

Functional Modification of Bacterial Cellulose and its Research Progress in the Field of Electrochemistry

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Abstract. Bacterial cellulose (BC) demonstrates unique application potential in the green electrochemical field due to its high-purity three-dimensional nanofiber network synthesized by microorganisms, extremely high specific surface area, excellent mechanical strength, and good biocompatibility. However, its inherent insulating property and the rigid demand of electrochemical devices for efficient electron conduction form a core contradiction, which requires functionalization modification to transform the microstructure into macroscopic performance. This study focuses on bacterial cellulose-based functional materials, systematically reviewing the principles and applicable boundaries of three technical routes: in-situ modification, post-functionalization modification, and blend regeneration modification. It also integrates their application progress in the regulation of ion transport in the separator of lithium-ion batteries, the construction of mechanical reinforcing phases, and the coordination of conductive networks. In the future, efforts should be made to develop multi-step hierarchical collaborative modification processes, establish multi-dimensional performance evaluation standards centered on ion conductivity, cycling stability, and mechanical strength, and promote the transformation of bacterial cellulose-based electrochemical materials from laboratory research to practical applications.

Keywords: Bacterial cellulose, functional modification, silicon-based anode, separator

1. Introduction

Bacterial cellulose (BC) is a kind of natural biomass nanomaterial with its unique three-dimensional network structure and renewable advantages, which has attracted extensive attention in the field of electrochemistry [1]. Although BC is an intrinsically insulating material, it needs to undertake efficient electron/ion conduction tasks in devices such as supercapacitors and batteries, which makes its direct application difficult [2]. Therefore, the functionalization modification of BC becomes the key path to break through this bottleneck: by introducing conductive components, constructing ion channels or regulating surface chemistry, the microscopic structural advantages of BC can be effectively transformed into macroscopic electrochemical performance, thereby providing a feasible technical solution for the development of green bioenergy materials [3].

To achieve this goal, existing research has developed three technical routes: in-situ modification, post-functionalization modification, and blend regeneration modification. These approaches have achieved significant progress in scenarios such as lithium-ion battery separators and silicon-based

negative electrodes [3-7]. For example, in situ addition of chito-oligosaccharide combined with covalent cross-linking can increase the Young's modulus of BC composite membrane [4]. The introduction of carboxyl groups by TEMPO oxidation can increase the conductivity of BC ions much higher than that of pure BC [5]; the lithium-ion migration number of BC separators modified with cationic polymer PDDA is much better than that of commercial separators [6]. However, the current modification methods still generally face common problems such as uneven dispersion of conductive components, poor coating stability, and damage to the natural crystalline structure. In addition, the application scenarios of various technologies still lack horizontal comparison, and the performance evaluation criteria have not formed a unified consensus [3-7].

This article systematically reviews the core characteristics of bacterial cellulose and its modification requirements in electrochemical applications. It focuses on summarizing the principles and application boundaries of three types of modification techniques: in-situ modification, post-functionalization modification, and blend regeneration modification. Furthermore, it summarizes three application directions of bacterial cellulose in silicon-based negative electrodes of lithium-ion batteries, namely regulation of ion transport in the separator, mechanical reinforcement construction, and synergy of conductive networks. This review aims at providing a bacterial cellulose functional modification systemic theory reference for the applications in the field of electrochemistry, and to outline expectations for subsequent multi-step collaborative modification processes in development and to provide a reference for the establishment of a comprehensive performance evaluation standard.

2. Core characteristics of bacterial cellulose and its modification requirements in electrochemistry

2.1. Core characteristics of BC

Bacterial cellulose (BC) is a natural nanoscale cellulose material secreted by microorganisms (mainly acetic acid bacteria such as *Komagataeibacter xylinus*, etc.) through the extracellular polysaccharide synthesis pathway. Its chemical structure is a linear chain of D-xylopyranose linked by β -1,4-glycosidic bonds. The chair-like conformation of adjacent units endows the molecular chain with excellent stability. The microbial synthesis pathway of BC determines its unique properties distinct from plant cellulose: during synthesis, no lignin, hemicellulose, etc. are produced; the cellulose content can reach over 95%, and no harsh bleaching and purification processes are required, which is in line with the requirements of green chemistry.

In supramolecular structures, BC chain through intensive intramolecular and intermolecular hydrogen bonding into highly ordered crystalline structure, and a significant degree of crystallinity is better than that of plant cellulose, and cellulose I crystal shape. The high crystallinity and high polymerization degree endow BC with excellent mechanical properties, with its Young's modulus and tensile strength at relatively high levels, and its tear resistance is significantly superior to that of traditional polymer films [3, 4]. BC is formed by the interweaving of nanofibers into a three-dimensional nano-porous network, with an extremely high porosity, large specific surface area, and strong water retention capacity. This unique nanofiber network not only provides abundant channels for ion transport but also provides sufficient active sites for the loading of functional substances [8-12].

In addition, the BC surface is rich in free hydroxyl groups, which endows it with excellent hydrophilicity and interface modification potential. It can be functionalized and modified through various chemical methods such as esterification, etherification, and graft copolymerization. BC also

has good biocompatibility, biodegradability, and low toxicity. Under the action of cellulase, it can naturally degrade into environmentally friendly small molecules such as glucose [1-3]. This provides a solid chemical foundation for its application in the fields of electrochemical energy storage and sensing.

2.2. Requirements for modification of BC

Although BC has the above outstanding characteristics, its native form has a series of inherent limitations in electrochemical applications, which need to be modified to achieve performance breakthroughs.

BC has environmental sensitivity to mechanical properties. The mechanical behavior of BC is closely related to the water-containing state. In a moist state, its elongation at break can reach 8% to 15%, showing certain toughness. However, after drying, hydrogen bonds rearrange to form a dense network, and the elongation at break drops sharply to about 3%, with a significant brittle characteristic. BC fibers present a directional arrangement during formation, resulting in obvious anisotropy in their mechanical properties, which limits their reliability in complex stress environments. In electrochemical systems such as silicon-based anodes, the volume expansion of active materials up to 300% during charging and discharging can easily lead to electrode powdering and structural collapse. Therefore, it is urgently necessary to introduce mechanical strengthening components to maintain the integrity of the electrode structure.

Lack of intrinsic conductivity is also the core problem of BC application in the field of electrochemistry. As an insulating polymer, BC cannot directly undertake the task of electron conduction required by electrode materials. As the electrode substrate for supercapacitors, the negative electrode framework for lithium-ion batteries, and the sensitive layer of electrochemical sensors, it needs to be endowed with conductive functions by introducing conductive components. The single chemical function of BC limits its diversified application scenarios. Although its superhydrophilicity is conducive to the infiltration of electrolyte, it is prone to dimensional changes and structural deformation in a humid environment, and has poor compatibility in hydrophobic electrolyte systems. BC itself does not possess electrochemical activity and is difficult to directly adapt to functional electrochemical scenarios such as medical dressings, antibacterial clothing, and intelligent wearable devices [2, 3, 7].

3. Modification techniques of bacterial cellulose in the field of electrochemistry

3.1. In-situ modification

In-situ modification refers to the process of directly intervening in the formation and performance regulation of the three-dimensional network structure of BC during its biosynthesis by adding functional substances or adjusting fermentation conditions in the culture medium [3, 4, 10]. The types of substances that can be added are diverse, including water-soluble polymers (such as chitosan oligomers, polyvinyl alcohol), insoluble fibers (such as microfibrillated cellulose), natural active substances (such as aloe vera gel), and various conductive fillers, etc. From the point of view of the mechanism of action, this modification mainly achieves performance improvement through three ways. The added functional substances can fill the network defects at the fiber scale, reducing stress concentration phenomena through physical filling [4, 9, 10]. Biological molecules such as chitosan oligomers or CBM3 can form a large number of hydrogen bonds with BC molecular chains, acting as an interface binder to enhance the bonding force between fibers. By adopting a two-step

fermentation strategy or adding specific inducers, the directional arrangement of fibers during the assembly process can also be regulated, thereby improving the performance imbalance caused by material anisotropy [10]. The advantage of in-situ modification lies in being able to achieve performance optimization while maintaining the integrity of the natural three-dimensional network structure of BC. However, conductive additives are prone to sedimentation in the culture system, resulting in an uneven distribution of them in the three-dimensional network. In addition, external substances may also interfere with the normal metabolic activities of bacteria.

3.2. Post-functionalization modification

Non-in-situ modification is carried out after the synthesis of BC. Through physical, chemical or morphological reconstruction methods, diverse functions such as conductivity and antibacterial properties are imparted to the BC on the pre-formed three-dimensional network [3, 11, 12]. Physical filling and impregnation are the most straightforward modification approaches, which are environmentally friendly. This method relies on the high-porosity three-dimensional network of BC, and through immersion, vacuum filtration or coating, conductive active substances (carbon nanotubes, graphene, nano-metal particles, conductive polymers, etc.) are physically loaded onto the surface or pores of BC fibers, achieving functionalization without chemical bonding [11]. Chemical group modification introduces specific functional groups or grafted functional molecules through covalent bonding onto the BC molecular chains, enabling precise performance control and long-term stability. Schiff base reactions, graft polymerization, TEMPO oxidation, etc. have been widely used to improve the antibacterial, hydrophobic/hydrophilic properties and ionic conductivity of BC. Although chemical modification can impart stable functional characteristics to BC, it is necessary to be vigilant about the toxicity and residue risks of reagents, and natural polysaccharides, plant extracts, etc. should be preferred as green modification agents. Nanomorphological reconstruction is another important non-in-situ modification path. Through physical fragmentation or acid treatment, the BC membrane is transformed into nanofibers (BCNF) or nanocrystals (BCNC). Utilizing their high specific surface area and good dispersibility as functional carriers, the material's adsorption, barrier, and electrochemical properties can be significantly enhanced [12].

3.3. Blend regeneration modification

As an additional technique apart from in-situ and non-in-situ modification, blending re-generation modification involves dissolving BC in a specific solvent system (such as ionic liquids, N-methylmorpholino-N-oxide, ZnCl_2 solution, etc.) and then mixing it with conductive fillers. Subsequently, the material is processed through regeneration, spinning, or casting membrane techniques to prepare conductive BC composite materials. This method enables the molecular-level uniform dispersion of conductive components within the BC matrix, and the material morphology has strong designability (fibers, membranes, aerogels, etc.). The high crystallinity of BC requires the use of strong polar solvents for its dissolution, and the viscosity of the dissolution solution is high, and its thermal stability is poor, which restricts further processing. Additionally, the dissolution process will destroy the original excellent crystalline structure and mechanical properties of BC.

4. Application status of bacterial cellulose in silicon-based negative electrodes of lithium-ion batteries

4.1. Regulation of lithium ion transport by bacterial cellulose-based functional diaphragms

In lithium metal batteries, the diaphragm plays a crucial safety function of isolating the positive and negative electrodes to prevent short circuits, directly affecting the kinetics of lithium ion transport and the uniformity of deposition, and is a core component determining battery performance [13]. The cation modification strategy has become an effective means for regulating ion transport in BC-based diaphragms, with the core being the use of strong electrostatic adsorption between positively charged polymers and negatively charged BC fibers to achieve charge modification and structural regulation of the BC fiber surface [6, 13]. Huang Jiajing et al. prepared a composite diaphragm by electrostatic self-assembly using polydiallyldimethylammonium chloride (PDDA) and BC. The introduction of PDDA made the fiber stacking change from dense to loose, and the Zeta potential changed from negative to positive [6]. This case proves that the electrostatic assembly strategy of cation polymers can simultaneously achieve physical structure regulation and selective optimization of charge transport, and is a simple and effective path for diaphragm functionalization. However, this method relies on physical adsorption for modification layer loading, and the coating stability still faces challenges in long-term cycling. Excessive introduction may lead to a decrease in diaphragm mechanical performance.

Apart from PDDA, the chemical grafting modification strategy also demonstrates effective control over ion transport. Cheng et al. prepared OBCS separators by grafting chitosan onto BC. After grafting, the fiber spacing increased, the dispersion uniformity improved, and both the porosity and ionic conductivity were enhanced [14]. This case indicates that covalent bonding chemical grafting can achieve a more stable modification effect than physical adsorption, avoiding the risk of coating detachment. However, the reaction conditions for grafting need to be strictly controlled, and there is an optimal range for the introduction of chitosan; excessive introduction may clog the pores and reduce the ion transport efficiency. Huang et al. prepared TOBC nanofiber membranes by oxidizing BC with TEMPO to convert hydroxyl groups into carboxyl and aldehyde groups, weakening the hydrogen bond between fibers and enhancing the porosity and the affinity of the separator to the carbonate-based electrolyte [5]. Its ionic conductivity exceeds that of pure BC by four times, and the cycling stability is excellent. Compared with physical coating, chemical grafting provides a more stable functionalized interface. The advantage of TEMPO oxidation is that it achieves permanent surface modification through chemical bonding, without the problem of coating detachment, and the oxidation reaction mainly occurs in the non-crystalline region, causing limited damage to the fiber skeleton. However, this method requires the use of chemical reagents such as TEMPO, the reaction conditions are sensitive to pH and temperature, and there are challenges in achieving consistent control during large-scale production.

4.2. Bacterial cellulose as a mechanical reinforcing phase inhibits the volume expansion of silicon-based anodes

At the application level of silicon-based anodes, researchers have recognized that the inherent mechanical properties of BC before carbonization are already a powerful tool for dealing with volume expansion [7]. Based on the theory of fiber reinforcement, the three-dimensional network of BC can maintain the structural integrity of the electrode by physically encapsulating and binding silicon particles, using the flexibility of the fibers to buffer volume changes, and the surface

hydroxyl groups can form strong hydrogen bonds with the silicon particles, optimizing stress transfer and distribution [3, 7].

Zhou Chuhan et al. prepared SiC@2%BC composite materials by uniformly coating BC on the surface of silicon-carbon particles using high-pressure homogenization and freeze-drying processes [7]. The core innovation of this approach lies in directly utilizing the intrinsic mechanical properties of BC before carbonization. Single-particle mechanical tests showed that the coating of BC enhanced the crushing strength and electrode DMT modulus, and significantly reduced the volume expansion rate. After cycling 100 times at 0.5C, the capacity retention rate of this modified electrode was much better than that of the unmodified electrode. This strategy was also successfully extended to the nano-silicon system, confirming its universality. However, its limitations are also obvious: although the coating strategy inhibited volume expansion, it failed to simultaneously solve the problem of overall electrode conductivity. When the active material loading increased, it was questionable whether the BC fiber network could effectively cover all the particles. It should also be noted that if the BC-coated composite materials are further carbonized, although the initial discharge specific capacity can be improved, due to the degradation of mechanical strength, the cycle stability actually decreases. This indicates that retaining the mechanical reinforcing function of BC is more crucial than simply pursuing conductivity.

4.3. Construction of efficient conductive networks and multifunctional composite systems with bacterial cellulose

To further balance the mechanical properties and conductivity of the electrode, the researchers designed BC in collaboration with components such as carboxymethyl cellulose (CMC), etc., to construct a functional network that combines mechanical reinforcement and efficient electron transport. Zhou Chuhan et al. carried out hydrothermal carbonization treatment on BC and CMC to obtain CBC-CMC composite additives [7]. On one hand, this material utilizes the dispersing effect of CMC to guide the uniform distribution of conductive carbon black Super P within the electrode, forming a "grapevine-like" efficient conductive network with multiple branched pathways. On the other hand, the high aspect ratio CBC-CMC fiber network significantly enhances the mechanical properties of the electrode. Experimental results show that the average response current of the SiO_x@CBC-CMC electrode is 4.4 times that of the SiO_x@PAA electrode, the DMT modulus increases by 58.4%, the volume expansion rate decreases by 70.9%; after cycling 300 times at 0.5C, there is almost no capacity decay. This case demonstrates that the fiber network of BC not only can serve as a mechanical reinforcement framework, but also can collaborate with CMC to construct a dual-functional composite system with stress dissipation and electron conduction. The limitation of this strategy is that it relies on hydrothermal carbonization treatment, which has more complex process steps than direct coating, and it is still necessary to study whether the partial sacrifice of the mechanical properties of BC fibers during the carbonization process will affect the enhancement effect in long-term cycling. Currently, this strategy has only been verified in the silicon oxide system, and whether it can be extended to pure silicon or high-capacity silicon-carbon alloy systems also requires further research.

BC can also be directly used as a functional binder or structural template in silicon-based anode systems. Park et al. combined BC with silicon nanoparticles and polyaniline (PANi-Si-BC), using BC as a structural template to fix the silicon particles, and using phytic acid modification to enhance the interface bonding, resulting in a composite material that maintained stable electrical conductivity after 100 repeated bending cycles, confirming the potential of BC in flexible energy storage devices [8]. Wang et al. constructed a one-dimensional carbon framework by pyrolyzing BC, combined with

magnesium thermal reduction to prepare a silicon-based nanorod negative electrode, and when the carbon content was controlled at 11 wt%, excellent electrochemical performance was exhibited [15].

5. Conclusion

Through the research, this article found that bacterial cellulose defects such as insulation and mechanical properties of anisotropic. Therefore, in situ modification, post-functional modification and blend regeneration modification should be adopted to adapt to different application scenarios. Among them, cationic modification can optimize the ion transmission selectivity of the separator; the three-dimensional network of un-carbonized bacterial cellulose can effectively buffer the volume expansion of the silicon-based anode during charging and discharging, and when combined with carboxymethyl cellulose for compounding, it can also simultaneously ensure the mechanical stability and conductivity of the electrode. It can be seen that the modification scheme needs to be selected according to the specific use requirements, and retaining the mechanical advantages of cellulose native skeleton is the core to improve the cycle life of silicon cathode. This article system combing three kinds of modified technology advantages and disadvantages and bacterial cellulose application in the field of cell membrane, silicon anode mechanism, perfect the review system of biomass electrochemical materials, designed for green energy storage field researchers composite electrode, the diaphragm materials provide a complete theoretical reference. At present, single modification methods generally have problems such as uneven dispersion of fillers and damage to the natural crystalline structure. Subsequently, multi-step collaborative modification processes should be developed, and a unified comprehensive performance evaluation standard should be established to promote the practical industrial application of bacterial cellulose-based electrochemical materials.

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