Application of Biomass Materials in Zinc−Ion Batteries

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Aqueous zinc-ion batteries (ZIBs), with large reserves of zinc metal and maturity of production, are a promising alternative to sustainable energy storage. Nevertheless, ZIBs also have many drawbacks, for instance, aqueous solution has poor frost resistance and is prone to side reactions. In addition, zinc dendrites also limit the performance of ZIBs. The deeper development and modification of ZIBs is crucial. Biomass, a green and sustainable resource with complex molecular structure and abundant functional groups, makes it have great application in ZIBs.

biomass zinc−ion battery electrode electrolyte separator binder

1. Introduction

Compared with the most widely used lithium-ion battery, aqueous zinc-ion battery has the advantages of high safety, non-toxicity and easy manufacture, which promotes the popularization of renewable energy. Zinc metal is stable in the natural environment and can be directly used to assemble batteries without assembly in harsh glove boxes, which greatly reduces the production cost and production conditions of zinc ion batteries. In addition, it uses water as an electrolyte, which has the advantages of environmental protection and safety compared with organic electrolytes [2, 3]. However, with the research of zinc ion batteries, the generation of zinc dendrites, the dissolution of electrodes, the occurrence of side reactions at the electrolyte and electrode-electrolyte interfaces, the ion transport properties of electrolytes and separators, and the viscosity and flexibility of binders will limit the development of zinc ion batteries.

Biomass, with unique structural and chemical properties, is a kind of renewable organic material [4]. After different processing, it can bear different functions. Biomass feedstocks, such as wood, crab shell, and waste, etc., can be used to produce porous carbon through physical/chemical activation, these as−prepared carbon can be used as electrode material for ZIBs [2].

Starting from the different components of zinc ion batteries, it is necessary to comprehensively summarize some problems existing in the batteries and solve these problems by using different components of biomass to realize the perfect combination of biomass and existing ZIBs commercial materials or develop innovative applications of biomass. It can provide a reference for the rational design and utilization of biomass and its derived materials to prepare zinc ion batteries with long life and high energy density, and provide a development direction for future zinc ion batteries and new energy storage.

2. Zinc−ion battery

Zinc−ion battery is mainly composed of positive and negative electrode materials, electrolyte, separator and binder. The reversible zinc stripping/electroplating of the negative electrode and the reversible Zn^{2+} insertion/extraction of the positive electrode realize the energy storage and release of the zinc−ion battery [12]. The electrolyte transmits the transport current to the ion medium, and its ionic conductivity and operating temperature range affect the performance and operating temperature of the entire battery [13,14]. The separator acts as a physical barrier between the electrodes to prevent internal short circuits, which is a key factor in determining the safety of zinc ion energy storage devices [15,16]. The binder is responsible for connecting the electrode materials together and then stably adhering them to the collector to provide good contact for the electron flow [17,18]. The charge storage process of a zinc−ion battery depends on the migration of Zn^{2+} between the anode and cathode. The charge storage mechanisms of Zn anode and cathode of a zinc−ion battery are briefly discussed as follows:

2.1. Charge Storage Mechanism of Zn Anode

The charge storage of zinc anode relies on the reversible zinc stripping/electroplating. As shown in Equation (1).

$$Zn^{2+}+2e^{-}\rightleftharpoons Zn \quad (1)$$

During the charging process of ZIB, Zn^{2+} in the electrolyte is reduced and deposited on the Zn anode. During the discharge process, the anode zinc is stripped and oxidized to soluble Zn^{2+}, which migrates to the cathode side [19,20]. However, Zn^{2+} is more inclined to deposit on the thread dislocation on the surface of Zn, and uneven stripping/plating leads to a series of side reactions such as zinc dendrites [19,21,22].

2.2. Charge Storage Mechanism of Cathode

At present, the energy storage mechanism of different cathode materials can be divided into four categories: traditional Zn^{2+} insertion/extraction, dual ions co−insertion, Zn^{2+} coordination/uncoordination and conversion reaction [12,19].

(1) Traditional Zn^{2+} insertion/extraction

Reversible Zn^{2+} insertion/extraction has been widely accepted as the main mechanism of most ZIB cathodes, which is suitable for cathodes with open structures, such as special channels and layered structures [19,23]. Taking the classical $\alpha-MnO_2$ tunnel structure as an example (Equation (2)), Zn^{2+} ions are extracted from the tunnel of $\alpha-MnO_2$ during charging, and Zn^{2+} ions dissolved from the Zn anode move rapidly and insert into the tunnel during discharging [20].

$Zn2^{+}+2e^{-}+2MnO_2 \rightleftharpoons ZnM_2O_4$ (2)

(2) Dual ions co−insertion

The large size of water and Zn^{2+} will produce strong electrostatic repulsion with other divalent ions, resulting in slow Zn^{2+} intercalation. Different from traditional Zn^{2+} insertion/extraction, the dual ions co−insertion mechanism is also demonstrated. In theory, the insertion of intercalation ions such as H^+, Li^+, and Na^+ with faster diffusion is allowed at the same time as the insertion of the host material, which effectively promotes the use of active sites in the host structure and improves the performance of zinc−ion batteries [12,24,25].

(3) Coordination/uncoordination reaction of Zn^{2+} with organic cathode

This principle is suitable for organic compound cathode materials with abundant electroactive groups, which act as excellent active sites for Zn^{2+} storage by rapid coordination with electropositive Zn^{2+} [19,20]. These organic cathodes include quinone compound [26], 2D covalent organic frameworks [27], metal−organic framework [28] and pyrene−4,5,9,10−tetraone [29], etc.

(4) Conversion reaction

The conversion reaction in the battery can directly carry out charge transfer. A reasonable conversion reaction can improve the performance of zinc−ion battery. There is a reversible conversion between α−MnO_2 and MnOOH in a mild $ZnSO_4$ aqueous electrolyte during the charging/discharging process of Zn/α−MnO_2 batteries [30].

The energy density of zinc−ion batteries varies from tens to few hundreds Wh kg^{-1}. For instance, the zinc−ion battery with the modulated $NiCO_2O_4$ nanosheets as the cathode can reach the energy density of 578.1 Wh kg^{-1} [31]. The development of zinc−ion batteries with high energy density is also one of the reasons for applying biomass to batteries.

3. Biomass for Electrodes

In general, the cathode materials of zinc−ion batteries include manganese−based oxides [30,32,33] as well as the prussian blue analogues [34,35], inorganic molybdenum sulfate [36], molybdenum oxide [8,37] and organic quinone compounds, which exhibit tunnel structure or layered structure. Zinc ions can be reversibly embedded and extracted in the cathode material. However, due to the tip effect, the microscopic protrusions on the surface of the metal zinc anode produce a strong local electric field during charging, attracting Zn^{2+} to deposit and grow into large−size zinc dendrites [38]. Biomass can enrich the active sites of electrode materials, expand the space for storing ions and electrons on the surface of electrode materials, and effectively solve the problem of zinc dendrites. Currently, a variety of biomass materials, such as yeast [39], collagen [40], gelatin and agar [41], and even biomass waste, can be used as electrode materials for zinc−ion batteries. In addition, organic polymer biomass, the coating of hydrophilic biomass, and the 3D modification of carbonized biomass are typical advanced biomass for electrode materials [42,43].

3.1. Pure Biomass for Organic Electrode Materials

Compared with conventional inorganic cathode materials, the organic cathode materials have the following advantages, such as environmentally friendly and renewable [44–46], adjustable structure [47], high charge and discharge rate. Generally, organic cathode materials only involve chemical absorption and ion doping during charging/discharging process, which cannot change their structure and valence bond, resulting in high charge and discharge rate [23], Quinones present completely insoluble in water, which have a variety of properties when applied to zinc−ion batteries [48]. Quinone organic materials have weak intermolecular van der Waals forces, which can produce moderate Coulomb repulsion to diffuse cations [49–51]. Moreover, their plasticity and soft lattice may allow molecules to reorient, which are conducive to form the reversible intercalation of Zn^{2+}. Therefore, the carbonyl reduction potential can be adjusted by modifying the function of quinone derivatives [52–54]. For example, the p−aminobenzoic acid is synthesized by using yeast and wheat bran as precursors, which presents a cavity structure. The carbonyl groups on and under the calix [4] quinone molecule with an open bowl structure and eight carbonyl groups can react with Zn^{2+}, which is more conducive to the absorption of Zn^{2+}, increasing the capacity and energy density of the battery [39]. At present, more than 2400 quinone compounds have been extracted from plants, animals, fungi and other biomass [55]. However, Zn anode is inevitably poisoned by adopting quinone compounds in aqueous solution. In this regard, ion exchange membrane is used to effectively inhibit the dissolution of discharge products [49,56].

3.2. Biomass with Surface Modification for Electrode Materials

The coating can act as a barrier on the electrode surface, physically inhibit the dissolution of the electrode and maintain the stability of the electrode structure [57]. Compared with common carbon−based coatings, biomass coatings have certain water absorption. For example, the coverage of cathode coatings, such as gelatin and agar, can reduce the interface impedance and increase the diffusion rate of Zn^{2+} on the electrode, so as to improve the capacity and cycle life of zinc−ion battery [57,58]. For instance, collagen can also form micro−skin on the electrode surface after hydrolysis, and adsorb dissolved Mn^{2+}, thus improving the reversibility of the total redox reaction of MnO_2/Mn^{2+} during charge and discharge, improving the cycle life of zinc−ion batteries [40].

The surface modification of the cathode material can slow down the occurrence of side reactions on the EEI effectively; thus, the introduced coating on the surface of the zinc anode can achieve a dendrite−free zinc anode, which is an effective strategy to induce uniform deposition of zinc [60]. MXene films prepared with chitosan can be used as coatings for zinc anodes [38]. The coating thickness also has an effect on the performance of zinc−ion battery. The thin coating can decrease the charge transfer resistance and improve the reversibility of the MnO_2/Mn^{2+} reaction. Nevertheless, the thick micro−skin coating increases the interface resistance and hinders the transmission speed of Zn^{2+}, reducing the specific capacity of battery. Therefore, coating can avoid direct contact with the electrolyte and reduce the occurrence of various corrosion and side reactions, regulating the coating thickness can effectively improve the performance of the battery [61].

3.3. Biomass Derived Carbon for Electrode Materials

Carbon materials usually have high conductivity, good chemical stability and rich pore structure, which can be combined with cathode−active materials to effectively improve their performance [62]. In general, activated carbon materials with rich porous structure can be obtained by biomass carbonization, the induced high porosity can promote the rapid transfer of electrons on composite materials [62]. For instance, carbon materials are prepared by chemical activation, and Mn_3O_4 particles are coated by deposition [62]. This obtained with an additional mesoporous structure, act as an environmentally friendly and efficient manganese oxide support for zinc−ion batteries [62]. The doping of heteroatoms such as N can effectively increase the surface roughness of biomass materials, increase their surface area and adjust the hydrophilicity of materials. In general, N atoms can exist in biomass−derived carbon skeletons in various forms, such as C−N, C=N, N−O, N−H, graphite N, pyridine− (N^+−O^-), pyrrole N, and pyridine N [65,66]. For instance, porous carbon is constructed by activation of N−doped corn silk, which is introduced into the zinc−based metal organic framework [67]. The N doping endows ZnO/N/C with a hierarchical porous structure [67]. The interconnection of macropores and mesopores can realize the rapid transport of zinc ions and improve the rate performance of ZIBs [68].

4. Biomass Used in Electrolytes

Biomass with hydrophilic functional groups, such as NH_2, −OH, −CONH−, $-CONH_2$ and $-SO_3H$, have high adsorption affinity for polar solvent molecules. Its strong interaction with salt anions can enhance the salt solubility and cation transport properties, promote the distribution of Zn^{2+} on the electrode surface more uniformly, thereby inhibiting the growth of Zn^{2+} crystals [69]. Biomass polymers, such as cellulose [70], guar gum [8], xanthan gum [71], carrageenan [56], sodium alginate [72], silk fibroin [73], can be used as electrolytes. Their mechanical stiffness and flexible combination can adapt to the changed electrode volume, resulting in a stable interface and the extended service life [74–76]. They can also be processed into customized shapes with uniform nanopore distribution to form a uniform metal ion flux at the electrode–electrolyte interface, which is conducive to providing stable zinc deposition/stripping, thereby effectively avoiding the generation of zinc dendrites [77].

4.1. Single Biomass Electrolyte

Single macromolecular biomass can coat on the target substrate to construct a solid−state zinc−ion battery, which can be beneficial to achieve a good bonding interface for charge and mass transfer, slowing down self−corrosion and eliminating a series of side reactions in aqueous solution [8,78]. Biomass such as cellulose, guar gum, gelatin and xanthan gum can be used as gel electrolytes for zinc ion batteries, giving ZIBs more excellent power density and rate performance [8], which can effectively alleviate the problem that gel electrolytes are difficult to adapt to rough zinc anodes [77]. A viscoplastic gel electrolyte is prepared with an interfacial adaptability by using cellulose as a precursor, which can optimize the contact interface between the electrode and the electrolyte, guiding the homogeneous epitaxial uniform deposition of zinc by adjusting the solvation structure of Zn^{2+} [79]. Compared with the conventional single strategy for regulating the nucleation of zinc crystals in the electrochemical process, the functionalized flexible gel electrolyte can achieve the stability of the zinc anode. The charged groups in the gel electrolyte construct a channel for the efficient movement of Zn^{2+} and homogenize the interfacial electric field of the zinc anode, which can realize the preferential growth of the zinc crystal plane (002) and optimize the deposition kinetics of Zn^{2+} (Figure 5b) [7,80–82].

4.2. Biomass Mixed Electrolyte

Biomass has upgraded the electrolyte of the zinc−ion battery from an aqueous solution system to a hydrogel or solid film package. However, the system with a large amount of water makes the battery perform poorly at low temperatures. The introduction of ethylene glycol, $Zn(ClO_4)_2$ and other substances in the biomass electrolyte can prevent the formation of an orderly hydrogen bond network between water molecules and reduce the freezing point of the water electrolyte, thereby developing a zinc ion battery with antifreeze performance of [17, 83, 84]. The introduction of humidity-sensitive biomass such as gelatin can also achieve rapid intelligent humidity plasticization of ZIBs [73].The gelatin−based three−dimensional network could effectively facilitate the Zn^{2+} transfer, reducing the energy loss during the ion migration process [73,87,88]. Moreover, gelatin has excellent temperature sensitivity and hydrophilicity. The absorption of water in the surrounding environment and the increase in temperature can make the gelatin liquefy, improve the corresponding efficiency of silk fibroin to water vapor, and realize rapid intelligent humidity plasticization [73]. Otherwise, the dried gelatin has excellent mechanical properties, which can effectively inhibit the growth rate of zinc dendrites, and has excellent waterproof and degradation properties [69,89].

4.3. Biomass−PAM Copolymer Electrolyte

Polyacrylamide (PAM) with certain electrical conductivity is widely used in water−soluble polymers. The active amide groups, anion and cation groups on the polymer chain can physically and chemically react with a variety of substances, enhancing the polymer framework and providing additional pore structure for the polymer [74]. The electrolyte prepared by cross-linking of biomass and PAM exhibits a certain degree of hierarchical porous network structure and provides a large number of ion channels [16, 92]. Biomass enriches the active sites of the electrolyte. The hierarchical porous network structure facilitates the capture of water in the network and the absorption of aqueous solutions, increasing the ionic conductivity by allowing free movement of Zn^{2+} ions. Based on the sodium alginate−polyacrylamide hydrogel electrolyte with a highly three−dimensional porous structure, ZIBs can be made more stable [93]. Similar to the transport of Zn^{2+} in polymer electrolytes, the zinc ion-polymer complex in the salt jumps from one coordination site of the functional group to another coordination site [98, 99]. The abundance of ion channels and active sites ensures uniform Zn^{2+} flux, greatly inhibits the growth of zinc dendrites, and effectively prevents the passivation of zinc anodes [102-104].

5. Biomass for Separator

The diaphragm acts as a physical barrier between the electrodes, it can allow the electrolyte ions to move freely. The regulation of ion deposition can be achieved to avoid zinc dendrites [105]. Excellent performance of the separator can help to achieve high ion exchange rate, good mechanical properties and flexibility. Biopolymers contain a large number of complex functional groups, which can enhance the toughness of the separator, enrich the channels of water and ions, and increase electrical conductivity [9,17]. It can also cross link with the electrolyte and form hydrogen bonds with H_2O, regulating the deposition of zinc anodes and inhibiting the dendritic failure in zinc−ion batteries [106]. At present, biomass as separators is mainly carried out by modifying separators and developing new biomass separators.

5.1. Biomass Modified Commercial Separator

As a widely used commercial separator, glass fiber has stable chemical properties, suitable ionic conductivity and good wettability. Nevertheless, it is easy for zinc dendrites with ultra−high Young's modulus (108 GPa) to penetrate the separator [81,107]. Currently, biomass with functional groups can effectively modify the glass fiber separator. Gelatin is introduced into bare glass fiber to obtain a separator, which can inhibit the occurrence of a violent disproportionation reaction on the cathode material, thereby protecting its spinel structure [63]. Gelatin becomes a film connected to the glass fiber, increasing the toughness, flexibility and mechanical strength of the separator. In addition, gelatin can chelate Zn^{2+} into $ZnGI^{+}$ during electroplating, which increases the charge transfer resistance and improves the capacity retention rate [108]. Furthermore, during the electroplating process, gelatin will adsorb on the surface of zinc and form a film, which can cover the active center on the battery electrode, reduce the nucleation rate and obtain a uniform dendrite−free coating and obtain a uniform dendritic−free coating [109]. Therefore, biomass can be modified to improve the mechanical properties of commercial separators and enhance the capacity retention.

5.2. Biomass Modified Nafion Membrane

The Nafion membrane is an excellent proton exchange membrane with stable performance and has an amazing long stripping/plating cycle life. Compared with commercial separators, the Nafion membrane has a better ion exchange performance. It can provide binding sites for Zn^{2+} ions, effectively inhibiting the dissolution of organic cathode discharge products, and solve the exposition of zinc (100) [9]. Biomass modification can construct more conductive channels in the Nafion membrane, which can further improve the ion exchange performance. The lignin is introduced into the Nafion membrane by simple scaling after solution casting, the casting membrane immersed in $ZnSO_4$ can convert the casting membrane into the Zn^{2+} type [94]. The obtained lignin@Nafion membrane not only has high conductivity, but also has a higher service life than that of commercial physical separators [9].

5.3. Biomass Directly Used as Separators

Metal−organic−framework−coated polyolefin separators, polyacrylonitrile and other new separators can also be used as ZIBs separators to inhibit the generation of zinc dendrites, but they are limited by the cumbersome synthesis process and environmental problems. Therefore, the commercial application of pure biomass separator is more promising. By comparing pure biomass separator and commercial glass fiber separator, biomass separator has the advantages of rich porosity and low surface energy, which can effectively buffer hydrogen evolution and side reactions, and improve the reversibility of zinc anode [110, 111]. Taking cellulose separator as an example, it has high strength modulus, abundant hydroxyl functional groups and uniform and dense nanopores, which make it have high ionic conductivity. These can promote the migration of ions and charges, reduce the desolvation energy barrier of hydrated zinc ions, and accelerate the zinc deposition kinetics at the zinc electrode/electrolyte interface. It can effectively inhibit the occurrence of harmful side reactions such as zinc dendrites [112].

6. Biomass Used in Binders

The binder can firmly bond the electrode material and its active substances and conductive agents to the current collector, providing a stable interface for the movement of ions and charges, solving a series of problems such as the dissolution of active substances, and giving the battery a longer service life [15,114]. Polyvinylidene fluoride (PVDF) as a common binder has strong electron−withdrawing functional groups and a high dielectric constant, which can improve ion transport, attract positively charged ions such as Zn^{2+}, and provide a high concentration of charge carriers. However, the PVDF binder is not environmentally friendly, the organic solvent used is not only flammable and volatile, but also expensive and difficult to recycle [115].

Biomass water−based binder has a low cost, no pollution, no strict processing requirements for air and humidity, and the solvent evaporation is fast. Moreover, the biomass water−based binder has an average swelling trend in the electrolyte. Its strong electron−withdrawing functional groups, carboxymethyl groups and other functional groups can also weaken the hydrogen bond between hydroxyl groups, promote the penetration of the electrolyte, and make the binder have a high degree of wettability and flexibility, which can improve the cycle stability of zinc−ion batteries [116,117]. The mixture of sodium carboxymethyl cellulose, sodium cellulose acetate, sodium alginate, sodium carboxymethyl cellulose and polyvinyl alcohol can be used as binders. The bonding performance of carboxymethyl cellulose is better than that of PVDF, which can be ascribed to the close connection of carboxymethyl cellulose and all components, reducing the influence of the phase change of the active material on the life of the battery (Figure 9c) [10,30,118]. Moreover, carboxymethyl cellulose has the most active sites, the O atoms of carboxylate and hydroxide groups of carboxymethyl cellulose form many binding sites with the Mn atoms of $\alpha-MnO_2$. In addition, ZIB/ carboxymethyl cellulose has the best cycle performance (Figure 9d) [10].

7. Conclusions and Foresight

Exploring the application of biomass in zinc−ion batteries is of great significance for energy storage and conversion and the development of new applications of biomass.

Biomass polymers can be extracted directly from biomass. Grafting modification or modification with active compounds can improve their mechanical properties, hydrophilicity and flexibility. The energy density and energy storage effect of biomass-based energy storage devices are much lower than those of traditional metal-based energy storage devices. The preparation of biochar can inherit the original structure of biomass and can also be reorganized to improve the porosity and better retain the original structure. It is usually prepared as a carbon material for battery electrodes or conductive additives. The heteroatoms can effectively increase the active sites and improve the coulombic efficiency of the electrode. In addition, according to the unique properties and characteristics of biomass, efforts should be made to realize the organic combination of biomass and ZIBs components, improve conductivity, and accelerate the commercialization of biomass electrolytes.