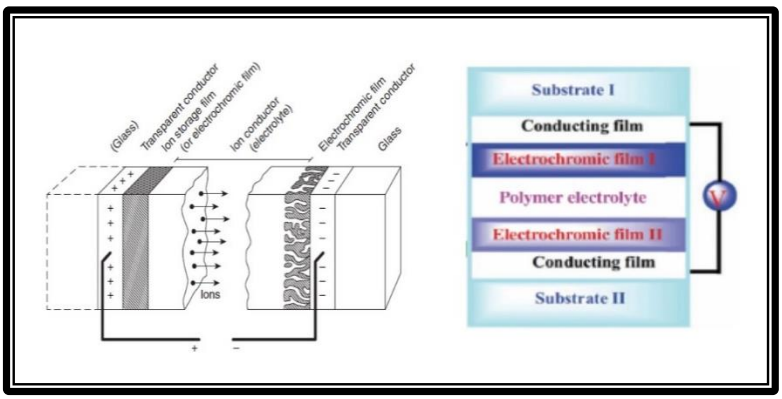


Figure 1.9 Schematic diagram and configuration of electrochromic device design [99]

The electrochromic display devices usually consist of multi-layered structures such as substrate, transparent conductor, electrochromic, electrolyte, ion storage/electrochromic layer, transparent conductor, and substrate as shown in Figure 1.9 [100]. In a typical electrochromic device, the transparent conductor (electronic conductor) works as a working electrode that needs to follow the electrochromic layer. The polymer electrolytes where conduction of ions takes place and supporting oxidation-reduction between the electrodes. The electrochromic layers change color under the application of the field. While the ion storage layer act as a buffer. When ions in the electrolyte are intercalated into the electrochromic layer, the ion storage provides ions to the electrolyte and captures ions. Nowadays, ion storage is replaced by an electrochromic layer. This electrochromic film is a mixed electronic-ionic conductor. The colorful responses of conjugated polymers to voltage are derived from the changes of electron states in molecules [101].

1.4.6 Sensors

Electrochemical sensors are studied widely and they are based on a redox reaction, at a working electrode resulting in a change in the electrical signal. The main principle of this device is monitoring change in electrical signal [45].

solid state sensors are commercially used to sense gases and ions in different systems. Solid-state sensors can be classified into two types (i) Impedance type (ii) Electrochemical type. In the first type of sensor, the conductivity of the solid electrolyte changes due to different gaseous atmospheres and is monitored. In the second type of sensor, electrochemical reactions (redox reaction) at the electrode/electrolyte interface are monitored. Polymer electrolyte-based sensors so far developed for gas sensing and humidity. Some examples are COx, NO_x, SO_x sensors for controlling pollution, ammonia sensors, oxygen sensors [102].

1.5 Motivation and Objective of The Present Work

As discussed above, the polymer electrolyte is an essential component as a separator in various electrochemical devices such as batteries, supercapacitors, solar cells, fuel cells, etc., The function and working of the device depend on the properties of the polymer electrolyte. The basic requirements of the polymer electrolyte are high ionic conductivity, wider electrochemical stability, high ionic transference number, good mechanical strength to withstand with electrodes, long life cyclability, etc., especially for the battery application. Various kind of polymer electrolyte systems using polymer hosts such as poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(vinyl chloride) (PVC), and poly(vinylidene fluoride) (PVDF) have been studied as discussed in the previous section. However, the solid polymer electrolytes system with the above said host polymer still faces the problem of low ionic conductivity of 10^{-5} to 10^{-7} S cm^{-1} which is not suitable for the battery application. Alternatively, the gel polymer electrolyte system has been found as a potential candidate due to its high ionic conductivity of the order of 10^{-4} to 10^{-3} S cm^{-1}. Apart from it, other interesting points are no leakage, ease to prepare and shaped it in the form of thin-film, no degradation, high compatibility with electrodes, high energy density, etc. Gel polymer electrolyte can be obtained by incorporating a large amount of plasticizers having the ability to dissolve the salt and provide a large number of free ions

for ion conduction. The plasticizer also maintained a liquid state in between polymer matrix owing to its non-volatile nature and ion transportation takes place through this liquid-rich swollen gel phase. The discussed parameters of polymer electrolyte depend on the properties of the individual constituent and their compatibility with each other while forming composition. Despite these outstanding properties of GPE, a large amount of plasticizer leads to poor mechanical strength and less compatibility towards the metal anode. Hence, in the present study rather than a single polymer, blending of the two polymers has been considered. As a host polymer poly(vinylidene fluoride - hexafluoropropylene) (PVDF-HFP) has been adopted due to its superb properties such as semi-crystalline nature which provide mechanical integrity and high dielectric constant $\varepsilon' \approx 8.4$ which helps for the higher dissociation of salt. Along with this, poly(methyl methacrylate) (PMMA) is blended with it owing to its amorphous nature which facilitates in increasing the amorphicity. A schematic diagram of the structure for the blended polymer electrolyte is shown in Figure 1.10.

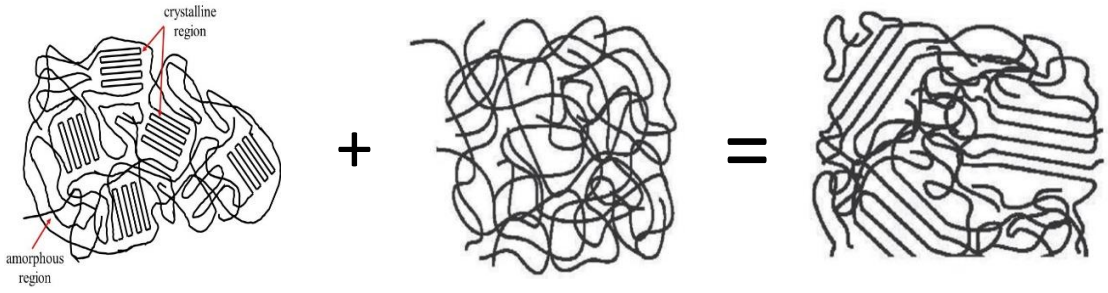


Figure 1.10 schematic diagram of the structure for the blended polymer electrolyte

Another required component is salt which should have a low lattice energy and small anionic radius so that the ion can diffuse easily through the polymer matrix. The present gel polymer electrolyte system consists of $LiClO_4$ as a salt due to its smaller dissociation energy and high solubility in the solvent. In gel polymer electrolyte, plasticizers play an important role which softens the polymer backbone as well as dissociates salt species that increases the number of free ions. Hence, high dielectric permittivity and low viscosity are essential properties of plasticizers to promote ion-pair dissociation. Hence in the present study the mixture of PC ($\varepsilon' \approx 64.4$, viscosity η at 25 °C ≈ 2.53 mPa S) and DEC ($\varepsilon' \approx 2.82$, viscosity η at 25 °C ≈ 0.748 mPa S) is taken. However, excessive use of plasticizers deteriorates its mechanical strength and makes the electrolyte non-compatible with the electrodes of the

battery system. To overcome this problem, the nano-particles are incorporated in the optimized gel polymer electrolyte system. It is expected that the combination of plasticizers and nano-particles would be of great importance to achieve desirable properties of polymer electrolytes for battery application. Al_2O_3 is chosen as a passive nano-filler to achieve nano-composite gel polymer electrolyte (NCGPE) because of its hydrophilic nature, high dielectric constant, and surface area. All these properties of the nano-filler lead to a decrease in the degree of crystallinity which enhances the free volume through the polymer matrix and consequently the number of free charge carriers increases.

After a deep literature review and with consideration of all discussed parameters above, the aim of the present study is to study the properties of the gel polymer electrolyte system for the Li^+ ion battery application. In the present work, the designed polymer electrolyte constitutes PVDF-HFP and PMMA as host polymer, $LiClO_4$ salt as an ion-conducting species, PC and DEC as plasticizers, and Al_2O_3 as nano-filler. The main objective of the present thesis is "**Electrochemical properties of nano-composite polymer blend gel electrolytes for battery applications**"

Prepared series in the current study are:

Series (a): PVDF-HFP:PMMA -PC:DEC (1:1)- x wt.% $LiClO_4$,
where x = 2, 4, 5, 7.5, 10

Series (b): PVDF-HFP:PMMA - 10 wt.% $LiClO_4$- x wt.% PC:DEC (1:1),
where x = 20, 30, 40, 50, 60

Series (c): PVDF-HFP:PMMA – 10 wt.% $LiClO_4$- 60 wt.% PC:DEC (1:1)- x wt.% Al_2O_3, where x = 0.5, 1, 2, 3, 4

To achieve the above objectives of the prepared gel polymer electrolyte system, it is necessary to understand the ion conduction mechanism, various physical characterization techniques such as X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), atomic force microscopy (AFM), impedance measurement, ion transport number, linear sweep voltammetry (LSV), cyclic voltammetry (CV), mechanical strength, etc. are must understand.

Therefore, following characterization with the above objectives of the thesis are discussed below.

- Gel polymer electrolytes system is synthesized by solution casting technique.
- The X-ray diffraction study to understand the increase or extent of amorphousity due to the addition of $LiClO_4$ salt, the addition of plasticizers, and dispersion of nano-fillers.
- Fourier transform infrared spectroscopy (FTIR) identifies the nature of bonding or complex formation after blending polymers, the addition of salt, plasticizers, and nano-fillers, and finally to understand the functional group present in samples.
- The change in the surface morphology with the change in compositions can be visualized by scanning electron microscopy (SEM) and atomic force microscopy (AFM).
- The thermal characterization is carried out to investigate the working temperature of the gel polymer electrolyte system for the batteries.
- Total ionic transport number (t_{ion}) was determined using Wagner's DC polarization technique to probe ionic nature.
- The electrochemical stability window and the cyclability of the present gel polymer electrolyte systems can be measured by linear sweep voltammetry (LSV) and cyclic voltammetry (CV) test.
- A mechanical study by a mechanical tester is a must to confirm the mechanical strength of the polymer electrolyte films.
- Electrical parameters were evaluated by using Electrochemical impedance spectroscopy (EIS) which is important for the measurement of electrical parameters such as bulk resistance, ionic conductivity, activation energy, dielectric properties, and electric modulus (bulk properties), and various relaxation processes in the gel polymer electrolyte system.
- Finally, the optimized gel polymer electrolyte films are selected as a separator in the fabrication of battery with a suitable anode and cathode material. The performance of the battery is studied by measuring the open-circuit voltage at no load and discharge characteristics at varying load conditions to estimate energy density, power density, etc. of the battery.

References

[1] C. Sequeira and A. Hooper, *Solid State Batteries*. Springer Netherlands, 1985.

[2] M. Z. A. Munshi and B. B. Owens, *Superionic Solids and Solid Electrolytes: Recent Trends*. Academic Press, New York, 1989, 1989.

[3] B. B. Owens and G. R. Argue, "High-Conductivity Solid Electrolytes: MAg_4I_5," *Science (80-.).*, vol. 157, no. 3786, pp. 308–310, 1967.

[4] Yung-Fang Yu Yao and J. T. Kummer, "Ion exchange properties of and rates of ionic diffusion in beta-alumina," *J. Inorg. Nucl. Chem.*, vol. 29, no. 9, pp. 2453–2475, Sep. 1967, doi: 10.1016/0022-1902(67)80301-4.

[5] R. Agrawal and R. K. Gupta, "Superionic Solids: Composite Electrolyte Phase - An Overview," *J. Mater. Sci.*, vol. 34, pp. 1131–1162, Mar. 1999, doi: 10.1023/A:1004598902146.

[6] M.Z.A.Munshi, "Handbook of Solid State Batteries and Capacitors." World Scientific, p. 740, 01-May-1995, doi: doi:10.1142/2385.

[7] A. Bunde, K. Funke, and M. D. Ingram, "Ionic glasses: History and challenges," *Solid State Ionics*, vol. 105, no. 1–4, pp. 1–13, Jan. 1998, doi: 10.1016/S0167-2738(97)00444-X.

[8] B. V. R. Chowdari and W. Wang, *Solid State Ionics*. WORLD SCIENTIFIC, 2000.

[9] J. N. Bradley and P. D. Greene, "Potassium iodide + silver iodide phase diagram. High ionic conductivity of KAg_4I_5," *Trans. Faraday Soc.*, vol. 62, no. 0, pp. 2069–2075, 1966, doi: 10.1039/TF9666202069.

[10] J. R. MacCallum and C. A. Vincent, Eds., *POLYMER ELECTROLYTE REVIEWS-I*, Elsevier A. Springer, 1987.

[11] S. Chandra, *Superionic solids: principles and applications*. Amsterdam, North Holland., 1981.

[12] M. Jacob, E. Hackett, and E. Giannelis, "From nanocomposite to nanogel polymer electrolytes," *J. Mater. Chem. - J. Mater. Chem.*, vol. 13, pp. 1–5, Dec. 2003, doi: 10.1039/b204458g.

[13] M. B. Armand, P. G. Bruce, M. Forsyth, B. Scrosati, and W. Wieczorek, "Polymer Electrolytes," *Energy Materials*. pp. 1–31, 09-Feb-2011, doi: doi:10.1002/9780470977798.ch1.

[14] R. J. Cava, F. Reidinger, and B. J. Wuensch, "Single-crystal neutron-diffraction study of AgI between 23° and 300°C," *Solid State Commun.*, vol. 24, no. 6, pp. 411–416, Nov. 1977, doi: 10.1016/0038-1098(77)91306-0.

[15] H. Ricker, "Solid Electrolytes. General Principles, Characterization, Materials, Applications. Herausgegeben von P. Hagenmuller und W. van Gool. Academic Press, New York 1978. XVII, 549 S., geb. $ 52.00," *Angew. Chemie*, vol. 91, no. 11, p. 947, Nov. 1979, doi: 10.1002/ange.19790911132.

[16] D. H. Rothman and S. Zaleski, "Lattice-gas models of phase separation: interfaces, phase transitions, and multiphase flow," *Rev. Mod. Phys.*, vol. 66, no. 4, pp. 1417–1479, Oct. 1994, doi: 10.1103/RevModPhys.66.1417.

[17] K. Funke, "Solid Electrolytes: Jump Relaxation and 'Universal' Dynamic Response," *MRS Proc.*, vol. 135, p. 43, 1988, doi: DOI: 10.1557/PROC-135-43.

[18] K. P. Padmasree, D. K. Kanchan, and A. R. Kulkarni, "Impedance and Modulus studies of the solid electrolyte system $20CdI_2$–$80[xAg_2O$–$y(0.7V_2O_5$–$0.3B_2O_3)]$, where $1 \leq x/y \leq 3$," *Solid State Ionics*, vol. 177, no. 5–6, pp. 475–482, Feb. 2006, doi: 10.1016/J.SSI.2005.12.019.

[19] J. P. Malugani and G. Robert, "Conductivite ionique dans les verres $LiPO_3LiX$ (X = I, Br, Cl)," *Mater. Res. Bull.*, vol. 14, no. 8, pp. 1075–1081, Aug. 1979, doi: 10.1016/0025-5408(79)90075-8.

[20] M. S. Jayswal, D. K. Kanchan, P. Sharma, and M. Pant, "The effect of PbI_2 on electrical conduction in Ag_2O-V_2O_5-B_2O_3 superionic glass system," *Solid State Ionics*, vol. 186, no. 1, pp. 7–13, Mar. 2011, doi: 10.1016/J.SSI.2011.01.016.

[21] O. L. Anderson and D. A. Stuart, "Calculation of Activation Energy of Ionic Conductivity in Silica Glasses by Classical Methods," *J. Am. Ceram. Soc.*, vol. 37, no. 12, pp. 573–580, Dec. 1954, doi: 10.1111/j.1151-2916.1954.tb13991.x.

[22] M. D. Ingram, M. A. Mackenzie, W. Müller, and M. Torge, "Cluster and pathways: a new approach to ion migration in glass," *Solid State Ionics*, vol. 28–30, pp. 677–680, Sep. 1988, doi: 10.1016/S0167-2738(88)80124-3.

[23] C. C. Liang, "Conduction Characteristics of the Lithium Iodide-Aluminum Oxide Solid Electrolytes," *J. Electrochem. Soc.*, vol. 120, no. 10, pp. 1289–1292, 1973.

[24] M. Nagai and T. Nishino, "Enhancement in conductivity for porous alumina-based AgI–Al_2O_3 composites by use of temperature and concentration gradient," *Solid State Ionics*, vol. 117, no. 3–4, pp. 317–321, Feb. 1999, doi: 10.1016/S0167-2738(98)00422-6.

[25] U. Lauer and J. Maier, "Conductivity enhancement and microstructure in AgCl/AgI composites," *Solid State Ionics*, vol. 51, no. 3–4, pp. 209–213, Apr. 1992, doi: 10.1016/0167-2738(92)90202-Z.

[26] J. T. Jow and J. Bruce Wagner, "The Effect of Dispersed Alumina Particles on the Electrical Conductivity of Cuprous Chloride," *J. Electrochem. Soc.*, vol. 126, no. 11, pp. 1963–1972, 1979.

[27] A. Bunde, W. Dieterich, and E. Roman, "Dispersed ionic conductors and percolation theory," *Phys. Rev. Lett.*, vol. 55, no. 1, pp. 5–8, Jul. 1985, doi: 10.1103/PhysRevLett.55.5.

[28] F. M. Gray, *Polymer Electrolytes Review -1*, Mac Callum. London: Elsevier, 1987.

[29] M. A. Ratner and D. F. Shriver, "Ion transport in solvent-free polymers," *Chem. Rev.*, vol. 88, no. 1, pp. 109–124, Jan. 1988, doi: 10.1021/cr00083a006.

[30] M. B. Armand, "Polymer Electrolytes," *Annu. Rev. Mater. Sci.*, vol. 16, no. 1, pp. 245–261, Aug. 1986, doi: 10.1146/annurev.ms.16.080186.001333.

[31] J. Y. Kim and S. H. Kim, "Ionic conduction behavior of network polymer electrolytes based on phosphate and polyether copolymers," *Solid State Ionics*, vol. 124, no. 1–2, pp. 91–99, Sep. 1999, doi: 10.1016/S0167-2738(99)00104-6.

[32] G. P. Pandey, S. A. Hashmi, and R. C. Agrawal, "Hot-press synthesized polyethylene oxide based proton conducting nanocomposite polymer electrolyte dispersed with SiO_2 nanoparticles," *Solid State Ionics*, vol. 179, no. 15–16, pp. 543–549, Jun. 2008, doi: 10.1016/J.SSI.2008.04.006.

[33] A. Karmakar and A. Ghosh, "Charge carrier dynamics and relaxation in (polyethylene oxide-lithium-salt)-based polymer electrolyte containing 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide as ionic liquid," *Phys. Rev. E*, vol. 84, no. 5, p. 51802, Nov. 2011, doi: 10.1103/PhysRevE.84.051802.

[34] S. D. Thompson, L. R. Jordan, and M. Forsyth, "Platinum electrodeposition for polymer electrolyte membrane fuel cells," *Electrochim. Acta*, vol. 46, no. 10–11, pp. 1657–1663, Mar. 2001, doi: 10.1016/S0013-4686(00)00767-2.

[35] T. Miyamoto and K. Shibayama, "Free-volume model for ionic conductivity in polymers," *J. Appl. Phys.*, vol. 44, no. 12, pp. 5372–5376, Dec. 1973, doi: 10.1063/1.1662158.

[36] M. Vogel and T. Torbrügge, "Ion and polymer dynamics in polymer electrolytes PPO-$LiClO_4$. I. Insights from NMR line-shape analysis," *J. Chem. Phys.*, vol. 125, no. 5, p. 54905, Aug. 2006, doi: 10.1063/1.2217945.

[37] D. E. Fenton, J. M. Parker, and P. V. Wright, "Complexes of alkali metal ions with poly(ethylene oxide)," *Polymer (Guildf).*, vol. 14, no. 11, p. 589, Nov. 1973, doi: 10.1016/0032-3861(73)90146-8.

[38] P. V Wright, "Electrical conductivity in ionic complexes of poly(ethylene oxide)," *Br. Polym. J.*, vol. 7, no. 5, pp. 319–327, Sep. 1975, doi: 10.1002/pi.4980070505.

[39] S. Chandra, S. B. Rai, P. K. Singh, K. Kumar, and A. Chandra, "On the correlation between the thermal and electrical transport in ionic conductors," *J. Phys. D. Appl. Phys.*, vol. 39, no. 16, pp. 3680–3683, 2006, doi: 10.1088/0022-3727/39/16/023.

[40] J. Y. Song, Y. Y. Wang, and C. C. Wan, "Review of gel-type polymer electrolytes for lithium-ion batteries," *J. Power Sources*, vol. 77, no. 2, pp. 183–197, Feb. 1999, doi: 10.1016/S0378-7753(98)00193-1.

[41] A. Arya and A. Sharma, "Polymer electrolytes for lithium ion batteries: a critical study," *Ionics (Kiel).*, vol. 23, pp. 497–540, Jan. 2017, doi: 10.1007/s11581-016-1908-6.

[42] M. Marcinek *et al.*, "Electrolytes for Li-ion transport – Review," *Solid State Ionics*, vol. 276, pp. 107–126, Aug. 2015, doi: 10.1016/J.SSI.2015.02.006.

[43] P. Sharma, "Study of conduction mechanism in PEO-PMMA polymer blend nano-composite electrolytes," The M.S.University of Baroda, Vadodara.

[44] J. Sharma, "Magnesium Ion Conducting Polymer Electrolytes For Solid-State Magnesium Batteries," University of Delhi, Delhi-110007, India, 2016.

[45] G. F.M., *Solid Polymer Electrolytes: Fundamentals and Technological Applications*. New York: VCH, 1991.

[46] M. H. Buraidah, L. P. Teo, S. R. Majid, and A. K. Arof, "Ionic conductivity by correlated barrier hopping in NH_4I doped chitosan solid electrolyte," *Phys. B Condens. Matter*, vol. 404, no. 8–11, pp. 1373–1379, May 2009, doi: 10.1016/J.PHYSB.2008.12.027.

[47] C. A. Angell, C. Liu, and E. Sanchez, "Rubbery solid electrolytes with dominant cationic transport and high ambient conductivity," *Nature*, vol. 362, no. 6416, pp. 137–139, 1993, doi: 10.1038/362137a0.

[48] A. Manuel Stephan, "Review on gel polymer electrolytes for lithium batteries," *Eur. Polym. J.*, vol. 42, no. 1, pp. 21–42, Jan. 2006, doi: 10.1016/J.EURPOLYMJ.2005.09.017.

[49] G. Feuillade and P. Perche, "Ion-conductive macromolecular gels and membranes for solid lithium cells," *J. Appl. Electrochem.*, vol. 5, no. 1, pp. 63–69, 1975, doi: 10.1007/BF00625960.

[50] S. Chintapalli and R. Frech, "Effect of Plasticizers on Ionic Association and Conductivity in the $(PEO)_9LiCF_3SO_3$ System," *Macromolecules*, vol. 29, no. 10, pp. 3499–3506, Jan. 1996, doi: 10.1021/ma9515644.

[51] G. B. Appetecchi and B. Scrosati, "A lithium ion polymer battery," *Electrochim. Acta*, vol.

43, no. 9, pp. 1105–1107, Apr. 1998, doi: 10.1016/S0013-4686(97)10117-7.

[52] G. B. Appetecchi, F. Croce, and B. Scrosati, "Kinetics and stability of the lithium electrode in poly(methylmethacrylate)-based gel electrolytes," *Electrochim. Acta*, vol. 40, no. 8, pp. 991–997, Jun. 1995, doi: 10.1016/0013-4686(94)00345-2.

[53] J. Y. Song, Y. Y. Wang, and C. C. Wan, "Conductivity Study of Porous Plasticized Polymer Electrolytes Based on Poly(vinylidene fluoride) A Comparison with Polypropylene Separators," *J. Electrochem. Soc.*, vol. 147, no. 9, p. 3219, 2000, doi: 10.1149/1.1393886.

[54] G. P. Pandey, R. C. Agrawal, and S. A. Hashmi, "Magnesium ion-conducting gel polymer electrolytes dispersed with nanosized magnesium oxide," *J. Power Sources*, vol. 190, no. 2, pp. 563–572, May 2009, doi: 10.1016/J.JPOWSOUR.2009.01.057.

[55] N.-S. Choi and J.-K. Park, "New polymer electrolytes based on PVC/PMMA blend for plastic lithium-ion batteries," *Electrochim. Acta*, vol. 46, no. 10, pp. 1453–1459, 2001, doi: https://doi.org/10.1016/S0013-4686(00)00739-8.

[56] A. Ponrouch, D. Monti, A. Boschin, B. Steen, P. Johansson, and M. R. Palacín, "Non-aqueous electrolytes for sodium-ion batteries," *J. Mater. Chem. A*, vol. 3, no. 1, pp. 22–42, 2015, doi: 10.1039/C4TA04428B.

[57] Z. H. Li, H. P. Zhang, P. Zhang, G. C. Li, Y. P. Wu, and X. D. Zhou, "Effects of the porous structure on conductivity of nanocomposite polymer electrolyte for lithium ion batteries," *J. Memb. Sci.*, vol. 322, no. 2, pp. 416–422, Sep. 2008, doi: 10.1016/J.MEMSCI.2008.05.074.

[58] B. Kumar and L. G. Scanlon, "Polymer-ceramic composite electrolytes," *J. Power Sources*, vol. 52, no. 2, pp. 261–268, Dec. 1994, doi: 10.1016/0378-7753(94)02147-3.

[59] B. Liang *et al.*, "Preparation and characterization of PEO-PMMA polymer composite electrolytes doped with nano-Al_2O_3," *Electrochim. Acta*, vol. 169, pp. 334–341, 2015, doi: https://doi.org/10.1016/j.electacta.2015.04.039.

[60] H. Zhang *et al.*, "Lithium bis(fluorosulfonyl)imide/poly(ethylene oxide) polymer electrolyte," *Electrochim. Acta*, vol. 133, pp. 529–538, 2014, doi: https://doi.org/10.1016/j.electacta.2014.04.099.

[61] S. Klongkan and J. Pumchusak, "Effects of Nano Alumina and Plasticizers on Morphology, Ionic Conductivity, Thermal and Mechanical Properties of PEO-$LiCF_3SO_3$ Solid Polymer Electrolyte," *Electrochim. Acta*, vol. 161, Apr. 2015, doi: 10.1016/j.electacta.2015.02.074.

[62] M. Kumaravadivel, J. Malathi, M. Hema, and S. Pandian, *Solid State Ionics: New Materials for Pollution Free Energy Devices*. Singapore: World Scientific, 2008.

[63] S. Ibrahim and M. Johan, "Thermolysis and Conductivity Studies of Poly(Ethylene Oxide) (PEO) Based Polymer Electrolytes Doped with Carbon Nanotube," *Int. J. Electrochem. Sci.*, vol. 7, pp. 2596–2615, Mar. 2012.

[64] G. Chiodelli, P. Ferloni, A. Magistris, and M. Sanesi, "Ionic conduction and thermal properties of poly (ethylene oxide)-lithium tetrafluoroborate films," *Solid State Ionics*, vol. 28–30, pp. 1009–1013, 1988, doi: https://doi.org/10.1016/0167-2738(88)90321-9.

[65] L. R. A. K. Bandara, M. A. K. L. Dissanayake, and M. B. E., *"Solid State Ionics - New Developments*. Singapore: World Scientific, 1996.

[66] S. Rajendran, M. R. Prabhu, and M. U. Rani, "Li ion conduction behavior of hybrid polymer electrolytes based on PEMA," *J. Appl. Polym. Sci.*, vol. 110, no. 5, pp. 2802–2806, Dec. 2008, doi: 10.1002/app.28701.

[67] M. Watanabe, M. Kanba, K. Nagaoka, and I. Shinohara, "Ionic conductivity of hybrid films based on polyacrylonitrile and their battery application," *J. Appl. Polym. Sci.*, vol. 27, no. 11,

pp. 4191–4198, Nov. 1982, doi: 10.1002/app.1982.070271110.

[68] H.-R. Jung and W.-J. Lee, "Electrochemical characteristics of electrospun poly(methyl methacrylate)/polyvinyl chloride as gel polymer electrolytes for lithium ion battery," *Electrochim. Acta*, vol. 58, pp. 674–680, Dec. 2011, doi: 10.1016/J.ELECTACTA.2011.10.015.

[69] S. R. Sivakkumar, D. R. MacFarlane, M. Forsyth, and D.-W. Kim, "Ionic Liquid-Based Rechargeable Lithium Metal-Polymer Cells Assembled with Polyaniline/Carbon Nanotube Composite Cathode," *J. Electrochem. Soc.*, vol. 154, no. 9, p. A834, 2007, doi: 10.1149/1.2750443.

[70] M. Alamgir and K. M. Abraham, "Room temperature rechargeable polymer electrolyte batteries," *J. Power Sources*, vol. 54, no. 1, pp. 40–45, Mar. 1995, doi: 10.1016/0378-7753(94)02037-4.

[71] D. Saikia and A. Kumar, "Ionic conduction in P(VDF-HFP)/PVDF–(PC + DEC)–$LiClO_4$ polymer gel electrolytes," *Electrochim. Acta*, vol. 49, no. 16, pp. 2581–2589, 2004, doi: https://doi.org/10.1016/j.electacta.2004.01.029.

[72] F. Groce, F. Gerace, G. Dautzemberg, S. Passerini, G. B. Appetecchi, and B. Scrosati, "Synthesis and characterization of highly conducting gel electrolytes," *Electrochim. Acta*, vol. 39, no. 14, pp. 2187–2194, 1994, doi: https://doi.org/10.1016/0013-4686(94)E0167-X.

[73] B. Lalia and S. Sekhon, "Polymer Electrolytes Based on Room Temperature Ionic Liquid: 2,3-Dimethyl-1-octylimidazolium Triflate," *J. Phys. Chem. B*, vol. 109, pp. 16539–16543, Oct. 2005, doi: 10.1021/jp051673c.

[74] M. Deka and A. Kumar, "Enhanced electrical and electrochemical properties of PMMA–clay nanocomposite gel polymer electrolytes," *Electrochim. Acta*, vol. 55, no. 5, pp. 1836–1842, Feb. 2010, doi: 10.1016/J.ELECTACTA.2009.10.076.

[75] S. Ramesh and L. C. Wen, "Investigation on the effects of addition of SiO_2 nanoparticles on ionic conductivity, FTIR, and thermal properties of nanocomposite PMMA–$LiCF_3SO_3$–SiO_2," *Ionics (Kiel).*, vol. 16, no. 3, pp. 255–262, 2010, doi: 10.1007/s11581-009-0388-3.

[76] B. Kumar and L. G. Scanlon, "Polymer–ceramic composite electrolytes: conductivity and thermal history effects," *Solid State Ionics*, vol. 124, no. 3–4, pp. 239–254, Sep. 1999, doi: 10.1016/S0167-2738(99)00148-4.

[77] Y.-J. Lim, Y.-H. An, and N.-J. Jo, "Polystyrene-Al_2O_3 composite solid polymer electrolyte for lithium secondary battery," *Nanoscale Res. Lett.*, vol. 7, p. 19, Jan. 2012, doi: 10.1186/1556-276X-7-19.

[78] F. Croce *et al.*, "Physical and Chemical Properties of Nanocomposite Polymer Electrolytes," *J. Phys. Chem. B*, vol. 103, no. 48, pp. 10632–10638, Dec. 1999, doi: 10.1021/jp992307u.

[79] Z. Li, G. Su, D. Gao, X. Wang, and X. Li, "Effect of Al_2O_3 nanoparticles on the electrochemical characteristics of P(VDF-HFP)-based polymer electrolyte," *Electrochim. Acta*, vol. 49, no. 26, pp. 4633–4639, Oct. 2004, doi: 10.1016/J.ELECTACTA.2004.05.018.

[80] D. Saikia and A. Kumar, "Ionic transport in P(VDF-HFP)–PMMA–$LiCF_3SO_3$–(PC + DEC)–SiO_2 composite gel polymer electrolyte," *Eur. Polym. J.*, vol. 41, no. 3, pp. 563–568, Mar. 2005, doi: 10.1016/J.EURPOLYMJ.2004.10.029.

[81] P. M. Shanthi, P. J. Hanumantha, T. Albuquerque, B. Gattu, and P. N. Kumta, "Novel Composite Polymer Electrolytes of PVdF-HFP Derived by Electrospinning with Enhanced Li-Ion Conductivities for Rechargeable Lithium–Sulfur Batteries," *ACS Appl. Energy Mater.*, vol. 1, no. 2, pp. 483–494, Feb. 2018, doi: 10.1021/acsaem.7b00094.

[82] H. Verma, K. Mishra, and D. K. Rai, "Sodium ion conducting nanocomposite polymer electrolyte membrane for sodium ion batteries," *J. Solid State Electrochem.*, vol. 24, no. 3, pp. 521–532, 2020, doi: 10.1007/s10008-019-04490-4.

[83] J. Li, R. Hu, H. Zhou, S. Tao, and Y. Wang, "Nano-SiO_2@PMMA-doped composite polymer PVDF-HFP/PMMA/PEO electrolyte for lithium metal batteries," *J. Mater. Sci. Mater. Electron.*, vol. 31, no. 3, pp. 2708–2719, 2020, doi: 10.1007/s10854-019-02811-x.

[84] L. Ye and Z. Feng, *Polymer Electrolytes – Fundamentals and Applications*, C. Sequeir. Oxford: Woodhead Publishing Limited, 2010.

[85] Y. Abu-Lebdeh and I. Davidson, *Nanotechnology for Lithium-Ion Batteries*. Springer US, 2013.

[86] B. E. Conway, *Electrochemical Supercapacitors-Scientific Fundamentals and Technological Applications*. Springer US, 1999.

[87] S. Chandra, *Superionic solids: Principles and applications*. Amsterdam: North Holland, 1981.

[88] A. González, E. Goikolea, J. A. Barrena, and R. Mysyk, "Review on supercapacitors: Technologies and materials," *Renew. Sustain. Energy Rev.*, vol. 58, pp. 1189–1206, May 2016, doi: 10.1016/J.RSER.2015.12.249.

[89] M. Kumar, "Ion Dynamic Studies of Few Sodium and Ammonium salt Containing Polymer Electrolyte Systems," Banaras Hindu University,Varanasi, 2014.

[90] O. Z. Sharaf and M. F. Orhan, "An overview of fuel cell technology: Fundamentals and applications," *Renew. Sustain. Energy Rev.*, vol. 32, pp. 810–853, Apr. 2014, doi: 10.1016/J.RSER.2014.01.012.

[91] A. Kirubakaran, S. Jain, and R. K. Nema, "A review on fuel cell technologies and power electronic interface," *Renew. Sustain. Energy Rev.*, vol. 13, no. 9, pp. 2430–2440, Dec. 2009, doi: 10.1016/J.RSER.2009.04.004.

[92] H. Gerischer, M. E. Michel-Beyerle, F. Rebentrost, and H. Tributsch, "Sensitization of charge injection into semiconductors with large band gap," *Electrochim. Acta*, vol. 13, no. 6, pp. 1509–1515, Jun. 1968, doi: 10.1016/0013-4686(68)80076-3.

[93] H. Tributsch, "Reaction of excited chlorophyll molecules at electrodes and in photosynthesis*," *Photochem. Photobiol.*, vol. 16, no. 4, pp. 261–269, Oct. 1972, doi: 10.1111/j.1751-1097.1972.tb06297.x.

[94] "https://en.wikipedia.org/wiki/Dye-sensitized_solar_cell." .

[95] B. Muthuraaman, G. Will, H. Wang, P. Moonie, and J. Bell, "Increased charge transfer of Poly (ethylene oxide) based electrolyte by addition of small molecule and its application in dye-sensitized solar cells," *Electrochim. Acta*, vol. 87, pp. 526–531, Jan. 2013, doi: 10.1016/J.ELECTACTA.2012.09.030.

[96] J. Gong, K. Sumathy, Q. Qiao, and Z. Zhou, "Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends," *Renew. Sustain. Energy Rev.*, vol. 68, pp. 234–246, Feb. 2017, doi: 10.1016/J.RSER.2016.09.097.

[97] G. A. Niklasson and C. G. Granqvist, "Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these," *J. Mater. Chem.*, vol. 17, no. 2, pp. 127–156, 2007, doi: 10.1039/B612174H.

[98] P. R. Somani and S. Radhakrishnan, "Electrochromic materials and devices: present and future," *Mater. Chem. Phys.*, vol. 77, no. 1, pp. 117–133, Jan. 2003, doi: 10.1016/S0254-

0584(01)00575-2.

[99] C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials*. Amsterdam: Elsevier, 1995.

[100] V. K. Thakur, G. Ding, J. Ma, P. S. Lee, and X. Lu, "Hybrid Materials and Polymer Electrolytes for Electrochromic Device Applications," *Adv. Mater.*, vol. 24, no. 30, pp. 4071–4096, Aug. 2012, doi: 10.1002/adma.201200213.

[101] H. Peng *et al.*, "Electrically Driving Sensors Based on Polymer," *Polym. Mater. Energy Electron. Appl.*, pp. 287–323, Jan. 2017, doi: 10.1016/B978-0-12-811091-1.00008-2.

[102] F. Opekar and K. Štulík, "Electrochemical sensors with solid polymer electrolytes," *Anal. Chim. Acta*, vol. 385, no. 1–3, pp. 151–162, Apr. 1999, doi: 10.1016/S0003-2670(98)00583-2.