

Chapter 1

CHAPTER 1

INTRODUCTION

Energy demand and intriguing requisite for clean energy steer mankind to look for efficient energy storage systems owing to the escalation of global environmental issues. Alternative energy sources have been on focus rather than relying on recurrent energy sources such as solar or wind energy. Hence establishing high-performing energy storage systems from renewable sources is the pressing priority to encounter the escalating energy challenge. The strategy of energy storage systems is in the level of infancy to offer ample energy at an affordable cost. This state of affairs has stimulated interest in clean energy storage technologies. A viable power solution for our modern electronic gadgets thrive researchers to innovate effective energy storage and the battery has a pivotal role which helps in the replacement of fossil fuels with renewable resources.

1.1 Energy Storage and Batteries

Energy storage has a crucial part to play between the utilization of natural energy and recompensating the energy requirements. Batteries can store energy in an electrochemical way. A battery is typically composed of an anode, a cathode, an electrolyte for ion conduction, and also a separator for insulating the two electrodes. State-of-the-art electrochemical storage devices employ liquid electrolytes for ion transport. The electrolyte is the key component that has to be explored to improve the performance of a battery since the potential depends on the transfer of ions within this electrolyte. Presently, the development of batteries is encountering bottlenecks, cramped by safety threats like leakage leading to explosions due to the disadvantages of the liquid electrolytes. The development of new materials for the preparation of solid electrolytes is carried out to improve the chemistry of batteries [1]. To explore the possibilities of new battery chemistry for safe battery technology, the research heads to understanding the interplay between the new electroactive bio-based materials as solid electrolytes to replace the current organic liquid and gel electrolytes. This leads to thinner electrolytes and much more compact packing with comparatively better performance in energy devices at a reduced environmental cost [2–4].

1.2 Solid Electrolytes

Efforts have been made to replace the existing organic liquid electrolyte with a high-performance and safe solid electrolyte, stable over a wide range of temperatures. A potential solid electrolyte should possess high ionic conductivity in the range of 0.1mS/cm with

negligible electronic conductivity. It must also have good electrochemical stability in the working potentials and good chemical stability within the operating temperature of the battery. The electrolyte materials must also be biodegradable, non-toxic, nonflammable, and also affordable [5, 6]. Solid electrolytes are membranes developed from blending metal salt in an appropriate polymer host which possesses ionic conduction properties, flexibility, lightweight, and a solvent-free system and advantages over liquid electrolytes are shown in Figure 1.1. Many polymers such as polyethylene oxide, poly (methyl methacrylate), polyvinyl alcohol, polyvinyl pyrrolidone, and polyacrylonitrile have been employed for the preparation of solid electrolytes [7–11]. Their noxious nature towards the environment stimulated the researchers to shift their interest to bio-based electrolyte materials.

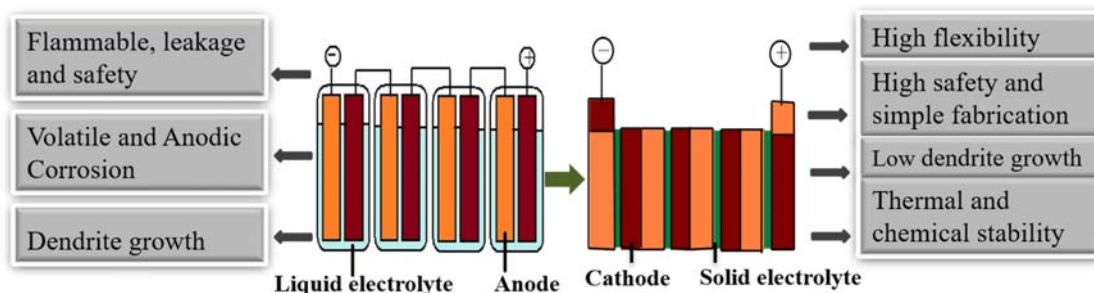


Figure 1.1: Advantages of Liquid Electrolyte over Solid Electrolyte

Over the past few decades, biopolymers have gained stupendous interest because of their remarkable properties including biodegradability, chemically harmless, low cost, and sustainability. Apart from polymer electrolytes, natural polymers have gained interest due to their easy availability, cost-effectiveness, sustainability, and environment-friendly nature [12, 13]. Natural or biopolymers are polymers obtained from naturally renewable sources such as alginate, chitosan, cellulose acetate, pectin, agar-agar, carrageenan, and tamarind seed polysaccharide [14–22]. Substantial research has been carried out on these biopolymers from synthesis techniques to the fabrication of cells. These materials possess the ease of fabrication, and safety along with competent ionic conductivity compared with synthetic polymers.

In this pursuit, biomass-based materials have gained interest in tackling global environmental issues for a prospective future. Former analysis has indicated that bio-based materials offer unique characteristics as their abundance in nature, their ability to form

membranes and has the ability to accommodate a wide range of charge carrier ions as salts in the host matrix. Primarily, these biomass-based materials such as plant seeds, tubers, cereal starch, and plant leaves have applications focused on pharmaceutical, agricultural, biological, food packaging, and wound healing [23–27]. Their properties provoked scientists to probe into the natural biomass-based materials to prepare bio-membranes with better electrochemical properties for energy storage devices like batteries [28–30].

1.3 Biopolymer electrolytes: An Insight

Biopolymers are materials that are derived from trees, plants, animals, or bio-synthesized by microorganisms. These polymers originated from plant biomass and essentially constitute repeating units constituting carbon in their chain. Owing to their abundance, renewability, non-toxic nature, and biodegradability these biopolymers possess a wide range of applications in bio-medical, agricultural, cosmetics, and also in industrial applications.

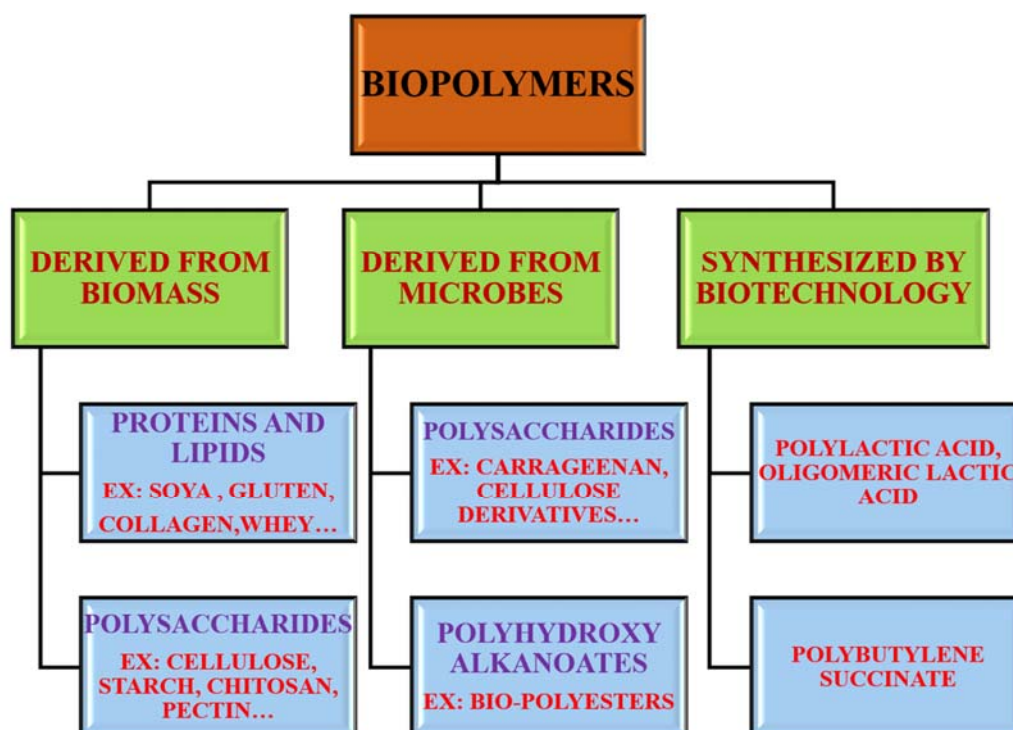


Figure 1.2: Classification of Biopolymers

1.3.1 Classification of Biopolymers

Biopolymers are broadly classified based on various scales as seen in Figure 1.2.

Based on their origin as

1. Natural biopolymers – biosynthesized by living organisms.
2. Synthetic biopolymers – obtained from natural renewable materials by biotechnology.
3. Microbial biopolymers – biosynthesized by microbes.

Based on the monomeric units as

1. Polysaccharides – carbohydrate chains. Ex. Starch, cellulose.
2. Proteins – amino acid chains. Ex. Collagen, fibrin.
3. Polynucleotides – nucleic acid chains. Ex. DNA, RNA.

1.4 Choice of the host biomass for the bio-electrolyte

Former research has evidenced the innate properties of biopolymers that are biodegradable and eco-friendly in nature. This provoked the desire to emulate them with diverse amalgamation techniques to meet the present criteria of the solid electrolyte with enhanced flexibility, mechanical and thermal stability, sufficient electrochemical stability, and virtuous ionic conductivity with no spillage or internal shortening in the cell. Owing to the above nature, biomass materials directly from natural sources are considered a propitious candidature with environmental compassion as an added advantage for battery devices. Hence, the contemporary analysis aims to develop solid electrolytes from three different biomass such as Corn Silk – a biowaste, seaweed – *Sargassum Muticum*, and plant exudate – *Salmalia Malabarica* gum and to investigate their compatibility in fabricating ion-conducting batteries with magnesium, lithium, and ammonium salts as their ionic dopants.

1.4.1 Corn-based biomass

Zea mays otherwise known as Corn is a cereal grown in many parts of the world in abundance. Corn is traditionally known for its medicinal value. Various parts and derivatives of Corn such as Corn Husk, Corn silk, Corn cob, Corn starch, Cornstalk, Corn straw, Corn kernel, and Corn leaves have been known for treating diabetes, possess anti-inflammatory

Properties [31, 32], anti-malarial, antioxidant, anticancer properties [33, 34], and antitumor activities [35–37]. Generally considered as a waste by-product, they possess many functional components beneficial and safe to mankind which are now the topic of interest. Notwithstanding the benefits of Corn silk considered a bio-waste has been found to possess potential moieties facilitating them as a biorefinery to produce green energy. The chemical composition of certain bioactive components present in different parts of Corn is schematically represented in Figure 1.3 [31, 38, 39].

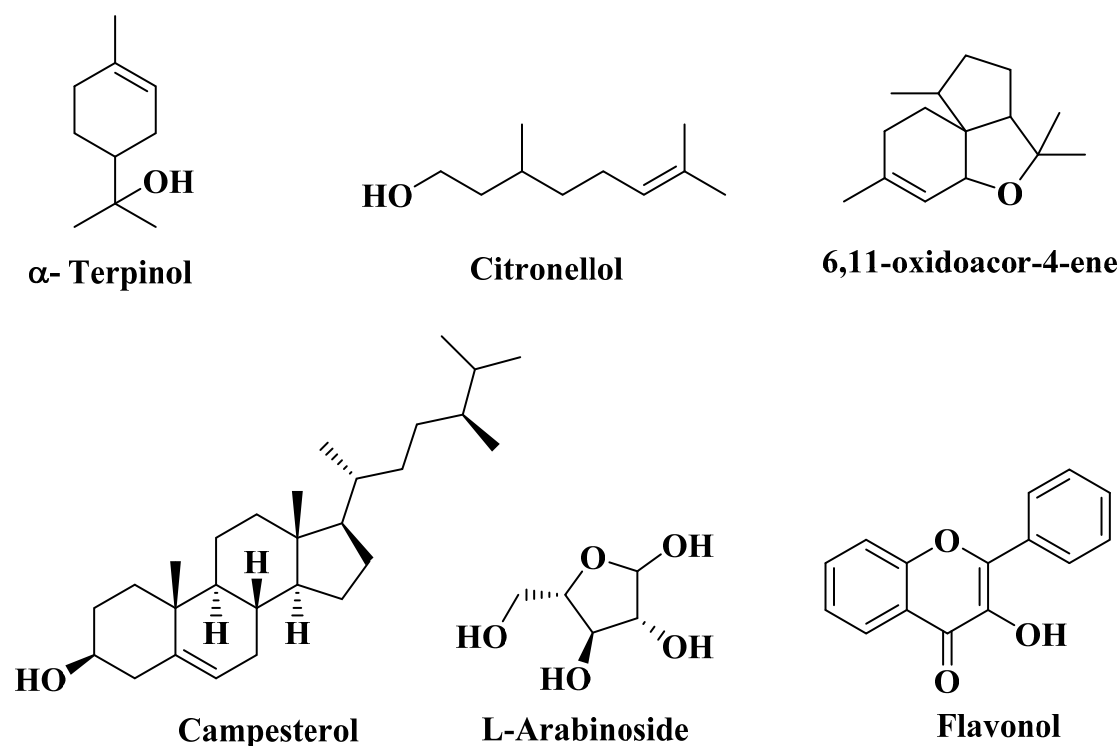


Figure 1.3: Bioactive Components present in various parts of Corn plant

Strenuous efforts have been accomplished to isolate many compounds from corn and to investigate biofuel and electrochemical energy storage applications [40]. The presence of potentially electroactive components like polysaccharides, flavonoids, and lignocellulosic compounds in the corn silk extract provoked the idea to explore the natural electrochemical properties. Thus, an attempt has been made to prepare a Corn Silk bio-membrane (CSBP) by blending Corn Silk Extract (CSE) with Polyvinyl Alcohol (PVA). The present investigation then aims to develop solid bio-electrolyte from CSBP with magnesium

chloride, lithium chloride, and ammonium formate as the ionic dopant. The aforesaid bio-electrolyte has been characterized and thus furnishes scope for a clean environment.

1.4.2 Seaweed-based biomass

To counterbalance the global crisis scenario and for the development of sustainable and clean energy, there is an escalating demand for new biomass-based materials. These bio-based materials are exploited for their application in various pharmaceutical, food, and cosmetic fields. *Sargassum Muticum* is an invasive seaweed that has been recognized as a source to produce biofuel because of its abundant nature and carbon-neutral emissions [41]. Hence the feasibility of implementing biomass – to – biofuel feasibility has been investigated. This seaweed *Sargassum Muticum* is an excellent source of potential electroactive metabolites such as proteins, polysaccharides, and many polyphenols, phlorotannin, and fucoidans [42]. These biologically active functionalities enable the seaweed to exhibit anti-inflammatory, antioxidant, antimicrobial, antitumor, anticancer, and even more properties [43–47] and are listed below in Figure 1.4.

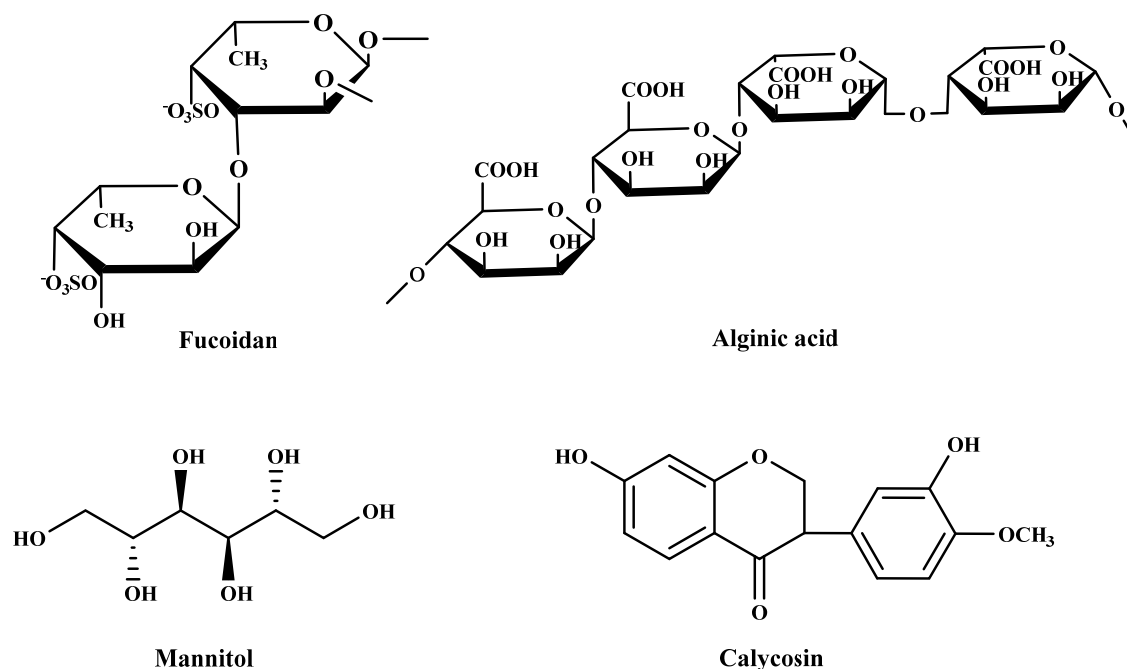


Figure 1.4: Bioactive Components present in Seaweed

A plethora of analyses and studies on the components of seaweed highlighted its continued interest in concerning to their application as bio-electrolyte for implementation in batteries as a biomass-energy source. Hence in our present investigation, a solid bio-membrane has been prepared from the ethanol extract of *Sargassum Muticum* by blending the seaweed extract with polyvinyl alcohol (PVA) with varying weight percentages and optimizing them. An ion conducting battery has been fabricated from each of the prepared bio-electrolyte with the ionic dopant salts Magnesium chloride, Lithium chloride, and Ammonium formate and characterized for better performance.

1.4.3 Plant biomass – *Salmalia Malabarica gum*

Plant gums with remarkable properties such as biocompatibility, biodegradability, and non-toxic nature with structural modification ability have propelled the research interests for electrolyte applications [48–55]. These biomass-based renewable materials possess plant gum polysaccharides that find their application in food packaging, wound healing, drug delivery, cosmetics, and medical fields [56–61].

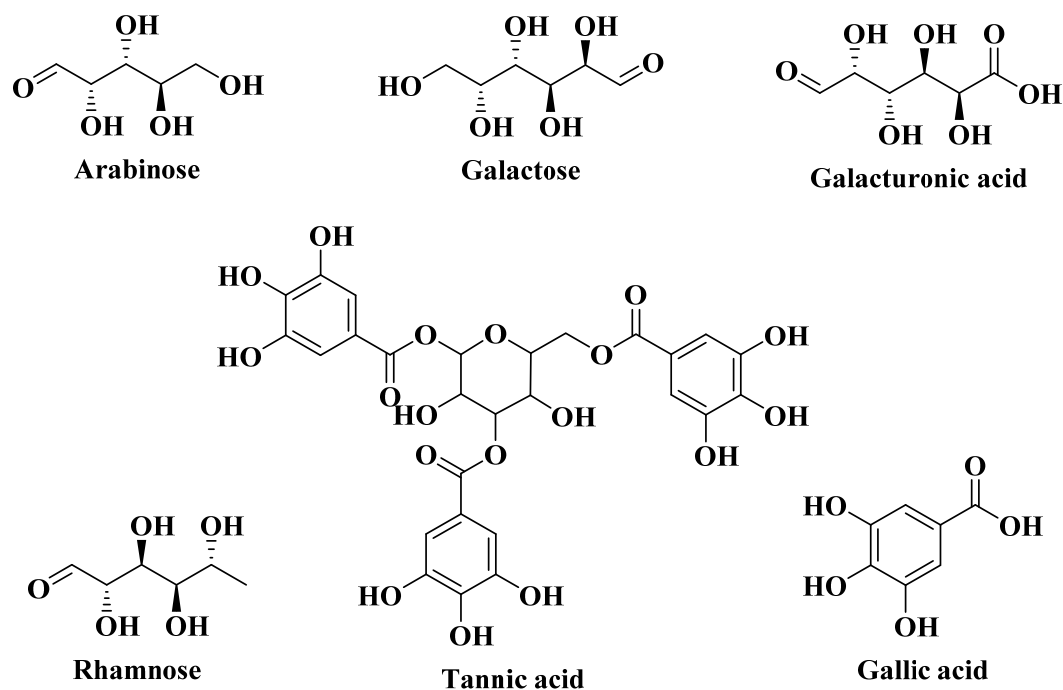


Figure 1.5: Bioactive components present in *Salmalia Malabarica gum*

Natural gums are generally heterogeneous and hence produce simple sugars on hydrolysis. Their structural components constitute carbohydrate polymers, thus making them electroactive with the hydroxyl, carboxyl, and carbonyl functional groups. This enables them to accommodate ionic dopant salts in their polymer host matrix and some of which are shown in Figure 1.5.

Plant gums are composed of polymers with different covalently bonded polysaccharides, which have been found to be an abundant industrial raw material due to their ease of chemical alterations [62]. As compared to biopolymers, gums are anionic functional moieties with greater charge density, thus attracting positive metal ions into the polymer structure [63]. Eventually, these metal ions contribute to the ionic conductivity of the gum-based membranes. Thus bio-membranes prepared from *Salmalia Malabarica* Gum (SMG) are then doped with magnesium chloride, lithium chloride, and ammonium formate salts to develop the respective metal ion conducting bio-electrolytes. The prepared bio-electrolytes are further characterized and studied for electrochemical applications.

1.5 Essential attributes of Solid Bio-Electrolyte for Electrochemical Devices

Preliminary investigations have ascertained the high salt-tolerant capacity and strong hydrogen-forming ability of the biomass-derived materials to their varied structural components and their ease of functional modifications. Solid bio-electrolytes are solvent-free thin membranes prepared by dissolving ionic salts into the host matrix [64, 65]. Solid electrolytes exhibit competent ionic conductivity, and high energy density with a wide electrochemical stability window, and are also compact and leakproof [66]. The biomass-derived materials are highly flexible and are cast into thin films which provide a good electrode-electrolyte interface during the fabrication of batteries. In this perspective and also considering their renewability, biodegradability, and non-lethal nature, biomass-derived materials are explored in the present investigation.

The following are the criteria for the bio-electrolyte to be a potential candidate for electrochemical devices.

- Bio-electrolyte should possess good mechanical and electrochemical stability.
- Bio-electrolyte must have low activation energy at their vacant and occupied sites in their structure matrix, hence hopping of ions from one site to the adjacent site is possible.

- Bio-electrolyte should exhibit good flexibility and ease of fabrication.
- Bio-electrolyte must acquire virtuous ionic conductivity.
- Bio-electrolyte should have a high cationic transference number.
- Bio-electrolyte should hold a good electrode-electrolyte interface.
- The biomass-derived materials must have high-metal salt tolerance and possess a large number of polar groups (N, O, S, etc.,) in their structure.
- Bio-electrolyte must maintain a low glass transition temperature for increased segmental motion in the host matrix.
- The biomass-derived materials should possess a framework structure through which the hopping mechanism of ion migration is possible.
- The biomaterials used for the preparation of bio-electrolyte should be biodegradable, non-lethal, and eco-friendly.
- The Bio-based materials must be cost-effective and abundant in nature.

1.6. Choice of salts for the bio-electrolytes

1.6.1 Criteria of salt for solid bio-electrolyte

As an ionic charge carrier, the added salt into the bio-electrolyte composition influences its electrolytic properties like ionic conductivity, thermal stability, and amorphous nature. The prerequisites for salt for the preparation of solid bio-electrolyte are:

- The lattice energy of the salt should be low for easy dissociation into the host matrix.
- The salt should compose of a large size anion and a smaller cation.
- The salt should be completely soluble in the solvent used.
- The anion of the salt should be stable during oxidative decomposition at the cathode.
- The salt should be thermally and chemically stable throughout the reaction.
- They should be also cost-effective and non-toxic.

1.6.2 Magnesium salt as conducting species for the bio-electrolytes

Magnesium has been found in abundance and is also safe to handle during the fabrication of batteries. They are also cost-effective and have a melting point of 649°C. The divalent property of Mg^{2+} provides them a high theoretical volumetric capacity of 3832 mAh.cm⁻³, compared to Li^+ of 2062 mAh.cm⁻³ [67]. The main advantage of employing magnesium for energy storage applications includes the chemical and electrochemical stability of magnesium metal anode and its high coulombic efficiency [68]. The required properties of a polymer electrolyte such as minimum interfacial impedance, high thermal stability, and neglectable electronic conductivity also enable the choice of magnesium metal as a potential applicant for the present work. In view of all the above facts, magnesium is considered the best alternative for next-level battery applications.

1.6.3 Lithium salt as conducting species for the bio-electrolytes

Lithium salts are the most preferred choice of ionic dopants owing to their small size and hence high gravimetric coulombic density, also a wide electrochemical stability window [69, 70]. Lithium chloride is a choice of ionic dopant due to its electropositive nature to give up electrons at ease to form Li^+ ions and its lightweight. They are also a promising material for the fabrication of high energy density batteries due to their high specific capacity of 3860 AhKg⁻¹. Lithium also possesses a high electrochemical reduction potential of -3.045 V and low activation energy. This also facilitates easy dissociation of the salt into the bio-host matrix.

1.6.4 Ammonium salt as conducting species for the bio-electrolytes

Proton conductors for solid bio-electrolytes consist of the mobile charge providers such as H^+ , NH_4^+ etc., H^+ ions are smaller in size and hence can be easily intercalated between the host of the bio-host matrix [71, 72]. Ammonium formate is a choice of ionic dopant in the present study. The ionic radii of H^+ are approximately 0.84fm [73] making it best suitable for intercalation into the layer matrix of the biomaterial structure. They are also electrochemically decomposed even at 1 to 2 V which additionally makes them suitable for proton battery fabrication [74–76]. Other advantages are their low cost, non-lethal nature, and safe handling process [77].

1.7 Ionic Transport Mechanism in Bio-Electrolyte

Ionic conduction is considered to be the fundamental characteristic considered for the evaluation of membranes as a candidature for electrochemical devices like batteries. The transport of ions in these biopolymers or any bio-based materials occurs through the segmental motion of the molecular segments in the structure of the host. The conduction mechanism is dependent on the number of free charge carriers, mobility of the charge carriers, the salt-tolerant capacity of the biomass-derived material to accommodate the charge carriers, the dielectric constant of the host biomaterial and the amorphous nature of the prepared bio-electrolyte. The ionic conductivity of the bio-electrolyte is dependent on the amorphous nature of the membranes owing to the increase in chain mobility. This enables the metal ions to move between the coordinating sites of the biomaterial structure either through inter-chain hopping or intra-chain hopping mechanism as shown in Figure 1.6.

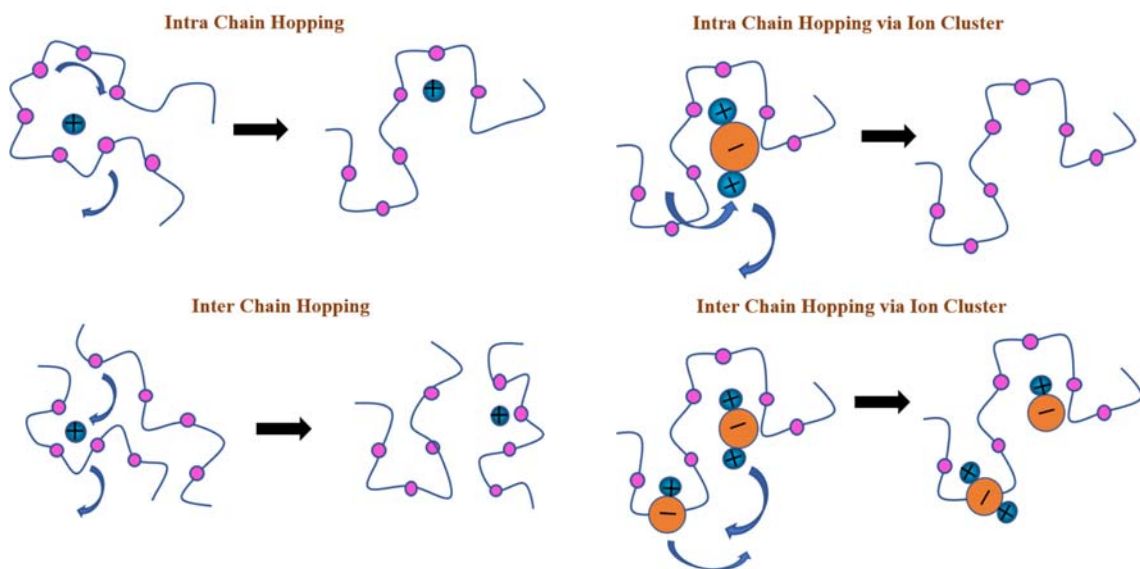


Figure 1.6: Ionic conduction in solid electrolyte by hopping mechanism

Initially, the crystalline nature of the bio-membrane prepared from the bio-based material has been found to be high, which is then suppressed by the inclusion of the ionic dopant into their structural matrix due to the plasticizing effect of the added salts. The mobility of the cations causes an increase in the conducting nature of the membrane by enhancing ionic diffusion [78]. In this regard, charge carriers curtail the movement of the ionic providers by preferably choosing them with a bulkier anion. The glass transition temperature displays the flexibility of the bio-membranes which enables the ease of the segmental motion of the bio-host backbone. In this perspective, a low glass transition temperature indicates the transition from the glassy state to a low energy rubbery state of the prepared bio-electrolyte which propels the ionic conductivity of the membranes [79].

In the proton conduction process, H^+ hops from one coordination site to another across the membrane composition. The H^+ produced from the added ammonium salt adheres to the ionic site of the functional group and then hops to the other coordination site. The proton from the bio-based material also contributes to the ionic conductivity of the bio-electrolyte membrane [80].

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