

Biopolymers as Solid Polymer Electrolytes: Advances, Challenges, and Future Prospects

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Abstract

Biopolymer electrolytes have emerged as a promising alternative to conventional synthetic materials for the development of electrolyte in electrochemical devices. These materials, derived from natural polymers, offer several advantages over synthetic polymer including biodegradability, environmental sustainability, and the potential for cost-effective production. This review provides a comprehensive overview of the current advancements in biopolymer electrolytes, focusing on their application in electrolyte thin films. The discussion encompasses various types of biopolymers, such as cellulose, chitosan, starch, pectin and their composites, which have been explored for their ionic conductivity, mechanical stability, and electrochemical performance. Key factors influencing the performance of biopolymer electrolytes, including polymer modification, ion transport mechanisms, and the incorporation of plasticizers and fillers, are critically analyzed. The review also highlights the challenges associated with the integration of biopolymer electrolytes in electrochemical devices, such as batteries, supercapacitors, and fuel cells, and explores potential strategies for overcoming these obstacles. Finally, the future outlook for biopolymer electrolyte-based thin films is discussed, emphasizing the need for further research to optimize their properties and expand their applications in next-generation energy storage and conversion systems.

Keywords- Biopolymers, Supercapacitors, Fuel cells, Solid polymer electrolytes (SPEs).

1. Introduction

Polymer electrolytes play a critical role in the fabrication of a wide range of electrochemical devices (Aaliya et al., 2021; Payne, 2007; Wang et al., 2021). Nowadays, liquid electrolytes are used in the majority of commercial electrochemical devices (Yue et al., 2016; Sun et al., 2017). But compared to liquid electrolytes, solid polymer electrolytes (SPEs), which are classified as synthetic polymers, have a number of benefits, including a higher energy density (Chiappone et al., 2011), more flexible configurations (Jian et al., 2020), enhanced safety (Xu et al., 2020), higher operating temperatures (Shah et al., 2024), and the removal of electrolyte leakage (Hallinan and Balsara, 2013). Among synthetic polymer electrolytes, metal salt complexes with high molecular weight polymers like polyethylene oxide (PEO) are the most extensively studied (MacCallum and Vincent, 1987; Gray, 1991; Kato et al., 2016). Despite their potential, PEO-based solid polymer electrolytes suffer from low ionic conductivity ($\sim 10^{-7}$ S/cm) at ambient temperature, limiting their practical application (Steinbüchel, 2003; Xue et al., 2015). As a result, several other synthetic polymers, including polymethyl methacrylate (PMMA), polyacrylonitrile (PAN), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP), have been explored for use in electrolyte applications (Chandra and Rustgi, 1998; Özdemir and Güner, 2007;

dos Santos and Lena, 2013; D'Amelia et al., 2014;). The environmental pollution caused by synthetic polymers, has become a significant concern that hinders use of these polymers (Rayung et al., 2020). Alongside environmental issues, the rising cost of fossil fuel-derived products has prompted researchers to shift their focus toward biodegradable polymers. Biopolymers, which are categorized under natural polymers, have become a major area of research interest. Since their introduction in the 1980s, a wide range of biodegradable polymers has been synthesized (Dumitriu, 2004; Finkenstadt and Willett, 2005; Smalley, 2005; Rees, 2012; Stephen and Phillips, 2016), with the primary goal of developing stable biopolymeric systems with excellent electrical and mechanical properties.

Biopolymer electrolytes (BPEs) are solid ionic conductors created by dissolving salts into high molecular weight polymers. They can be produced in semi-solid or solid form using cost-effective and reliable processes (Finkenstadt, 2005; Habibi and Lucia, 2012). BPEs exhibit several advantageous properties, high energy density, a wide electrochemical stability window, solvent-free and leak-proof operation, ease of processing, and lightweight—attributes. This makes these electrolytes suitable for various electrochemical devices including fuel cells, supercapacitors, batteries (Tarascon and Armand, 2001; Ozer et al., 2002; Fonseca et al., 2006; Stephan, 2006), and dye-sensitized solar cells (DSSCs). Batteries are widely recognized as the dominant energy storage solution, particularly in the automotive sector and portable electronics (Scrosati and Garche, 2010). Among these, lithium-ion batteries (LIBs) are preferred for applications such as electric vehicles, grid energy storage, and flexible electronics due to their high energy and power density (Scrosati and Garche, 2010). Key components of rechargeable batteries include the anode, cathode, and electrolytes (Singh et al., 2022b). Traditional electrolytes, typically liquid-based and containing organic solvents, are flammable and volatile, posing risks of leakage and internal short circuits in LIBs, often caused by lithium dendrite growth on the anodes. This raises significant safety concerns, especially in high-demand applications. To address these challenges, the development of solid-state electrolytes has become a key area of research (Singh, 2023). Currently, researchers are focused on creating energy storage devices that are lightweight, safe, environmentally friendly, and cost-effective. Although biopolymers offer advantages in terms of safety, environmental impact, and weight reduction, there is concern that their use in energy applications could lead to higher food prices or even exacerbate food shortages (Malhotra et al., 2015). However, considering that energy is one of the most pressing global issues, addressing energy challenges can have a positive cascading effect on other problems, including water scarcity, food insecurity, poverty, and environmental degradation. Therefore, neglecting energy-related issues could potentially have more serious consequences for food availability than utilizing biopolymers in energy storage. Cellulose, one of the most abundant and well-known biopolymers, stands out due to its widespread availability (Rasali et al., 2020), ease of recycling, and extensive research into its use as a bio-based polymer electrolyte component.

In this review, the unique properties of biopolymers that contribute to their application as bio-based electrolytes are elaborated. The development of these bio-based polymer electrolytes not only addresses environmental concerns associated with synthetic alternatives but also opens up new avenues for innovation in energy storage solutions (Larrabide et al., 2022). The applications of biopolymers in energy products highlight their versatility and potential to enhance performance. However, thorough characterization of biopolymer-based energy products is essential to ensure their effectiveness and reliability. As we face challenges in scalability, cost, and performance optimization, the future prospects for biopolymers in this field remain promising, paving the way for sustainable energy solutions that align with global environmental goals.

2. Classification of Biopolymers

The term "biopolymer" originates from the Greek words "bio" and "polymer," meaning derived from living organisms. Biopolymers are large macromolecules composed of repeating monomeric units (Ezeoha and Ezenwanne, 2013) typically produced by living organisms. These monomers are linked through covalent bonds to form long polymer chains. Common illustrations of biopolymers include DNA, RNA, fatty acids, gelatin, keratin, cellulose, and starch. Certain biopolymers, such as DNA and RNA, play a crucial role in transmitting genetic material across generations. Cellulose and starch, on the other hand, serve as the primary structural components in plants (Ali et al., 2013). Biopolymers have been present on Earth for billions of years, much longer than synthetic polymers, which have more uniform and random structures. In contrast, biopolymers are arranged in highly organized structures, allowing for their breakdown into smaller chains through biological processes (Thomas et al., 2020). The degradation of biopolymers is facilitated by their low carbon-carbon bond energy, making them susceptible to degradation through enzymes, moisture, heat, and other environmental factors. This is largely due to the presence of hydroxyl groups in their structure. Many biopolymers are hydrophilic, meaning they easily degrade upon water absorption. However, no standardized testing method currently exists for the characterization of their degradation. Biopolymers can also be produced through hydrolysis and condensation reactions, such as in the case of carbohydrates and proteins. Synthetic biopolymers like polylactic acid (PLA), poly (vinyl alcohol) (PVA), and polycaprolactone (PCL) are typically produced through hydrolysis, although there are subtle differences between the two mechanisms. Biopolymers cover a broad range of materials, including chitosan derived from crustaceans, plant derivatives like xanthan, gums, starch, and protein-based materials such as casein and gelatin. The growing reliance on fossil fuels and the ongoing oil crisis have spurred the need to shift toward the use of biopolymers. In response, many polymer industries have begun exploring biopolymers as alternatives to synthetic raw materials. For instance, Imperial Chemical Industries pioneered the development of thermoplastic biopolymers under the brand "BIOPOL." Historically, biopolymer production required more energy than synthetic polymers. However, recent advances in scientific techniques are leading to the development of energy-efficient, commercially viable biopolymers (Leja and Lewandowicz, 2010).

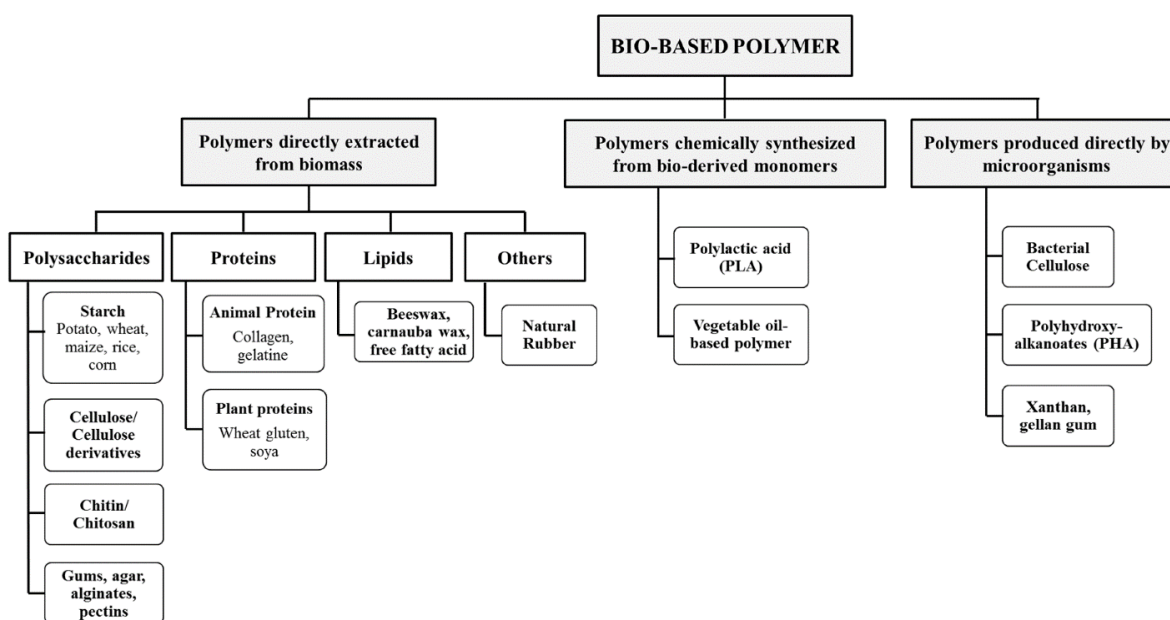


Figure 1. The categorization of bio-based polymers (Malhotra et al., 2015, Open access).

3. Challenges with Biopolymers for their use as Electrolyte

Despite their environmental benefits, biopolymers like starch, cellulose, and chitosan often have lower ionic conductivity and mechanical strength which are vital for various applications (mostly energy storage). Biopolymer electrolytes can be crucial for various applications such as renewable energy systems, enhancing the sustainability and efficiency of dye-synthesized and perovskite solar cells, and contributing to lightweight, flexible supercapacitors for wind energy storage. They also improve ion transport in microbial fuel cells. The use of biopolymers as electrolytes in energy storage devices presents both promising opportunities and significant challenges. While these materials offer environmental benefits due to their renewable and biodegradable nature, they often fall short in two critical performance areas: ionic conductivity and mechanical strength (Rasali et al., 2020). Addressing these limitations is essential to fully harness the potential of biopolymer electrolytes in sustainable energy applications.

3.1 Ionic Conductivity

One of the primary challenges facing biopolymer electrolytes is their relatively low ionic conductivity compared to synthetic polymers and liquid electrolytes. This limitation arises from the typically dense structure of biopolymers, which lacks a sufficient number of free ions, consequently restricting ion mobility through the material. Since ionic conductivity directly influences the charge-discharge rate and overall efficiency of energy storage devices, it is crucial to improve this property. Recent research has explored several strategies to enhance the ionic conductivity of biopolymer-based electrolytes such as blending biopolymers with other polymers or incorporating ionic salts and plasticizers has shown promise in improving ion transport. This approach creates a more flexible polymer matrix and increases the availability of free ions, both of which are conducive to better ionic conductivity. The addition of nanomaterials, such as graphene oxide, silica, or carbon nanotubes, has been found to enhance the ionic pathways within the biopolymer matrix. These nanofillers create a more conductive network, facilitating improved ion transport. Functionalizing the biopolymer backbone by introducing polar or ion-conducting groups—such as carboxyl, hydroxyl, or amine groups—can significantly increase ion conductivity. These modifications enhance ion interaction and mobility within the material, offering a viable path to more conductive biopolymer electrolytes. **Table 1** comparing the conductivity of different biopolymers.

Table 1. Table comparing the ionic conductivities of biopolymers.

Biopolymer	Additive	Conductivity [σ (S/cm)]	References
Agarose/Agars	KI	9.02×10^{-3}	Singh et al. (2013)
Carrageenans	Chitosan+carrageenan+ NH_4NO_3	2.39×10^{-4}	Shuhaimi et al. (2008)
Cellulose	NH_4NO_3	2.1×10^{-6}	Shuhaimi et al. (2010)
Pectin	Amidated pectin+Glutaraldehyde (GA)	1.098×10^{-3}	Mishra et al. (2009)
Corn Starch	NH_4Br	5.57×10^{-5}	Shukur and Kadir (2015)
Chitin/Chitosan	EMImSCN-NaI	2.60×10^{-4}	Singh et al. (2010)
Methylcellulose (MC)	NH_4NO_3	2.10×10^{-6}	Shuhaimi et al. (2010)

3.2 Mechanical Robustness

Another major challenge for biopolymer electrolytes is their lack of mechanical robustness. This weakness can hinder the material's ability to withstand the stresses encountered in energy storage devices, leading to structural degradation over repeated cycles, particularly in flexible or wearable applications. Efforts to enhance the mechanical strength of biopolymers, while preserving or even improving ionic conductivity, have included the following approaches like the use of crosslinking agents can result in a more stable, interlinked structure within the biopolymer matrix, enhancing the material's mechanical durability. Similar to their impact on ionic conductivity, nanofillers also contribute to mechanical reinforcement. By

embedding nanomaterials within the polymer matrix, the overall strength and resilience of the material can be significantly increased. Some studies have investigated the development of hybrid systems, which combine biopolymers with synthetic polymers or ceramics. These hybrid materials aim to strike a balance between flexibility, mechanical strength, and ionic conductivity, enabling biopolymer electrolytes to meet the rigorous demands of energy storage applications. The pathway to overcoming these challenges lies in continued research into novel biopolymer formulations, functional modifications, and composite structures. With targeted advancements in ionic conductivity and mechanical strength, biopolymer electrolytes could play an essential role in the development of sustainable and high-performance energy storage technologies.

4. Bio-Based Polymers Used as Electrolytes

Polysaccharides, proteins, lipids, and natural rubber are examples of the first class of bio-based polymers, which are those that are directly derived from biomass resources. Among these, polysaccharides have garnered the most attention in the field of polymer electrolytes, as indicated by the literature. Their accessibility, widespread availability, and abundance make them particularly attractive for research. Plants, as the primary source of polysaccharides, play a crucial role in their production. This section will focus on polymer electrolytes derived from polysaccharides, proteins, and natural rubber. **Figure 1.** Represents the categorization of bio-based polymers.

4.1 Starch

Extensive research has explored starch due to its wide variety, biodegradability, availability, and abundance in nature. Starch is a natural carbohydrate-based polymer and the final product of photosynthesis in plants, primarily sourced from corn, potatoes, wheat, tapioca, and rice. While starch is commonly used in food products, its applications extend to various other industries, including its use as binders, adhesives, absorbents, and encapsulants. Starch consists of two primary components: linear amylose (poly(α -1,4-d-glucopyranose)) and α -1,6-branched amylopectin, with their proportions varying depending on the plant source (Khair and Arof, 2010; Kumar et al., 2012). **Figure 2** depicts the structures of amylose and amylopectin.

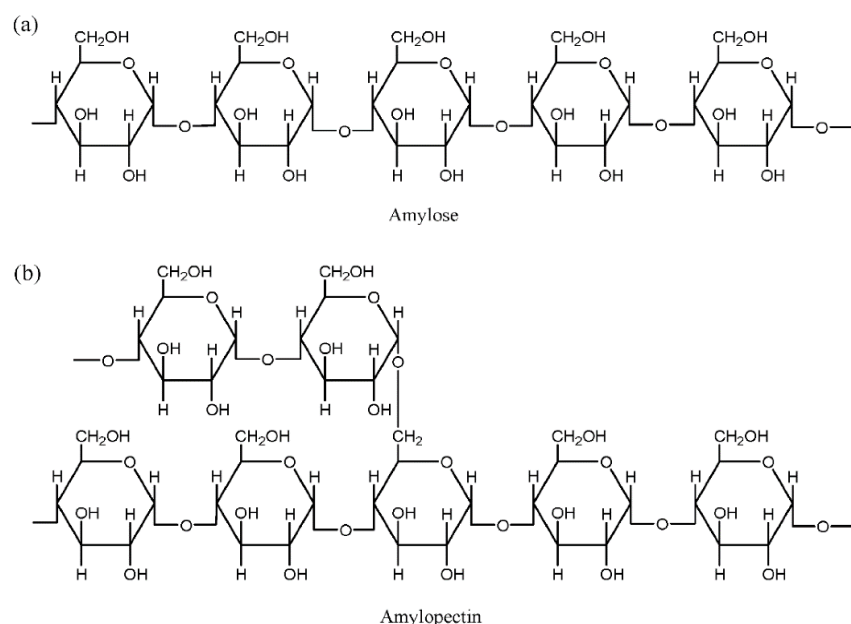


Figure 2. Structures of amylose and amylopectin (Rayung et al., 2020, Open access).

Due to the presence of hydroxyl groups in both compounds, starch-based polymers have emerged as promising candidates for use as polymer hosts in electrolyte applications. **Table 2** presents the aggregate data of earlier research on bio-based polymer electrolytes of starch.

Table 2. Summary of former study on starch based polymer electrolytes.

Polymer (Starch)	State	σ (S/cm)	Stability (V)	T_g (C)	Structure	Device	References
Rice starch–LiI–MPII–TiO ₂	Solid	3.6×10^{-4}	0.22 eV	–	Amorphous	DSSC	Khanmirzaei and Ramesh (2014)
Corn starch–LiPF ₆ –[BmIm][PF ₆]	Solid	1.5×10^{-4}	–	–	–	Super-capacitor	Liew and Ramesh (2014)
Corn starch–LiPF ₆ –[BmIm][Tf]		3.2×10^{-4}	–	–	–		
Corn starch–LiClO ₄	Solid	1.6×10^{-6}	0.64 eV	64	–	–	Teoh et al. (2014)
Corn starch/chitosan–NH ₄ I–glycerol	Solid	1.3×10^{-3}	0.18 eV	–	–	–	Yusof et al. (2014)
Starch/chitosan–NH ₄ I	Solid	3.0×10^{-4}	0.20 eV	–	Amorphous	–	Teoh et al. (2015)
Starch/chitosan–NH ₄ Cl–glycerol	Solid	5.1×10^{-4}	0.19 eV	–0.37	–	–	Khanmirzaei et al. (2015a)
Starch/chitosan–NH ₄ Br–EC	Solid	1.4×10^{-3}	0.17 eV	–	Amorphous	EDLC	Khanmirzaei et al. (2015b)
Corn starch–LiClO ₄ –SiO ₂	Solid	1.2×10^{-4}	0.25 eV	–	–	EDLC	Gandini and Lacerda (2015)
Rice starch–LiI	Solid	4.7×10^{-5}	–	–12	Amorphous	DSSC	Johari et al. (2011)
Rice starch–NH ₄ I		1.4×10^{-4}	–	–38	Amorphous		
Rice starch–NaI		4.8×10^{-4}	–	–42	Amorphous		
Rice starch–NaI–MPII	Solid	1.2×10^{-3}	–	–58	Amorphous	DSSC	Harun et al. (2011)

4.2 Cellulose

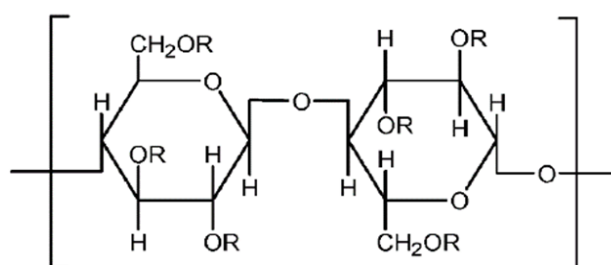
The most prevalent and vital renewable resource in the world is cellulose. It is the main structural element that gives plant cell walls their mechanical support and structural integrity. A linear homopolysaccharide with a high molecular weight, cellulose is made up of β -d-glucopyranose units in the 4C1 conformation connected by (1→4) glycosidic linkages. Two anhydroglucose subunits make up each repeating unit. The microscopic structure of the fiber assembly determines the proportions of the crystalline and amorphous areas that make up the helically structured microfibrillar form of cellulose (Harun et al., 2012).

Table 3. Overview of previous research on cellulose-based polymer electrolytes.

Polymer (Cellulose)	State	σ (S/cm)	T_g (C)	Structure	Device	References
Cellulose acetate–NH ₄ BF ₄ –TiO ₂	Gel	1.4×10^{-2}	–	–	Battery	Harun et al. (2013)
Cellulose acetate–NH ₄ BF ₄ –PEG	Solid	1.4×10^{-5}	–	–	–	Asghar et al. (2012), Samsudin et al. (2012)
CMC–DTAB	Solid	7.7×10^{-4}	0.09 eV	Amorph	–	Huang et al. (2012)
PEG/network cellulose–LiClO ₄	Gel	10^{-4}	–	Amorph	–	Ramesh et al. (2012a)
CN–HPC–LiI–I ₂ –MHII	Gel	2.5×10^{-3}	–	Amorph	DSSC	Ramesh et al. (2012b)
Cellulose acetate–LiTFSI–DES	Gel	2.6×10^{-3}	4.23 kJ/mol	Amorph	–	Ramesh et al. (2013), Sahli (2012)
Cellulose acetate–LiTFSI–[AmIm][Cl]	Solid	1.8×10^{-3}	–	Amorph	–	Shuhaimi et al. (2012)
Methyl cellulose–LiCF ₃ SO ₃	Solid	2.1×10^{-5}	–	Amorph	–	Selulos (2012)
Methyl cellulose–PEG–NH ₄ NO ₃	Solid	10^{-6}	–	Amorph	EDLC	Majid and Arof (2005)
Methyl cellulose–KOH–DMC	Solid	10^{-5}	–	–	–	Aziz and Abidin (2015)
PE/PVDF/Cellulose acetate butyrate–LiPF ₆ –EC/EMC	Gel	2.5×10^{-3}	–	–	Battery	Bakar et al. (2015)

The three hydroxyl groups in the anhydroglucose units can be partially or totally reacted with various chemicals to create cellulose derivatives. A wide range of cellulose derivatives has been thoroughly studied, such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, cellulose acetate, cellulose triacetate, cellulose acetate butyrate, hydroxypropyl methyl cellulose, and carboxymethyl cellulose. The structures of cellulose and its derivatives are shown in **Figure 3**.

The summarized data from previous studies on bio-based polymer electrolytes derived from starch are presented in **Table 3**.



Cellulose	R=H
Methyl Cellulose (MC)	R=H or CH ₃
Ethyl Cellulose (MC)	R=H or CH ₂ CH ₃
Hydroxyethyl Cellulose (HEC)	R=H or CH ₂ CH ₂ OH
Cellulose Acetate (CA)	R=H or COCH ₃
Cellulose Triacetate (TCA)	R=COCH ₃
Cellulose Acetate Butyrate (CAB)	R=H or COCH ₃ or COCH ₂ CH ₂ CH ₃
Hydroxypropyl Methyl Cellulose (HPMC)	R=H or COCH ₃ or COCH ₂ CH(OH)CH ₃
Carboxymethyl Cellulose (CMC)	R=H or CH ₂ OH ₂ COONa

Figure 3. Representative units of cellulose and cellulose derivatives (Rayung et al., 2020, Open access).

4.3 Chitosan

Chitosan has garnered significant attention in the field of polymers due to its unique properties, including non-toxicity, biodegradability, and biocompatibility. Chitosan is made up of 1,4-linked units of 2-deoxy-2-aminoglucose, which are derived from the deacetylation of chitin. Chitin, a natural polysaccharide, is found in the exoskeletons of arthropods like shrimp, crabs, and lobsters, as well as in various fungi. **Figure 4** illustrates the molecular structure of chitin and its deacetylation process, which results in the formation of chitosan (Buraidah et al., 2016). **Table 4** presents a compilation of previous findings on starch-based bio-polymer electrolytes.

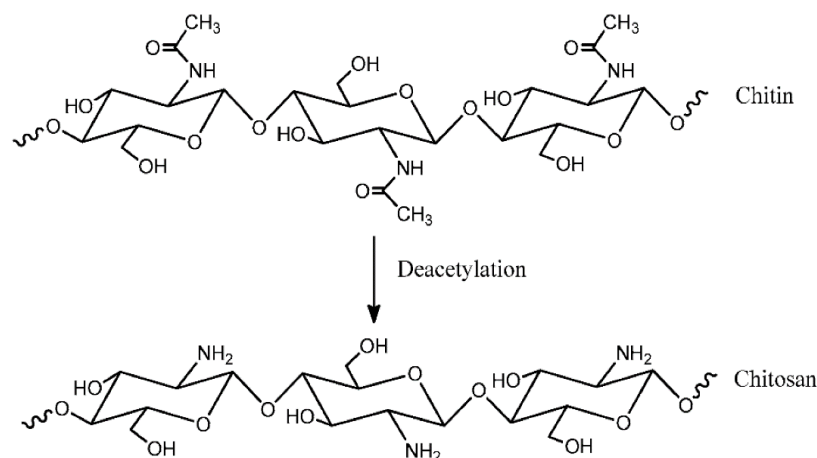


Figure 4. Molecular structure of chitin and chitosan (Majid and Arof, 2005, Open access).

Table 4. Overview of previous research on chitosan-based polymer electrolytes.

Polymer (Chitosan)	State	σ (S/cm)	T_g (C)	Structure	Device	References
Chitosan–NaCF ₃ SO ₃ –Al ₂ O ₃	Solid	–	–	Amorphous	–	Sudaryanto et al. (2016)
CMCh–DTAB	Solid	1.9×10^{-6}	–	–	–	Kalaiselvimary et al. (2016)
Chitosan/PEO–NH ₄ I	Solid	3.7×10^{-6}	–	Amorphous	DSSC	Yusuf et al. (2016)
Chitosan–LiClO ₄ –ZrO ₂	Solid	3.6×10^{-4}	–	Amorphous	–	Fadzallah et al. (2016)
Chitosan–perchloric acid	Solid	5.9×10^{-4}	–	–	–	Shirdast et al. (2016)
N-phthaloyl chitosan–TPAI–I ₂ –EC	Solid	5.5×10^{-3}	0.11 eV	Amorphous	DSSC	Aziz (2016)
Chitosan–oxalic acid	Solid	4.1×10^{-5}	–	–	–	Alves et al. (2016a)
Sulfonated chitosan–sulfonated GO	Solid	7.2×10^{-3}	–	–	–	Alves et al. (2016b)
Chitosan–LiCF ₃ SO ₃ –Al ₂ O ₃	Solid	10^{-6}	–	Amorphous	–	Gaikwad and Pande (2013)
Chitosan–Ce(CF ₃ SO ₃) ₃ –glycerol	Solid	1.7×10^{-5}	–	Amorphous	–	Alves et al. (2016b)
Chitosan–Eu(CF ₃ SO ₃) ₃ –glycerol	Solid	1.5×10^{-6}	–	Amorph	–	Alves et al. (2016a)

5. Development of Bio-Based Polymer Electrolyte

A typical PE consists of an inorganic salt embedded in a polymer matrix, forming a conductive solid system where the salt dissociates into ions, thereby improving conductivity. The development of this field began with the 1973 discovery of poly (ethylene oxide) (PEO) doped with alkali metal ions. Extensive studies have since demonstrated that various factors—such as electrolyte components, preparation methods, and thermal history influences the electrochemical, thermal, and mechanical properties of polymer electrolytes. The effectiveness of these electrolytes depends largely on ionic conductivity and transport properties, which are influenced by factors like polymer chain mobility, polymer host dielectric constant, salt dissociation level, concentration, and ion aggregation (Varshney and Gupta, 2011).

When constructing polymer electrolytes, several factors need careful consideration, such as the choice of polymer host, ion source (salts or acid dopants), solvents, and other additives. The polymer host should provide stability in terms of chemical, electrochemical, and photochemical properties, along with thermal and mechanical durability. Hosts with a high density of polar groups (such as O, NH, CN, F) are favored for improved ion transport. Additionally, an amorphous polymer state with low glass transition temperature

improves ion diffusivity and segmental motion, enhancing electrolyte performance. Polar polymers with these qualities are commonly used as hosts (Aziz et al., 2018).

The choice of salts in polymer electrolytes is critical as they supply the charge carriers necessary for conductivity. Salts of alkali, alkaline earth, and transition metals are commonly used, where metal cations interact with the polymer's polar groups. The segmental motion of the polymer creates free volume, allowing ions to migrate more freely and improving conductivity. Salts influence conductivity through complex formation, polymer chain cross-linking, and salt dissociation. Additionally, proton-conducting electrolytes are formed by swelling the polymer in proton-donor solutions. The solvent used must dissolve salts effectively, with high dielectric constant, low vapor pressure, low viscosity, and chemical inertness (Raphael et al., 2010; Liew and Ramesh, 2013).

The use of bio-based polymers in polymer electrolytes is not a new concept and has been explored for several years. However, it is only in the past three decades that these materials have been extensively studied within this field. To make these bio-based electrolytes commercially viable, improvements in their properties are necessary. The key challenge is to develop an electrolyte system with high ionic conductivity while maintaining suitable electrochemical, thermal, and mechanical characteristics. Various strategies have been explored to overcome these challenges, such as blending the bio-based polymer with other well-suited polymers, adding fillers, and incorporating plasticizers. Blending involves combining at least two polymers or copolymers, with each component typically comprising more than 2 wt% of the mixture. This approach is favored for its simplicity and the ability to modify physical properties through adjustments in composition (Gaikwad and Pande, 2013). Plasticizers can improve conductivity by lowering the glass transition temperature, which increases ion mobility and aids in the dissociation of ion aggregates. Plasticizers with a high dielectric constant can also help solvate more salt, thus increasing the concentration of free ions (Shukur et al., 2013). Additionally, incorporating organic or inorganic fillers can reduce crystallinity, enhancing both the mechanical and electrochemical properties. Conductivity is particularly influenced by the size and concentration of the filler particles, with smaller particles in lower concentrations generally leading to improved conductivity (Audeh et al., 2014).

Numerous nanoparticles, extensively detailed in literature, are used in nanocomposite production. These nanoparticles are typically classified by their nanoscale dimensions into categories: fibers (1D), nanoplatelets (2D), and particles (3D). They differ significantly from microparticles commonly utilized in composites due to their greater surface area. Nanofillers, widely available and frequently studied, are the focus of commercial trials. There are various dimensional nanofillers which have been significantly discussed here such as:

- **1- Dimensional**

One-dimensional (1D) nanomaterials, such as nanorods, nanotubes, and nanowires, extend beyond nanoscale in a single direction, resulting in a needle-like shape. They may be amorphous or crystalline, pure or mixed, standalone or within a matrix, and can be metallic, ceramic, or polymeric. Highly conductive 1D materials like silver nanowires (AgNWs) serve as effective conductive additives alongside carbon nanotubes (CNTs), facilitating the dispersion of conductive particles in polymer solutions. This structure enables the integration of graphene's properties into macroscopic forms for flexible, wearable electronics. Recently, room temperature ionic liquids (RTILs) have emerged as promising alternatives to traditional organic solvents. RTILs are molten salts made up of large, asymmetric organic cations and highly delocalized inorganic anions. These liquids offer several beneficial properties, such as exceptional thermal and chemical stability, high ionic conductivity, non-volatility, non-flammability, and a broad electrochemical potential range (Yin et al., 2016; Motsoeneng et al., 2020).

• 2- Dimensional

Two-dimensional (2D) nanomaterials have a plate-like structure, including nanofilms, nanolayers, and nanocoatings. These materials can be either amorphous or crystalline, composed of various chemical elements, used in single or multi-layer forms, and can be integrated into different matrices such as metallic, ceramic, or polymeric substrates. Graphene is a prime example: it consists of a single atomic layer of sp^2 -hybridized carbon atoms in a honeycomb structure, offering high surface area, electrical and thermal conductivity, and robust mechanical properties, which make it ideal for enhancing polymer characteristics (Ahmad et al., 2015; Pramanik et al., 2017; Nasir et al., 2018).

• 3- Dimensional

Bulk nanomaterials are characterized by dimensions larger than the nanoscale, exceeding 100 nm in all three dimensions. Structurally, they can include various nanocrystalline formations, typically with nanoscale crystals arranged in multiple orientations. These 3D nanomaterials may incorporate nanoscale features, such as dispersions of nanoparticles, clusters of nanowires, nanotubes, or layered structures composed of multiple nanolayers. Immiscible polymer blends generally consist of two distinct phases, where a particular filler can be selectively localized. The placement of this filler significantly influences the final properties of the blend composites. Various factors affect the filler's preferred localization, primarily thermodynamic interactions—especially polar interactions—between fillers and polymer phases. Studies show that fillers often locate in the phase with higher affinity, reducing interfacial energy. Additionally, fillers tend to favor the less viscous phase to further minimize interfacial energy during the mixing process (Pramanik et al., 2017; Kabir et al., 2018; Motsoeneng et al., 2020).

6. Applications

6.1 Lithium-Based Batteries

The application of biopolymers in lithium–sulfur batteries has recently garnered attention due to the high energy density of these systems, approximately 2600 W h kg^{-1} (Yuan et al., 2019). The integration of Carbon-containing, fibrous biomaterials offers several advantages for Li-S battery, including robust physical and chemical adsorption properties, truncated cost, and ecological sustainability. Materials such as soy protein, chitosan, cellulose, and fungi have also been explored for their potential to enhance lithium batteries (Fu et al., 2019). Guo et al. recently proposed synthesis methods using carbon-based hydrogels derived from materials like gelatin, which further optimize the performance of these batteries (Guo et al., 2019). **Table 5** presents a compilation of data on the use of biopolymers as components in lithium batteries.

Table 5. Applications of biopolymers in lithium battery components.

Application	Function	Initial reversible capacity	Coulombic efficiency	Cycling stability	References
Silk-derived hierarchical porous nitrogen-doped carbon nanosheets	Anode in Li-ion	$1913 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ at $0.1 \text{ A} \cdot \text{g}^{-1}$	49.2% at $0.1 \text{ A} \cdot \text{g}^{-1}$	9% loss after 10000 cycles	Hou et al. (2015)
Carbonized silk fibroin nanofibre film	Cathode and anode interlayers in Li/S	1164 mA h g^{-1} at 0.2 coulomb (C)	97.3% at 1.0 C	69% retention after 200 cycles	Wu et al. (2019)
Silk-derived N/P co-doped porous carbon mixed with sulfur	Cathode in Li/s	$888.5 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ at 1.0 C	97.6% at 1.0 C	0.032% loss per cycle over 500 cycles at 1.0 C	Thiyagarajan et al. (2021)
Keratin-derived carbon added to TiNb_2O_7	Anode in Li-ion	$356 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ at 0.1 C	55.0% at 0.1 C	85% retention after 50 cycles at 1 c	Shao et al. (2022)
Keratin-derived carbon combined with $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles.	Anode in Li-ion	$1690 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ at 0.2 C	75% at 0.2 C	1000 mA h g^{-1} 0.2 C after 200 cycles	Ramakrishnan et al. (2018)

6.2 Zinc-Based Batteries

Zinc metal batteries are another promising category of electrochemical materials, offering benefits such as reusability, high energy density, affordability, lower environmental impact, and scalability. However, their performance is frequently hindered by zinc deposition, which occurs when the aqueous electrolyte interacts with the zinc. This problem, along with the growth of dendrites, limits the potential of zinc-based batteries by creating undesired contact between the cathode and anode, resulting in corrosion. To address these challenges and enhance the viability of this sustainable battery technology, the incorporation of biopolymers can help minimize undesirable interactions. The collective data of biopolymer applications as zinc based battery components is presented in **Table 6**.

Table 6. Biopolymer applications as zinc based battery components.

Material	Function	Initial reversible capacity	Coulombic efficiency	Cycling stability	References
Silk II–silk	Coating for Zn anode	189 mA h g ⁻¹ at 0.1 A g ⁻¹	As high as 99.7%	As long as 3300 h at 10 mA cm ⁻² and 10 mA h cm ⁻²	Zhou et al. (2021)
Gelatin–silk protein film	Electrolyte film	311.7 mA h g ⁻¹	Greater than 90% Over 100 cycles	Greater than 90% Over 100 cycles	Lee et al. (2011)
Carrageenan and wool keratin biogel	Electrolyte film	271.6 mA h g ⁻¹ at 0.1 A g ⁻¹	~98%	96% capacity retention, ~70% over extended cycles	Xu et al. (2020)
Chitosan-based gel electrolyte with poly-vinyl alcohol (PVA)	Electrolyte film	310 mA h g ⁻¹ at 0.1 A g ⁻¹	96.5% at 0.5 A g ⁻¹	Retention after 300 cycles	Poosapati et al. (2021)
A sustainable chitosan-zinc electrolyte for high rate zinc metal batteries	Electrolyte	208 mA·h·g	99.7%	Greater than 400 cycles	Song et al. (2019)

6.3 Capacitors

Like in batteries, biopolymers can enhance the electrical properties of conventional electrode materials in capacitors. Capacitors offer an alternative energy storage solution with the advantage of faster charging, though they are limited by lower energy density. Supercapacitors, a specific type of capacitor, combine the characteristics of both capacitors and batteries by storing energy within the electrolyte (Ramakrishnan et al., 2018). **Table 7** represents the applications of biopolymers in capacitor components.

Table 7. Biopolymer applications as capacitor components.

Material	Function	Capacitance	Surface area	Cycling stability	References
Graphene-infused porous carbon resulting from collagen	Electrode	365 F·g ⁻¹ at 1 mV·s ⁻¹	1087 m ² ·g ⁻¹	97% capacitance	Dong et al. (2015)
Nitrogen-doped carbon nanosheets from collagen cross-linked with paraformaldehyde	Electrode	102 F·g ⁻¹ at 25 mV·s ⁻¹	695 m ² ·g ⁻¹	80% capacitance	Lu et al. (2022)
Collagen fiber sheath cross-linked with oxidized sodium alginate	Electrolyte locked separator.	143.07 F g ⁻¹ at 5 Mv s ⁻¹	-	99.99% capacitance	Wu et al. (2022)
Keratin-derived reduced graphene oxide combined with MoO ₂	Electrode	256 F g ⁻¹ at 0.02 A g ⁻¹	2042 m ² ·g ⁻¹	86% capacitance	Subhani et al. (2022)
Carbonized keratin combined with sulfuric acid	Electrode	270 F g ⁻¹ at 1 A g ⁻¹	2684 m ² ·g	98% capacitance	Wu et al. (2021)

7. Characterization and Analysis of Biopolymer-Based Materials for Energy Applications

An essential phase in the production of biopolymer-based energy products is confirming that the desired material properties are attained in the final product. Various methods are utilized to analyze samples after fabrication. Field emission scanning electron microscopy (FESEM) is commonly used to examine the structural stability and morphology of biopolymers integrated into battery materials, allowing for detailed visualization of membrane porosity and other features (Zeng et al., 2019). X-ray photoelectron spectroscopy (XPS) is another valuable tool for identifying the chemical composition of the final product, particularly important in heteroatom-doped scaffolds (Wang et al., 2012). Similarly, Raman spectroscopy aids in characterizing doped materials by analyzing D, G, and 2D band peaks, providing insights into surface defects, as doped materials often feature smaller crystallites. Thermal characteristics are evaluated through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), which measure thermal transitions and degradation. Mechanical properties are evaluated through stress-strain testing and nanoindentation, assessing both bulk and nanoscale material strength (Arico et al., 2005). To assess the battery's performance and longevity, methods like electrochemical impedance spectroscopy and cyclic voltammetry are employed to examine the impact of individual elements within the energy storage system. Additionally, samples undergo testing for biodegradability, structure (using X-ray diffraction and Fourier transform infrared spectroscopy), and morphology at various scales via atomic force microscopy, scanning electron microscopy, and transmission electron microscopy (Ma et al., 2022). Apart from these techniques, X-ray absorption spectroscopy is also effectively used for characterization of these electrolytes (Singh et al., 2022a).

8. Challenges and Future Prospective

Biopolymers present an exciting frontier for the development of next-generation energy storage materials. Due to their unique properties, a wide range of biopolymers are suitable for various roles within energy storage devices, offering potential solutions to challenges faced by current technologies. The key advantages of natural biopolymers lie in their biodegradability, biocompatibility, and renewability. This review focuses on classes of biopolymers used in energy storage applications like Starch, Agrose, and cellulose etc. In order to design efficient energy storage devices, an in-depth understanding of electrical laws and principles is essential to optimize various components. Key performance metrics include total capacity, capacity retention after multiple charge cycles, and capacitance, particularly for supercapacitors. Energy storage devices usually consist of five main constituents: an anode, cathode, electrolyte, separator, and current collector. By understanding the theory underlying the function of each component, researchers can optimize biopolymer-based materials to meet the specific requirements of these roles. Several fabrication techniques have been developed to convert biopolymers into structures proper for energy storage tenders. Solution casting is an effective method for producing membranes for biopolymer electrolyte applications, while electrospinning allows for the creation of tunable nanofibers with precise control over material properties. Three-dimensional printing offers unique control over the final structure, with processes such as ball milling, grinding, and extrusion enabling the production of biopolymer filaments for 3D printing. Once fabricated, rigorous testing is required to ensure that the biopolymer materials possess the necessary structural and functional properties. A diverse range of biopolymers can be used in different battery parts to improve overall capacity, energy density, or to reduce problems such as dendrite growth. While lithium-ion batteries continue to be the benchmark for rechargeable energy storage, materials based on biopolymers present opportunities for advancement. Zinc batteries, which have lower environmental and economic costs compared to lithium-ion batteries, encounter challenges due to zinc deposition and dendrite formation. However, promising biopolymers like silk, keratin, and chitosan have demonstrated potential in addressing dendrite issues and enhancing battery performance. In supercapacitors, biopolymers such as collagen, keratin, and cellulose offer promising pathways for optimization by enhancing charging rates through porous separator structures, although this typically comes with a trade-off in energy density.

Despite the potential of biopolymer-based materials in energy storage, several challenges remain, including the cost of manufacturing, limited shelf life, and the question of whether these materials can consistently outperform conventional alternatives. Further research is required to advance biopolymer science, with the ultimate goal of developing fully biodegradable energy storage devices. Incorporating biopolymer-based components into energy storage systems allows for the utilization of their natural properties, low environmental impact, and ease of integration with other conductive materials. As the demand for advanced energy storage solutions continues to grow, biopolymers offer a promising avenue for the development of more sustainable and efficient technologies.

9. Conclusion

Biopolymers as solid polymer electrolytes (SPEs) represent a promising pathway toward sustainable, eco-friendly, and high-performance energy storage solutions. Through recent advancements, biopolymers like cellulose, chitosan, starch, and their composites have demonstrated the potential to meet the functional demands of modern energy storage devices, including batteries and supercapacitors. However, several challenges remain, particularly in enhancing their ionic conductivity, mechanical strength, and moisture resistance, all of which are crucial for their wide-scale adoption in commercial applications. While biopolymer-based SPEs offer inherent advantages such as biodegradability, low toxicity, and environmental compatibility, their performance still lags behind synthetic polymer-based alternatives. The integration of nanotechnology, composite engineering, and advanced processing techniques such as 3D printing presents opportunities to overcome these challenges and develop next-generation biopolymer SPEs with superior properties. Looking forward, further research is essential to address existing limitations, particularly in improving ionic conductivity and stability under operational conditions. The continued exploration of novel biopolymers, hybrid systems, and functionalized materials will be key in driving future innovations in this area. As the demand for sustainable energy storage grows, biopolymer-based SPEs stand poised to play a significant role in advancing the field, combining environmental benefits with technological advancements. Among the various biopolymers explored as solid polymer electrolytes, starch, cellulose, and chitosan have attracted significant attention due to their availability, biodegradability, and film-forming properties. Starch-based electrolytes offer flexibility and ease of modification through plasticization, yet their crystallinity often limits ion conductivity. In comparison, cellulose, with its rigid structure and high mechanical strength, demonstrates enhanced stability but requires chemical modifications to increase its ion transport properties. On the other hand, chitosan, a derivative of chitin, exhibits inherent ionic conductivity due to the presence of amino groups, making it a promising candidate for ionic applications. However, its poor solubility in water restricts its direct use without further modifications. Each biopolymer presents unique advantages and challenges in the development of efficient solid polymer electrolytes.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AI Disclosure

During the preparation of this work the author(s) used generative AI in order to improve the language of the article. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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