Biomaterials for High-Energy Lithium-Based Batteries: Strategies, Challenges, and Perspectives

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Developing high-performance batteries through applying renewable resources is of great significance for meeting ever-growing energy demands and sustainability requirements. Biomaterials have overwhelming advantages in material abundance, environmental benignity, low cost, and more importantly, multifunctionalities from structural and compositional diversity. Therefore, significant and fruitful research on exploiting various natural biomaterials (e.g., soy protein, chitosan, cellulose, fungus, etc.) for boosting high-energy lithium-based batteries by means of making or modifying critical battery components (e.g., electrode, electrolyte, and separator) are reported. In this review, the recent advances and main strategies for adopting biomaterials in electrode, electrolyte, and separator engineering for high-energy lithium-based batteries are comprehensively summarized. The contributions of biomaterials to stabilizing electrodes, capturing electrochemical intermediates, and protecting lithium metal anodes/enhancing battery safety are specifically emphasized. Furthermore, advantages and challenges of various strategies for fabricating battery materials via biomaterials are described. Finally, future perspectives and possible solutions for further development of biomaterials for high-energy lithium-based batteries are proposed.

1. Introduction

1.1. High-Energy Lithium-Based Batteries and Their Critical Issues

Rapid development of consumable electronics, electric vehicles, and grid-scale stationary storage has triggered ever-growing demands for advanced energy storage systems being able to offer sufficient energy at a reduced cost. This circumstance has stimulated the interest of new energy economy based on sustainable, inexpensive, and high-performance energy supply.[1] Thus, numerous efforts have been contributed to developing various clean energy storage technologies, in particular, on electrochemical energy storage/conversion systems. State-of-the-art electrochemical storage systems include rechargeable batteries, supercapacitors, fuel cells, and so forth. They are typically composed of a cathode and an anode coated on metallic current collectors, an electrolyte allowing ion transport, and a separator insulating the two electrodes. Among the various energy storage systems, rechargeable batteries such as lithium ion batteries (LIBs) have gained great commercialization success and have been applied as power supplies in many personal and industrial areas. Unfortunately, state-of-the-art LIBs using an Li-compound cathode (e.g., LiCoO₂) and a graphite anode approach their theoretical energy limits, making them barely sufficient to meet high-demanding needs for such as long-range electric vehicles.[2,3] Therefore, advanced LIBs with innovative high-capacity electrodes, e.g., metal oxides, silicon, etc. are of great interest, which are able to generate much higher energy density.[4] More significantly, next-generation batteries, “beyond LIBs” (e.g., lithium–sulfur (Li–S) and lithium–oxygen (Li–O₂) batteries, etc.), have emerged as a type of attractive energy storage devices, which feature ultrahigh energy density tremendously exceeding today’s LIBs.[5,6] In short, developing advanced high-energy Li-based batteries (i.e., LIBs and beyond “LIBs”) is of great significance for satisfying the needs by booming expansion of power supply markets.

For realization of high-energy Li-based batteries, in recent decades, advanced high-capacity electrodes have received considerable attention, which enable to store much more energy than currently used conventional electrodes. Namely, silicon anode is well known by its ultrahigh theoretical capacity of 4200 mA h g⁻¹[7] compared with 372 mA h g⁻¹ for graphite anode.[8] Meanwhile, various high-capacity anodes based on metal oxides such as Fe₂O₃, TiO₂, Co₃O₄, etc.[9–11] and high-capacity cathodes (e.g., Li-rich, Ni-rich cathodes, etc.[12,13]) have been widely studied for developing high-energy LIBs. Besides the high-capacity cathodes, high-voltage cathodes such as spinel LiMn₂O₄ and its high-voltage derivatives have become more and more prevailing today.[14,15] Furthermore, rechargeable Li metal batteries directly using Li metal as the anode are emerging as very promising battery systems, which are also known as “beyond LIBs.”[16,17] It is noted that Li metal when used as an anode, exhibits remarkable advantages of ultrahigh theoretical capacity (3860 mA h g⁻¹), the lowest redox potential (~3.04 V vs the standard hydrogen electrode) and low bulk...
density (0.53 g cm\(^{-3}\)).\(^{18,19}\) In this regard, Li–S, Li–O\(_2\), and solid-state Li metal batteries are the most significant categories. “Beyond LIBs” can provide extremely high energy density, e.g., 2600 Wh kg\(^{-1}\) for Li–S batteries,\(^{20}\) 3458 Wh kg\(^{-1}\) for Li–O\(_2\) batteries,\(^{21}\) compared with 387 Wh kg\(^{-1}\) for a LiCoO\(_2/\)graphite LIB,\(^{22,23}\) and thus hold great promise as next-generation rechargeable batteries.

Despite that the abovementioned battery systems show great potential for becoming the future energy storage devices, the broad practical applications are still limited today. The primary issues of high-energy Li-based batteries are illustrated in Figure 1: 1) The most fundamental issue is the low electrical conductivity of the electrodes. High-capacity electrodes such as silicon, metal oxides, sulfur, etc. all suffer from poor electrical conductivity and sulfur is even insulative.\(^{24–26}\) This results in poor electron-conduction networks inside electrodes and impedes accepting electrons from current collectors. 2) For high-voltage cathodes (e.g., LiMn\(_2\)O\(_4\)), the side reactions at the electrode/electrolyte interphase when being charged to high voltage lead to unstable formation of solid electrolyte interphase (SEI) and consumption of electrolytes.\(^{27,28}\) 3) High-capacity electrodes especially alloying-type ones share one big challenge, that is, the notable volume expansion in cycling processes. This causes electrode pulverization and unstable SEI, and thus finally fast capacity decay.\(^{29,30}\) 4) Sulfur and high-voltage cathodes experience dissolution/diffusion of electrochemical intermediates or “pollutants” (e.g., lithium polysulfides for sulfur cathode, Mn ions for LiMn\(_2\)O\(_4\) cathode), which greatly corrodes Li metal anodes and deteriorates the capacity and cycle life.\(^{31,32}\) 5) It is especially critical for Li metal batteries that the uncontrollable growth of Li dendrites poses severe safety concerns such as internal short circuit and even thermal runaway.\(^{33,34}\) It is, therefore, anticipated that stabilizing electrodes, capturing electrochemical intermediates, and protecting Li metal/enhancing safety are the primary targets of people’s efforts in order to achieve high-performance Li-based batteries for widespread applications.

1.2. Overview of Biomaterials for Energy Storage

Since battery performance is a result of collective contributions from various battery components, engineering of each component is essential for successful development of advanced Li-based batteries. The naturally diverse and complex structures/compositions of biomaterials bring about abundant functional groups, special structures, and unique physicochemical properties. These attractive attributes endow biomaterials with multifunctionalities, modification possibilities, and compatibilities with existing battery components. At the same time, adopting biomaterials strongly benefit the development of clean and sustainable energy economy. In fact, biomaterials have been widely employed in a vast variety of energy storage devices such as alkali-ion batteries (e.g., Li-ion, Na-ion, K-ion batteries),\(^{35–40}\) flow batteries,\(^{41–43}\) supercapacitors,\(^{44–47}\) etc. In this review, we particularly focus on the scope of Li-based batteries. Specifically, biomaterials can find their roles in boosting energy storage by means of making or modifying key battery components for addressing the critical issues of high-energy Li-based batteries shown in Figure 1. To this end, the main strategies are exploiting biomaterials for electrode, electrolyte, and separator engineering as illustrated in Figure 2. State-of-the-art studies have concentrated on utilizing a variety of biomaterials mainly based on mono-/poly-saccharides, proteins, lignin, fungus, etc. for enhancing performance of Li-based batteries. Representative biomaterials include cellulose, soy protein,
gums, alginate, etc., and the usage of them for specific engineering strategies is also depicted in Figure 2.

Biomaterials for electrode engineering are applied in four aspects, including structure design of active materials (AMs), electrode framework, electrode channel, and binder engineering. The aims of electrode engineering are to stabilize electrode structures and interphases, and even to prevent the diffusion of electrochemical intermediates. Because biomaterials comprise rich carbon moieties, carbonization of these materials leads to various carbonaceous materials. The resulting carbonaceous materials with unique architectures are used for design of advanced AM structures for improving stabilities of electrodes and electrode/electrolyte interphases, and/or for adsorbing electrochemical intermediates. Moreover, biomaterials are also exploited as electrode frameworks for loading AMs and as unique electrode channels for fabricating thick electrodes with oriented conduction pathways. It is noted that in addition to the aforementioned strategies for electrode engineering, biomaterials can be directly adopted as AMs for energy storage.\textsuperscript{[68–63]} The AMs are mainly classified into two categories: organic electrodes\textsuperscript{[52–56]} and carbon-based anodes.\textsuperscript{[57–61]} There are several comprehensive reviews describing the applications of biomaterials or carbonaceous materials derived from biomaterials directly as AMs, which are not included in this review. Detailed information can be referred in refs. \textsuperscript{[62–64]}. Additionally, binder as an important ingredient of an electrode controls the electrode microstructures and structural stability. In studies of binder engineering, researchers mainly capitalize on good physicochemical/mechanical properties of biomaterials for resolving the structural instability issue of electrodes. Some biobased binders even possess effectiveness for stabilizing electrode/electrolyte interphases and for capturing the electrochemical intermediates dissolved in organic liquid electrolytes. Electrolyte engineering by biomaterials has been focusing on substituting widely used organic liquid electrolytes by solid-state or quasi-solid-state electrolytes (e.g., gel electrolytes). Biomaterials that feature good solubility of Li salts and robust mechanical properties are appropriate electrolyte hosts or reinforcing agents. In electrolyte engineering strategies, various biobased solid electrolytes, gel electrolytes, and composite electrolytes have been reported, which are able to address the safety issues of Li-based batteries, in particular, Li metal batteries. Applying biomaterials for separator engineering aims to develop advanced separator alternatives for addressing the safety issues and boosting the electrochemical performance. Therefore, numerous efforts have been put to research new biobased separator materials featuring good mechanical strength, thermal stability, and high wettability. Moreover, separator coatings based on biomaterials are of great interest for trapping the dissolved electrochemical intermediates.

Figure 3 depicts the guidelines of appropriate protocols by applying biomaterials for rational design and fabrication of
advanced battery materials to address the corresponding critical issues. Specifically, the various abovementioned strategies play pivotal roles in stabilizing electrodes, trapping electrochemical intermediates, and protecting Li metal anodes/enhancing safety. It is reported that design of advanced AM structures, binder engineering, separator engineering, and electrolyte engineering by biomaterials make a contribution to trapping electrochemical intermediates. Using biomaterials for separator and electrolyte engineering helps to protect Li metal anode and enhance battery safety. Electrode engineering by biomaterials, including AM structure design, electrode framework, electrode channel, and binder engineering, is effective for stabilizing electrodes. Here in this review, we shed light on recent significant advancements in applications of biomaterials for boosting high-energy Li-based batteries, underlying their roles in stabilizing electrodes, capturing electrochemical intermediates, and protecting Li metal anodes/enhancing safety. The various strategies by using biomaterials for electrode, electrolyte, and separator engineering, and their contributions to battery performance are covered. The advantages and challenges of these strategies are discussed as well. Finally, we propose future perspectives and possible solutions for improving various energy materials by biomaterials.

2. Electrode Engineering

Based on the picture in Figure 2, electrode engineering by biomaterials is classified into four categories: AM structure design, electrode framework, electrode channel, and binder engineering. In this section, we summarize the significant progresses using biomaterials for AM structure design, electrode framework, electrode channel in several typical high-energy Li-based battery systems. Binder engineering, though it belongs to a part of electrode engineering, will be discussed in the next section independently.

2.1. Active Material (AM) Structure Design

The critical challenges of high-capacity electrodes (sulfur, silicon, etc.) fundamentally stem from low electrical conductivity and large volume deformation of AMs, and/or dissolution of AMs in organic liquid electrolytes. These three factors lead to poor electron conduction, severe electrode pulverization as well as loss of AMs in cycling processes, which eventually worsens the battery performance. Reducing the AM size down to nanosize is an effective way for shortening the ion-diffusion distance, improving the surface area for electron conduction, and more importantly, alleviating the strain from volume expansion. To further enhance the electrode properties, rational design of AM structures in multiscale represents an attractive strategy. Based on biomaterials, there are generally two routes for rationally designing AM structures: one is to create unique structures of AMs such as porous AMs, and the other one is to build desired architectures for composites of AMs and conductive agents, such as core–shell and porous AM composites. In this regard, core–shell and porous structured AMs and AM composites have been extensively studied by adopting biomaterials as sources for carbon and heteroatoms and as templates.

2.1.1. Core–Shell AM Composites

Core–shell structure strategy usually encapsulates AMs inside a conductive shell, e.g., carbon shell derived from biomaterials. As most AMs are in the form of particles, creating core–shell structures represents the most universal strategy for addressing the critical issues of AMs, especially high-capacity AMs. Designing a core–shell structure brings about three benefits depending on the AM properties. First, encapsulating AMs into a conductive shell promotes the electrical conductivity of every individual AM particle; thus, it helps to construct continuous and stable electron-conduction pathways and make full use of AMs in an electrode body. Second, the outer shell is conducive to withstand the notable volume change during lithiation/delithiation processes and stabilize SEI formation. Last, for some specific AMs such as sulfur that generates electrochemical intermediates (lithium polysulfides), the conductive shell plays an important role in preventing the diffusion of intermediates. The following sections describe two types of AMs: one experiences large volume change such as silicon and metal oxide anodes, and the other one is characterized by dissolution/diffusion of electrochemical intermediates such as sulfur cathodes.

Silicon Anodes: Among the various high-capacity anode materials, silicon has been recognized as the most promising
anode owing to its extremely high theoretical capacity of 4200 mA h g⁻¹, nontoxicity, and low cost.[83–88] However, the lithiation/delithiation processes induce a dramatic volume change >300%[69] resulting in electrode pulverization, unstable formation of SEI, and disconnection of electron-conduction pathways. Creating a conductive shell (e.g., carbon shell) on the silicon surface can effectively buffer the volume expansion, stabilize SEI formation, and provide continuous and stable electron-conduction pathways.

A good number of core–shell structured carbon/silicon composites have been reported by using such as glucose,[70–72] rice husk,[73,74] etc. as carbon sources. The battery performance has been dramatically enhanced by adopting the core–shell silicon anodes. For example, Li et al.[75] reported a core–shell structured silicon/carbon composite embedded in a sheet-like carbon film via carbonization of glucose and removal of NaCl template. The carbon film and hollow structure of the core–shell silicon/carbon spheres provided good electrical conductivity and buffering effect for the volume expansion of silicon. As a result, the researchers demonstrated excellent battery performance with a high capacity retention of 93.6% (=1018 mA h g⁻¹) after 200 cycles at 1 A g⁻¹. In Figure 4a–d, a recent work by Shao et al.[65] demonstrated that a porous carbon shell was able to further enhance the electrode performance, because the large pore volumes increased the contact area between the electrode and electrolyte. In their work, the researchers dehydrated glucose first and assembled it with a soft template (Pluronic F127) that was coated on silicon surface in Figure 4a. After undergoing a hydrothermal treatment and carbonization, a core–shell silicon/porous carbon (N-SPC) composite was fabricated as shown in Figure 4b,c. Benefitting from the unique structures, the SEI layer and structures of the silicon anodes were effectively stabilized. As a result, the battery with N-SPC anode delivered very stable cycling performance with a capacity of 1607 mA h g⁻¹, which was substantially higher than that of native silicon electrode in Figure 4d.

In addition, heteroatom-doping into the carbon network, especially nitrogen-doping (N-doping), can effectively enhance the capacity and cycling performance of silicon anodes.[76] This mainly results from the improvement in electrical conductivity and electrochemical activity.[77–79] Specifically, heteroatom-doping brings about several advantages: 1) the larger electronegativity of heteroatoms (e.g., N (3.04), C (2.55)) helps the electron transfer; 2) the heteroatoms generate more edges and vacancy defects for efficient Li-ion storage and Li-ion diffusion; 3) the heteroatoms show high binding energies with Li ions and thereof increase the capacity.[76,79–82] Kim et al.[86] reported a study of using glucosamine, a kind of amino sugar containing N atoms, for fabricating core–shell silicon/N-doped carbon composites in Figure 4e. The researchers applied a facile solution-coating method for coating carbon precursors, i.e., glucose and glucosamine, on the silicon surface. Carbonization of these two mixtures led to two kinds of core–shell silicon/carbon composites: core–shell silicon/carbon (C–Si) by glucose and core–shell silicon/N-doped carbon (NC-Si) by glucosamine (Figure 4f,g). By comparing the cycling and rate performance in Figure 4h,i, it was found that NC-Si exhibited much higher capacity and cycling stability than C–Si and bare Si.

Metal Oxide Anodes: Metal oxides such as SnO₂, Co₃O₄, MnO₂, FeO₂, CuO, etc.[83–88] have emerged as promising anode candidates, which provide higher capacity than today’s graphite anode. In contrast to intercalation chemistry, metal oxides can interact with Li ions based on conversion mechanism (MOₓ + 2xLi ↔ M + xLi₂O), where M indicates the metal.[90] In other words, insertion and extraction of Li ions for metal oxides exceeds 6 Li ions per formula unit compared with graphite anode.[100] Therefore, metal oxides usually possess much higher theoretical capacity; for example, CuO obtains a theoretical capacity of 674 mA h g⁻¹ with two electrons transferred.[91] At the same time, metal oxides feature good chemical stability, low cost, and abundance in nature. However, similar to other high-capacity electrodes, metal oxide anodes present unsatisfactory electrical conductivity and undergo large volume change in electrochemical reactions, which greatly limits their broad applications.[26,92] Thus, core–shell structure also makes a contribution to improving the electrochemical performance of metal oxide anodes. Compared with silicon anodes, constructing core–shell metal oxide anodes via biomaterials has been less intensively reported; however, there are still some impressive studies.

As shown in Figure 5a, Hong et al.[83] demonstrated a one-pot synthesis strategy for double-shelled yolk-shell SnO₂ electrode by carbonization of sucrose and combustion/removal of carbon as the template to generate voids. Yolk–shell structure provided two benefits here. First, unlike hollow structure with low packing density and energy density, yolk–shell structure increased the weight percentage of AMs for improving the energy density. Second, the voids between the core and the shell acted as buffering space for accommodating the volume expansion of SnO₂. The resulting double-shelled yolk–shell SnO₂ powders exhibited uniform size distribution in Figure 5b,c. At varying current densities such as 1 C and 5 C, double-shelled yolk–shell SnO₂ outmatched the dense SnO₂ spheres, which was verified by the significantly higher capacities for double-shelled yolk–shell SnO₂ in Figure 5d. Another work by Wen et al.[84] reported a core–shell structured composite CuO electrode (CuO@C) with carbon as the shell by carbonization of Cu₂O that adsorbed humic acid (HA) as shown in Figure 5e. The resulting CuO@C composite presented a disordered wormhole-like structure with amorphous carbon as the shell in Figure 5f,g. The core–shell CuO delivered much better performance in cycling stability and rate capability compared with unmodified CuO. As shown in Figure 5h,i, core–shell CuO@C (CC-550) showed negligible capacity decay and much higher capacities over various current densities. This indicated that the core–shell structure helped to withstand the volume change and thus improved the stability of SEI and continuance of electron-conduction networks for the CuO@C electrode.

Sulfur Cathodes: Although sulfur cathodes present high theoretical specific capacity (1675 mA h g⁻¹)[93,94] and theoretical energy density (2600 Wh kg⁻¹),[95,96] their practical applications are still severely hindered. This is because sulfur suffers from not only huge volume expansion (+80%) in alloying/dealloying processes with Li ions, but also dissolution of sulfur-related species in liquid electrolytes during electrochemical cycling.[97] The dissolution of sulfur-related species, e.g., lithium polysulfides, leads to the great loss of sulfur AMs and the notorious
“shuttle effect,” which corrodes Li metal anode and highly deteriorates the battery performance.\cite{98,99} At the same time, sulfur is insulative, indicating that a large quantity of conductive agents is needed to add in the electrodes, which sacrifices the energy density.\cite{100} Therefore, core–shell structure is significant for sulfur cathodes. Creating a conductive shell on the sulfur particle surface can effectively solve the principal issues of sulfur cathodes. Specifically, the shell helps to reduce the stain from volume change, increase the electrical conductivity of sulfur AMs, and importantly, block the diffusion of polysulfides.

Li et al.\cite{101} reported a core–shell structured sulfur cathode by encapsulating sulfur into a microporous carbon shell based on carbonization of amylose. Such core–shell sulfur/carbon composite presented a high surface area of 672.6 m² g⁻¹ and an initial discharge capacity as high as 1490 mA h g⁻¹. Zhang et al.\cite{93} reported an interesting study of impregnating sulfur into a double-shelled carbon spheres to generate a core–shell structured sulfur/carbon composite (DHCS-S) as shown in Figure 6a,b. In the strategy of synthesizing double-shelled hollow spheres, the researchers used SnO₂ hollow spheres as a type of hard template and coated glucose-derived polysaccharide
on both interior and exterior surfaces of the spheres. The double-shelled hollow spheres were generated by carbonization of polysaccharide and removal of the SnO2 template. Compared with native sulfur cathode (CB-S), DHCS-S showed obviously improved capacity and long-term performance with smaller capacity decay, owing to the stabilized electrode structure and trapped polysulfides by the double shell in Figure 6c. Meanwhile, in Figure 6d, the rate capability of DHCS-S was also enhanced as compared with CB-S, attributed to the improved electrical conductivity by the carbon shell, which promoted the charge-transfer kinetics. Zhang et al.[94] reported a core–shell structured carbon-coated sulfur/activated carbon (AC-S) composite via solution coating and hydrothermal carbonization of glucose (Figure 6e–g). As shown, the AC-S composite was covered by a layer of uniform amorphous carbon with numerous nanopores, which increased the accommodation space for trapping polysulfides. The core–shell carbon coated AC-S showed much higher capacity and much better stability in 50 cycles in Figure 6h as compared with AC-S, which was an indicator for the effectiveness of the carbon coating for trapping and reutilizing polysulfides. The rate capability of core–shell AC-S was also obviously improved in Figure 6i, owing to the promoted charge-transfer kinetics by the core–shell structure. Brun et al.[102] used monosaccharides such as glucose and xylose as carbon sources for fabricating hollow carbon spheres and infiltrated sulfur into them to form core–shell sulfur/carbon composites. The resulting Li–S batteries delivered stable capacities >800 mA h g\(^{-1}\) at 1 C compared to the untreated sulfur cathode with a capacity of only 300 mA h g\(^{-1}\).

2.1.2. Porous AMs and AM Composites

Biomaterials, acting as sources for carbon and even AMs, and as templates, have been widely investigated for fabrication of porous AMs and AM composites. To this end, studies have mainly focused on fabricating porous structured AMs or loading AMs into a porous host, usually a porous carbon host derived from biomaterials. Porous structure generates multiple advantages. First, porous structured AMs provide immense
surface area, which increases the contact area between AMs and electrolytes and thus improves the ion-conduction kinetics. Second, porous structured AMs are able to mitigate the volume change. Third, for AM composites such as AM/carbon composites, a porous carbon matrix improves the capacity for hosting AMs and electrolyte permeation. For specific electrodes such as sulfur cathodes, the porous structure is helpful for adsorbing electrochemical intermediates, polysulfides. In a word, for those AMs (e.g., silicon, metal oxides, etc.) that experience large volume deformation, porous AMs and AM/carbon composites have proved effective for overcoming the volume expansion problem; for the ones (e.g., sulfur) emitting electrochemical intermediates, porous AM/carbon composites have been the main research focus.

Silicon Anodes: Creating porous silicon is an attractive solution for buffering volume expansion and stabilizing formation of SEI. The vast resources of silicon in nature have inspired tremendous studies of extracting silicon from biomaterials, which is of great significance for sustainable energy supply.\cite{103,104} Rice husks (RHs)\cite{67} are the most intensively studied silicon source, which are the most common agricultural byproducts containing main components such as lignin,
cellulose, and 15–20 wt% silica. Liu et al. demonstrated an energy-efficient and scalable method in Figure 7a for producing nanosilicon (nano-Si) from RHs. The researchers first converted raw RHs to nano-SiO₂ via thermally decomposing the organics and then magnesiothermally reduced nano-SiO₂ to nano-Si. They revealed that the weight loss at 300–550 °C was due to cellulose/hemicellulose/lignin degradation and 23 wt% mass remained as the SiO₂ product from
thermogravimetric analysis (TGA) results. The obtained nano-Si showed a porous structure with a surface area of 245 m$^2$ g$^{-1}$ as illustrated in Figure 7b,c. In comparison of metallurgical-grade Si particles, the nano-Si derived from RHs delivered much higher capacity and more stable cycling performance in Figure 7d. The good performance of nano-Si resulted from the porous structure that shortened the ion-diffusion distance and the high internal porosity that enabled the volume change of Si without breaking the SEI layer on the exterior surface. Based on RHs, porous Si-based anodes such as Si/C or SiO$_2$/C composite anodes can also be fabricated. For example, Yu et al.\cite{106} reported a porous Si/C/graphene composite via calcination of RHs and subsequent thermal treatment by Mg powders in an inert gas. Subsequently, the as-prepared samples were dispersed in graphene oxide suspensions and then calcinated to obtain the final product. The Si/C/graphene composite anode exhibited a capacity of 760 mA h g$^{-1}$ after 80 cycles at 0.1 A g$^{-1}$. Cui et al.\cite{107} reported a type of microsized porous SiO$_2$@C composite by aluminothermic reduction from RHs. The researchers carbonized RHs in argon gas and activated the product by ZnCl$_2$ to generate porous carbonized RHs. Finally, the porous SiO$_2$@C composite was prepared after undergoing aluminothermic reduction and removal of Al$_2$O$_3$ by HCl. The SiO$_2$@C composite anode delivered a high reversible capacity of 1230 mA h g$^{-1}$ at 0.1 A g$^{-1}$. In addition to RHs, other abundant natural resources are also proper materials to produce Si and Si/C composites. For example, Praneetha et al.\cite{108} developed a rapid microwave assisted process for preparing Si from RHs, bamboo culm, and sugarcane bagasse. They found that the Si particles obtained from the three kinds of sources were all nanoporous. Wang et al.\cite{109} produced ultrafine mesoporous Si particles derived from bamboo leaf, which delivered a high capacity of 1800 mA h g$^{-1}$ at 0.2 C.

Heteroatom-doped (e.g., N-doping) Si composites have been of great interest as well, which has proved effective for further improving the battery performance owing to the enhancement in electrical conductivity and electrochemical activity by the heteroatoms, as discussed above in Section 2.1.1. Zhang et al.\cite{104} reported a 3D porous Si/N-doped carbon composites (Si@N/C) derived from bamboo charcoal as shown in Figure 7e. In their work, 3D porous Si particles were first obtained by extraction from bamboo charcoal followed by magnesiothermic reduction. Then polyacrylonitrile (PAN) was coated on the Si surface and was carbonized to eventually generate 3D porous Si@N/C. The Si@N/C showed a highly porous and nanonose-like structure in Figure 7f. As a result, Si@N/C showed much improved battery performance such as cycle and rate performances as well as Coulombic efficiency compared to porous Si particles in Figure 7g.h. This was owing to the porous nanostructure with N-doped carbon on the outer surface, which enhanced the capacity and helped to sustain the volume expansion of Si and stabilize the SEI layer. Another work by He et al.\cite{108} demonstrated the use of horse-tail for extracting Si nanoparticles and generated N-doped Si/C composites by coating polypropylene (PPy) and carbonizing this coating layer. Such N-doped Si/C composite delivered a high capacity of 1047.1 mA h g$^{-1}$ at 0.5 A g$^{-1}$ after 450 cycles.

Metal Oxide Anodes: Fabrication of porous structured metal oxides has been intensively studied, because synthesis of metal oxides is versatile by adapting various precursors with doping materials.\cite{110,111} Via utilizing biomaterials as template or carbon source, manifold porous metal oxides or metal oxide composites with different morphologies of 0D nanoparticles,\cite{112-114} 1D nanorods/nanotubes,\cite{115-117} and 2D nanosheets,\cite{118,119} etc. have been reported. As shown in Figure 8a, porous Co$_3$O$_4$ hollow nanorods were reported by Shim and coworkers\cite{110} who used a type of bacteria, Bacillus subtilis, as the soft template along with binding/reduction of the metal ions on the bacteria and spontaneous oxidation. The final porous Co$_3$O$_4$ hollow nanorods were achieved by thermal treatment at 300 °C for removing the bacterial template, which exhibited a rough surface (Figure 8b) and mesoporous structure with a surface area of 73.3 m$^2$ g$^{-1}$ (Figure 8c). The resulting porous Co$_3$O$_4$ hollow nanorods as anodes presented good reversible capacities in Figure 8d, which was contributed by the porous nanostructures for effectively accommodating the mechanical strain from volume expansion. Liu et al.\cite{115} studied a type of porous hollow NiO nanotubes by covering NiO gel on filter paper as the template and then calcinating the NiO/filter paper composite to result in the final product. The porous hollow structure did offer not only high surface area for AM/electrolyte contact, but also sufficient space for buffering volume change without pulverization. Such an NiO anode delivered a very stable reversible capacity of 620 mA h g$^{-1}$ and maintained over 600 mA h g$^{-1}$ after 100 cycles.

In addition, a significant number of studies on fabricating various metal oxide/carbon composites have been reported. Compared with pure metal oxides, compositing with carbon can obviously increase the electrical conductivity of metal oxide AMs. For example, Xia et al.\cite{112} reported an interesting study of using lotus pollen grains as both carbon source and template for generating porous structured NiO/C composite AMs. The porous NiO/C composite spheres presented a rough surface assembled by porous sculptures and had both meso- and macropores with a surface area of 171.58 m$^2$ g$^{-1}$. Another study of synthesizing Mn$_2$SnO$_4$/Sn/C composite cube was reported by Liang et al.\cite{111} in Figure 8e. The researchers used (–)fructose as the carbon source and synthesized the composite cubes by a simple hydrothermal process. It was revealed in Figure 8f that the composite cube actually obtained different components such as Sn, Mn$_2$SnO$_4$, and C. The porous Mn$_2$SnO$_4$/Sn/C composite cube showed the lowest charge-transfer resistance as compared with Mn$_2$SnO$_4$ and Mn$_2$SnO$_4$/C composite, mainly due to the doping effect of carbon as shown in Figure 8g. Naturally, the rate capability of Mn$_2$SnO$_4$/Sn/C composite cube was the highest among the three kinds of AMs, benefiting from the porous structure for accommodating the volume expansion and the carbon portion for improving the electron-conduction ability in Figure 8h. Xia et al.\cite{113} adopted microalgae as the template and carbon source for fabricating porous-structured hollow MnO/C microspheres via a simple solution-coating and carbonization method. The unique nanostructure led to a high reversible specific capacity of 700 mA h g$^{-1}$ at 0.1 A g$^{-1}$.

Sulfur Cathodes: In studies of addressing the critical problems of sulfur cathodes, one finds that rational design of porous materials for hosting sulfur AMs has been accepted to be the most important strategy. A highly porous carbon improves the loading capacity for sulfur and ion-conduction kinetics. Researchers have put tremendous efforts to fabricate various
types of porous carbon or heteroatom-doped porous carbon from numerous biomaterials, such as rice,[120] hair,[121] pig bone,[122] tuna bone,[123] silk coconut,[124] bamboo,[125] mono-/poly-saccharides,[126,127] banana peel,[128] wheat straw,[129] proteins,[130–132] and so forth. These studies mainly applied a carbonization process together with chemical activation (e.g., using KOH) or etching (e.g., using HF) to generate porous carbonaceous materials and then infiltrated sulfur into the pores.
by heat melting or solution infusion. Recently, an interesting porous structure, porous macrocellular carbon, inspired by popcorn was reported by Zhong et al.\cite{120} As shown in Figure 9a, the researchers puffed rice in a sealed device at a high temperature of 200–300 °C and a high pressure of 0.5–1.5 MPa, which resulted in a 3D macrocellular foam-like structure. Then they carbonized the puffed rice and used NiCl2 etching to create carbon/Ni (PRC/Ni) composite derived from highly porous puffed rice, with enhanced electrical conductivity of $7.2 \times 10^4$ S m$^{-1}$ by embedded Ni particles. After impregnating sulfur into PRC/Ni, a porous macrocellular PRC/Ni/S composite was fabricated as shown in Figure 9b. The Nyquist plots in Figure 9c confirmed that the PRC/Ni/S composite showed the lowest charge-transfer resistance due to the improved electrical conductivity by Ni particles and porous structure for reducing ion-diffusion distance. As a result, an excellent cycling performance and high Coulombic efficiency of the PRC/Ni/S electrode even with a high sulfur loading of 4 mg cm$^{-2}$ was demonstrated in Figure 9d. The good battery performance proved that such nanostructure effectively improved the utilization of sulfur AMs and stability of electrodes as well as reduced the loss of sulfur species.

Heteroatom-doping such as N-doping,\cite{133–135} O-doping,\cite{136–138} S-doping,\cite{139–141} etc. has played important roles in electrochemical performance of sulfur cathodes. Particularly, nitrogen is one of the most attractive doping atoms since it can increase electrical conductivity, carbon wettability, and more importantly offers strong interactions with polysulfides for reducing the polysulfide diffusion.\cite{142,143} Yu et al.\cite{122} reported a graphene wrapped hierarchical structured sulfur/carbon composite derived from hair. Hair acted as both carbon and nitrogen sources in their work. As illustrated in Figure 9e, the researchers first carbonized and activated hair to result in microporous N-doped carbon, and then infiltrated sulfur by heat-melting diffusion. Finally, they introduced positive charges by cetrionium bromide (CTAB) for wrapping graphene oxide (GO) nanosheets followed by reduction to form graphene (rGO). The TEM and EDS mapping images in Figure 9f indicated homogeneous distribution of C, N, O, and S elements in the composite. The C/S composite without graphene wrapping showed high initial discharge capacities of 1041 and 930 mA h g$^{-1}$ at 0.2 C and 0.5 C respectively, indicating that the porous N-doped carbon had some effects on preventing diffusion of polysulfides in Figure 9g. When wrapping the C/S composite by graphene nanosheets as additional physical barriers, the battery performance was further improved in Figure 9h that the capacity decay was substantially suppressed. Chen et al.\cite{130} reported a nitrogen and oxygen dual-doped honeycomb-like porous carbon derived from soy bean. The dual-doped porous carbon exhibited an extremely high surface area of 2690.3 m$^2$ g$^{-1}$ and the resulting sulfur composite cathode delivered a high reversible capacity of ~698.5 mA h g$^{-1}$ at 1 C. Schipper et al.\cite{144} synthesized a series of N-doped and S-doped porous carbon based on various carbon precursors (e.g., glucose, glucosamine) using a sol–gel process. They concluded that the sulfur/heteroatom-doped carbon composites presented obviously decreased capacity fading and polarization throughout cycling testing.

2.2. Electrode Framework

Differentiating from nanostructure design of AMs discussed above, electrode frameworks derived from biomaterials work as platforms or skeletons for loading AMs, which are able to realize the following desirable targets: 1) improve the overall structural stability and flexibility of the electrodes; 2) provide express electron conduction in a timely way; 3) improve the dispersion quality of AMs and the contact area of internal AMs with liquid electrolytes; 4) help to withstand the volume change of AMs; 5) increase the weight fraction of AMs warranted by a binder-free design. Most electrode frameworks are electrically conductive for facilitating the electron transfer, and therefore, biomaterials have great potential to act as electrode frameworks after carbonization. Moreover, biomaterials are very attractive electrode framework candidates because some of them can assemble into unique structures, such as 1D nanofibers, 2D nanosheets, and 3D continuous networks and foams. For example, Lv et al.\cite{145} synthesized a series of 1D metal oxide/carbon composites based on seaweed fibers, where metal oxide particles were embedded in the seaweed-derived carbon fibers. Zhu et al.\cite{112} developed 2D porous carbon nanosheets derived from soy bean hulls for loading sulfur AMs.

Compared to 1D or 2D structured electrode frameworks, 3D structured ones show notable advantages in providing more stable electrode structures and electron-conduction networks. Benefiting from these merits, Kuang et al.\cite{146} reported a thick electrode based on cellulose nanofibers (CNFs) in Figure 10a. In their work, the researchers fabricated conductive CNFs by mixing carbon black (CB) particles with CNFs, and then the AMs, LiFePO4 (LFP), were introduced into the networks. The thick electrode was realized by packing the CNF-based electrode layer by layer and applying compression (Figure 10b). As shown in Figure 10a,c, for the CNF-based electrode, the CB particles bonded to CNF network resulting in interconnected 3D conduction networks around LFP, compared to the conventional LFP electrode with random conduction networks. Huang et al.\cite{90} reported a binder-free and flexible Fe2O3 electrode by coating amorphous Fe3O4 on carbonized bacterial cellulose nanofibers (A-Fe2O3@CBC) where the CBC acted as an electrode framework in Figure 10d. Such A-Fe2O3@CBC showed a relatively rough surface due to the coating of amorphous Fe3O4 nanoshells. Zhou et al.\cite{147} reported an interesting work of fabricating a 3D carbon foam derived from elastin-like polypeptides (ELP-16) for hosting metal vanadium phosphate (MVP) AMs, specifically Li$_3$V$_2$(PO$_4$)$_3$ (LVP) and Na$_3$V$_2$(PO$_4$)$_3$ (NVP). The researchers took advantage of the interactions between MVP precursors and ELP-16 that assembled into a 3D fibrous structure, which finally led to a 3D carbon foam with MVP particles embedded into it as shown in Figure 10e. Via utilizing the 3D electrode frameworks, the electrochemical performance of the electrodes were significantly enhanced. For example, the areal capacity of the thick LFP electrode was much higher than that of conventional LFP electrode (Figure 10f) mainly due to the improved ion-/electron-conduction kinetics by the conductive framework. In addition, the long-term performances were excellent for A-Fe2O3@CBC and MVP 3D foam in Figure 10g,h, which was attributed to the much more stable electrode structure maintained by the frameworks. Zheng et al.\cite{148} coated
MnO on carbonized cotton fibers (MnO/CCFF) as the support for fabricating free-standing anodes. The resulting MnO/CCFF anode presented a high reversible capacity of 1081 mA h g\(^{-1}\) after 200 cycles at 0.1 mA cm\(^{-2}\). Hu et al.\[^{149}\] reported a Si-coated conductive nanopaper for flexible Si anode, via fabricating 3D porous carboxymethylated nanofibrillated cellulose/carbon nanotubes (NFC/CNT) conductive aerogels. The researchers deposited Si by plasma-enhanced chemical vapor deposition (PECVD) on the aerogel nanopaper and the resulting Si-nanopaper anode exhibited a stable capacity of 1200 mA h g\(^{-1}\) for 100 cycles. More information about typical AMs or AM composites derived from various biomaterials and their electrochemical performance is summarized in Table 1.

2.3. Electrode Channel

Above discussion has presented the fabrication of various types of nanostructured electrodes for realizing high-energy Li-based batteries. These attempts have made significant progresses, but most electrodes possess randomly distributed conduction networks resulting in poorly controlled ion-conduction and prolonged ion-diffusion distance. This effect becomes more prominent for thick electrodes and thereof limits the performance and even realization of them. As is well known that the porosity and tortuosity are the two decisive factors for ion-conduction kinetics of the electrodes. Particularly, tortuosity plays a critical role in the rate performance\[^{160}\] and minimizing tortuosity is significant for realizing fast ion transport. It is therefore encouraging to develop a low-tortuosity electrode architecture, which is especially essential for thick electrodes.

Nowadays, people are inspired by the aligned microchannels of wood for water-transport and exploited a variety of vertical carbon microchannels derived from wood for fabricating advanced electrodes. Intensive studies have reported using wood-derived carbons for fabricating various high-performance energy storage devices such as LIBs,\[^{161,162}\] Li–O\(_2\) batteries,\[^{163,164}\] Li–S batteries,\[^{165,166}\] supercapacitors,\[^{167,168}\] and so on. To name a few, Lu et al.\[^{161}\] fabricated thick LiCoO\(_2\) (LCO) electrodes based on pinewood-derived carbon microchannels as shown in Figure 11a. The microchannels brought about 1.5 times lower of the tortuosity and about 2 times greater of the ionic conductivity compared with the conventional LCO electrodes with randomly packed structures. They used a sol–gel
process, in which LCO precursor gel was infused into the vertical wood microchannels and then calcinated to generate thick LCO electrodes. The SEM images of the top view (Figure 11b) and cross-section view (Figure 11c) verified that such a thick LCO electrode exhibited vertically aligned open microchannels that loaded LCO AMs. It was interestingly found that ultrahigh

Table 1. Summary of typical AMs or AM composites fabricated by biomaterials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Biomaterial/Usage</th>
<th>Structure</th>
<th>Current rate</th>
<th>Capacity [mA h g(^{-1})]</th>
<th>Coulombic efficiency [%]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-based anodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si/C</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>400 mA g(^{-1})</td>
<td>1607</td>
<td>99.1</td>
<td>[65]</td>
</tr>
<tr>
<td>Si/C</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>200 mA g(^{-1})</td>
<td>2045</td>
<td>90.0</td>
<td>[70]</td>
</tr>
<tr>
<td>Si/C</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>1000 mA g(^{-1})</td>
<td>1018</td>
<td>93.6</td>
<td>[75]</td>
</tr>
<tr>
<td>Si/C</td>
<td>Citric acid/Carbon source</td>
<td>Core–shell</td>
<td>100 mA g(^{-1})</td>
<td>1489</td>
<td>N/A</td>
<td>[150]</td>
</tr>
<tr>
<td>Si/C</td>
<td>Reed/Si source Glucose/C source</td>
<td>Porous</td>
<td>0.5 C</td>
<td>1050</td>
<td>N/A</td>
<td>[151]</td>
</tr>
<tr>
<td>Si/N-doped C</td>
<td>Glucosamine/C, N sources</td>
<td>Core–shell</td>
<td>2000 mA g(^{-1})</td>
<td>1735</td>
<td>99.5</td>
<td>[66]</td>
</tr>
<tr>
<td>Si/N-doped C</td>
<td>Rice husk/Si source</td>
<td>Not specific</td>
<td>500 mA g(^{-1})</td>
<td>1031</td>
<td>≈100</td>
<td>[74]</td>
</tr>
<tr>
<td>Si/graphite/C</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>0.1 C</td>
<td>637.7</td>
<td>≈99.5</td>
<td>[72]</td>
</tr>
<tr>
<td>Si/graphite/C</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>60 mA g(^{-1})</td>
<td>602.7</td>
<td>N/A</td>
<td>[152]</td>
</tr>
<tr>
<td>Nano-Si</td>
<td>Rice husk/Si source</td>
<td>Not specific</td>
<td>1 C</td>
<td>1120</td>
<td>99.3</td>
<td>[103]</td>
</tr>
<tr>
<td>Si</td>
<td>Rice husk/Si source</td>
<td>Porous</td>
<td>1 C</td>
<td>2000</td>
<td>99.7</td>
<td>[105]</td>
</tr>
<tr>
<td>SiO(_2)/C</td>
<td>Rice husk/SiO(_2) C source</td>
<td>Not specific</td>
<td>74 mA g(^{-1})</td>
<td>485</td>
<td>97</td>
<td>[73]</td>
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<tr>
<td>Si@SiO(_2)/C</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>150 mA g(^{-1})</td>
<td>1100</td>
<td>&gt;99</td>
<td>[71]</td>
</tr>
<tr>
<td>Metal oxide anodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO(_2)</td>
<td>Sucrose/template</td>
<td>Core–shell</td>
<td>625 mA g(^{-1})</td>
<td>642</td>
<td>&gt;95</td>
<td>[83]</td>
</tr>
<tr>
<td>NIO</td>
<td>Filter paper/template</td>
<td>Hollow nanotube</td>
<td>200 mA g(^{-1})</td>
<td>620</td>
<td>99.1</td>
<td>[115]</td>
</tr>
<tr>
<td>CeO(_2)</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>0.2 C</td>
<td>355</td>
<td>N/A</td>
<td>[153]</td>
</tr>
<tr>
<td>NiO/C</td>
<td>Lotus pollen grains/C source, template</td>
<td>Porous</td>
<td>100 mA g(^{-1})</td>
<td>698</td>
<td>97.4</td>
<td>[112]</td>
</tr>
<tr>
<td>Mn(_2)SnO(_4)/Sn/C</td>
<td>(\alpha)-(\text{-})-fructose/C source</td>
<td>Porous</td>
<td>500 mA g(^{-1})</td>
<td>908</td>
<td>≈100</td>
<td>[111]</td>
</tr>
<tr>
<td>MnO/C</td>
<td>Glucose/C source</td>
<td>Porous</td>
<td>100 mA g(^{-1})</td>
<td>1691</td>
<td>N/A</td>
<td>[154]</td>
</tr>
<tr>
<td>CuO/C</td>
<td>Humic acid/C source</td>
<td>Core–shell</td>
<td>0.1 C</td>
<td>607.8</td>
<td>100</td>
<td>[84]</td>
</tr>
<tr>
<td>Fe(_2)O(_3)/C</td>
<td>Cotton/C source</td>
<td>Fibrous</td>
<td>200 mA g(^{-1})</td>
<td>1070</td>
<td>99</td>
<td>[155]</td>
</tr>
<tr>
<td>Fe(_2)O(_3)/Fe/C</td>
<td>Cotton/C source</td>
<td>Fibrous</td>
<td>1 A g(^{-1})</td>
<td>472</td>
<td>≈100</td>
<td>[88]</td>
</tr>
<tr>
<td>Fe(_2)O(_3)/C</td>
<td>Filter paper/C source</td>
<td>Fibrous</td>
<td>100 mA g(^{-1})</td>
<td>1826</td>
<td>≈100</td>
<td>[156]</td>
</tr>
<tr>
<td>NO(_2)/Ni/C</td>
<td>Sodium alginate/C source</td>
<td>Fibrous</td>
<td>72 mA g(^{-1})</td>
<td>793</td>
<td>N/A</td>
<td>[145]</td>
</tr>
<tr>
<td>MnO/C</td>
<td>Cotton/C source</td>
<td>Fibrous</td>
<td>0.1 mA cm(^{-2})</td>
<td>1.54 mA h cm(^{-2})</td>
<td>99.1</td>
<td>[148]</td>
</tr>
<tr>
<td>Co(_3)O(_4)/C</td>
<td>Murdannia simplex stalk/C source</td>
<td>Nanosheet</td>
<td>100 mA g(^{-1})</td>
<td>429</td>
<td>83.9</td>
<td>[11]</td>
</tr>
<tr>
<td>Sulfur cathodes</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S/C</td>
<td>Monosaccharide/C source</td>
<td>Core–shell</td>
<td>1 C</td>
<td>≈800</td>
<td>≈100</td>
<td>[102]</td>
</tr>
<tr>
<td>S/C</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>800 mA g(^{-1})</td>
<td>880</td>
<td>95</td>
<td>[94]</td>
</tr>
<tr>
<td>S/C</td>
<td>Pitch/C source</td>
<td>Core–shell</td>
<td>0.5 C</td>
<td>974</td>
<td>96</td>
<td>[157]</td>
</tr>
<tr>
<td>S/C</td>
<td>Glucose/C source</td>
<td>Core–shell</td>
<td>0.1 C</td>
<td>690</td>
<td>N/A</td>
<td>[93]</td>
</tr>
<tr>
<td>S/C</td>
<td>Amylose/C source</td>
<td>Core–shell</td>
<td>0.1 C</td>
<td>798</td>
<td>95</td>
<td>[101]</td>
</tr>
<tr>
<td>S/C</td>
<td>Soybean/C source</td>
<td>Porous</td>
<td>0.5 C</td>
<td>450</td>
<td>99</td>
<td>[132]</td>
</tr>
<tr>
<td>S/C</td>
<td>Coconut shell/C source</td>
<td>Porous</td>
<td>0.5 C</td>
<td>1030</td>
<td>N/A</td>
<td>[158]</td>
</tr>
<tr>
<td>S/C</td>
<td>Banana peel/C source</td>
<td>Porous</td>
<td>1 C</td>
<td>570</td>
<td>90</td>
<td>[128]</td>
</tr>
<tr>
<td>S/C</td>
<td>Starch/C source</td>
<td>Porous</td>
<td>0.5 C</td>
<td>683</td>
<td>≈100</td>
<td>[126]</td>
</tr>
<tr>
<td>S/C</td>
<td>Wheat straw/C source</td>
<td>Porous</td>
<td>1 C</td>
<td>445</td>
<td>95</td>
<td>[129]</td>
</tr>
<tr>
<td>S/N-doped C</td>
<td>Sild cocoon/C, N sources</td>
<td>Porous</td>
<td>2 C</td>
<td>383</td>
<td>≈100</td>
<td>[124]</td>
</tr>
<tr>
<td>S/N, O-doped C</td>
<td>Soybean/C, N, O sources</td>
<td>Porous</td>
<td>0.2 C</td>
<td>857.2</td>
<td>98.0</td>
<td>[130]</td>
</tr>
<tr>
<td>S/N, S, O-doped C</td>
<td>Tuna bone/C, N, S, O sources</td>
<td>Porous</td>
<td>0.2 C</td>
<td>1044.5</td>
<td>&gt;99</td>
<td>[123]</td>
</tr>
<tr>
<td>S/N,S-doped C</td>
<td>Cellulose nanocrystals/C source</td>
<td>Porous</td>
<td>2 C</td>
<td>365</td>
<td>93</td>
<td>[159]</td>
</tr>
</tbody>
</table>

and cross-section view (Figure 11c) verified that such a thick LCO electrode exhibited vertically aligned open microchannels that loaded LCO AMs. It was interestingly found that ultrahigh
loading of LCO AMs was achieved (LCO-1: \( \approx 96 \text{ mg cm}^{-2} \), LCO-2: \( \approx 207 \text{ mg cm}^{-2} \)), but much higher specific capacities than that of conventional LCO electrode were still delivered in Figure 11d. The corresponding areal capacities for LCO-1 and LCO-2 were 13.3 and 24.5 mA h cm\(^{-2} \), which were significantly higher than existing LIBs (4 mA h cm\(^{-2} \)). This study proved that the vertically aligned carbon microchannels led to high utilization of LCO, fast ion-transport process and good mechanical support for realization of thick electrodes. Similar to this idea, Chen et al.\(^{[162]} \) filled LiFePO\(_4\) nanoparticles into the aligned microchannels of carbonized basswood via vacuum infiltration. They successfully demonstrated 800 \( \mu \text{m} \) thick electrodes with ultrahigh AM loading of 60 mg cm\(^{-2} \) that delivered a high areal capacity of 7.6 mA h cm\(^{-2} \). Li et al.\(^{[165]} \) reported high loading sulfur cathodes based on the vertically aligned microchannels. They carbonized basswood slice to result in open porous

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**Figure 11.** Oriented channels for advanced electrodes. Wood-derived vertical microchannels for thick LiCoO\(_2\) (LCO) electrodes. Reproduced with permission.\(^{[161]} \) Copyright 2018, Wiley-VCH: a) Schematic illustration of synthesis strategy for thick LCO electrodes by sol–gel process based on wood-derived carbon microchannels; SEM images of b) top view and c) cross-section view of the thick LCO electrode; d) Comparison of specific capacity versus discharge rate for thick LCO electrode compared with control LCO cathode. Crab shell derived carbon nanochannels for sulfur and silicon electrodes. Reproduced with permission.\(^{[169]} \) Copyright 2013, American Chemical Society: e) Schematic illustration of fabrication of carbon nanochannel arrays derived from stone crab shell for encapsulating sulfur or silicon AMs; f) SEM image of carbon-coated nanochannel arrays; g) SEM image of sulfur encapsulated into the nanochannel arrays; h) EDS spectrum of sulfur cathode embedded in electrode nanochannels; i) Cycling performance of sulfur cathodes.
microchannels that were vertically aligned. The low tortuosity greatly shortened the ionic transport pathways and the good electrical conductivity supported powerful electronic transport. Then graphene was infiltrated into the microchannels followed by impregnation of sulfur by heat melting infusion. As a result, sulfur cathodes with a high sulfur loading of 21.3 mg cm\(^{-2}\) and a high areal capacity of 15.2 mAh cm\(^{-2}\) were demonstrated.

In addition to wood, Yan et al.\(^{[160]}\) reported fabrication of nanochannel arrays derived from stone crab shell for sulfur and silicon electrodes in Figure 11e. In their work, the researchers adopted crab shell with oriented nanochannels as the template and then acquired carbon-coated carb shell by coating polypyrrole followed by carbonization. Subsequently, they infused sulfur by heat melting and silicon by chemical vapor deposition (CVD) into the carbon-coated crab shell and removed CaCO\(_3\) framework finally. As shown in Figure 11f, the carbon-coated crab shell actually exhibited aligned nanochannel arrays with open porous structure. The average diameter of the nanochannel was determined to be about 70 nm. Taking sulfur cathode as an example, uniform nanochannel array structures of the sulfur/carbon composite was observed in Figure 11g, and the EDS spectrum in Figure 11g indicated a full incorporation of sulfur into the hollow nanochannels without impurities. The sulfur cathode based on such nanochannel arrays presented very stable cycling performance in Figure 11i, which resulted from the nanochannel structures for confining AMs, facilitating fast ion-conduction in a timely direction and accommodating the volume change. Similar conclusions were also drawn for silicon anode system.

2.4. Summary

With the diverse compositions and structures, biomaterials have been demonstrated to be appropriate materials for engineering of electrodes. First, for AM structure design, biomaterials that were well dissolved in specific solvents and showed good interactions with AMs were suitable materials for forming core–shell structures. Porous structures have been shown to be generated from versatile biomaterials by methods such as chemical/physical activation, templating, freeze-drying, etc. Biomaterials comprising rich heteratoms (e.g., N, O, S, etc.) were ideal precursors for deriving heteratom-doped carbonaceous materials that further enhanced the battery performance. Second, regarding electrode framework strategy, biomaterials with unique microstructures (e.g., fiber-like, sheet-like, etc.) and good mechanical properties were fabricated into electrode frameworks for feeding AMs. The mechanical flexibility and structural stability of resulting electrodes were substantially improved. Finally, for electrode channel strategy, biomaterials with well-defined microstructures such as aligned channels were appealing materials for generating electrode channels for loading AMs. This strategy effectively facilitated conduction for both ions and electrons in a controllable way.

3. Binder Engineering

The above discussion has underlined the strategies for electrode engineering in terms of rational design of AM nanostructures and the overall electrode architectures. In fact, the electrode structure is also strongly affected by the binder. Binder is an important component for gluing all solid particles, i.e., AMs and conductive fillers, into an electrode configuration. In spite of its low fraction in an electrode (<10 wt%), binder impacts the interactions among all the electrode components and the overall microstructures of the resulting electrodes.\(^{[170,171]}\) In this section, we summarize the significant progresses via exploiting biobased binders for achieving high-performance electrodes, especially silicon and metal oxide anodes, sulfur and high-voltage cathodes.

3.1. For Silicon and Metal Oxide Anodes

The main efforts on developing advanced biobased binders for silicon and metal oxide anodes have been put on those possess good mechanical properties and adhesion properties. Due to the extreme volume change of the AMs, robust mechanical properties help to withstand the volume variation, while a strong adhesion benefits the interfacial contacts among electrode components and the interfacial contact between electrode laminates and current collectors. Particularly for silicon anodes, immense studies have concentrated on biobased binders with carboxylic acid and/or hydroxyl groups to form hydrogen bonding with silicon.\(^{[172]}\) Such binders mainly include carboxy-methylcellulose (CMC),\(^{[172–175]}\) alginate,\(^{[176–178]}\) amylose,\(^{[179,180]}\) chitosan,\(^{[19,181]}\) guar gum,\(^{[182–184]}\) gum arabic,\(^{[185]}\) locust bean gum,\(^{[186]}\) karaya gum,\(^{[187]}\) β-cyclodextrin,\(^{[172,178]}\) lignin,\(^{[188]}\) and so on. Among these aforementioned binders, β-cyclodextrin (β-CD) that was first reported as a binder for silicon anode by Choi and coworkers,\(^{[172]}\) showed exceptional adhesion properties by its hyperbranched network structure. Such a structure was able to provide multiple noncovalent interactions with silicon, compared to 1D linear structured polymeric binders. The researchers demonstrated that hyperbranched β-cyclodextrin (β-CDp) presented higher adhesion strength and better mechanical properties compared with alginate, leading to much improved electrochemical performance of the resulting silicon anodes. The research group\(^{[188]}\) further developed a dynamic cross-linking strategy based on β-CDp and a cross-linker consisting of six tetrathylene glycol substituted adamantane units (6AD) for silicon anodes as shown in Figure 12a. This dynamic “host-guest” (binder as the host, cross-linker as the guest) cross-linking gave rise to not only better structural integrity of the resulting silicon anodes, but also a self-healing effect during lithiation/delithiation processes. Such dynamic cross-linking effectively enabled formation of stable SEI and self-healing as indicated in Figure 12b that after 150 cycles, no cracks were observed. The researchers also compared three types of CDp with six to eight (1,4)-α,β-glucopyranose units, that is, α,β-p,β-p,β-p. As shown in Figure 12c, all types of CDp presented comparative capacity retentions without dynamic cross-linking, but β-CDp with cross-linking (β-CDp/6AD) showed obviously the highest capacity retention up to 90%. Meanwhile, when compared with other binders such as CMC, alginate and polyacrylic acid (PAA), silicon anode with β-CDp/6AD binder exhibited ultra-stable cycling performance in Figure 12d, which indicated...
that the “host–guest” cross-linking interactions significantly enhanced the battery performance by stabilizing the electrode structures and SEI formation.

Moreover, Ling et al.\cite{185} reported a study of using gum arabic (GA) as a dual-functional binder for advanced silicon anodes inspired by the concept of fiber-reinforced concrete in
Figure 12e. Specifically, the rich hydroxyl groups of the polysaccharide in GA enabled formation of hydrogen bonding with silicon, and the long chain glycoproteins tolerated the mechanical deformation of silicon AMs. At the same time, the polar groups of GA increased the adhesion strength of the electrode laminate to the current collector compared with the electrode with CMC binder, as indicated by the peeling-off testing in Figure 12f. As a result, the silicon anode with GA (Si@GA) exhibited much more stable cycling performance and higher capacity even at a high current rate of 2 C compared with Si@CMC in Figure 12g. GA is also widely applied in metal oxide anodes due to its remarkable mechanical properties and adhesion strength. For example, Zhou et al.\cite{190} fabricated high-performance NiFe$_2$O$_4$ nanotubes (NFNTs) anode by using GA as the binder (NFNTs-GA). The researchers found that NFNTs-GA electrode presented much better mechanical properties, which helped to maintain structural integrity and form stable SEI. As shown in Figure 12h, the reduced modulus and hardness of the NFNTs-GA electrode were greater than that of the electrode with polyvinylidene fluoride (PVDF) binder. Benefiting from the advantages of the GA binder, the electrochemical performance of the anodes was notably enhanced. The NFNTs-GA anode in Figure 12i showed remarkably better rate performance with small capacity decay and variation with increase of current densities in comparison of NFNTs-PVDF anode. At the same time, the cycling stability of NFNTs-GA was also improved, which delivered much higher capacity of about 976 mA h g$^{-1}$ compared with PVDF case with a capacity of only 288 mA h g$^{-1}$ in Figure 12).

3.2. For Sulfur Cathodes

Biomaterials usually obtain many oxygen-containing or nitrogen-containing functional groups, making them appealing materials for adsorbing polysulfides thanks to the possible dipole–dipole interactions.\cite{191–194} At the same time, the rich functional groups lead to a variety of interactions with current collectors and electrode components. These attributes warrant the advantages of biobased binders for fabricating advanced sulfur cathodes. The use of biobased binders for sulfur cathodes dates back to decades ago and many biobased binders have been demonstrated to present effectiveness for enhancing the properties of sulfur cathodes. To name a few, CMC,\cite{196,197} gelatin,\cite{197–199} β-Cyclodextrin,\cite{200,201} guar gum,\cite{192,202} alginate,\cite{195,203} gum arabic,\cite{204} calcium lignosulfonate,\cite{205} etc. have been extensively studied. Among them, proteins are important category of biobased binders for sulfur cathodes. The different kinds of amino acids of proteins bring about abundant polar functional groups. These functional groups present strong dipole–dipole interactions with polysulfides for reducing the shuttle effect. The use of protein binders for sulfur cathodes dates back to a decade ago. Sun et al.\cite{197} first developed a gelatin binder for preparing sulfur cathodes. They explored that gelatin showed good adhesion strength and electrochemical stability as well as good dispersing ability for sulfur AMs. As a result, the sulfur cathode with gelatin as the binder showed much higher capacity and more stable cycling performance than a polyethylene oxide (PEO) binder system. A recently reported work by Fu et al.\cite{191} demonstrated a robust and ion-conductive protein-based binder for high-performance sulfur cathodes as shown in Figure 13a. In their work, the researchers incorporated soy protein with PAA to generate a robust multifunctional binder (SP–PAA). The synergistic effect from soy protein and PAA enhanced the performance of sulfur cathodes from three aspects: 1) improved the electrode microstructures by PAA; 2) adsorbed dissolved polysulfides by soy protein; 3) promoted the ion transport by soy protein. They found that the modulus of SP was 0.91 GPa, and the SP–PAA binder exhibited an improved modulus of 1.39 GPa owing to the network structure and the high modulus of PAA. The SP–PAA binder also showed an increased liquid electrolyte uptake of 9% compared with pure SP (0%). As shown in Figure 13b, the microstructures of the sulfur cathode with SP–PAA showed no cracks and sulfur AMs were thoroughly covered by conductive fillers. The photograph in Figure 13c verified that SP–PAA binder showed exceptional adsorption of polysulfides, due to the abundant functional groups of soy protein. At the same time, the adhesion property of the sulfur cathode was also improved by SP–PAA in Figure 13d. Naturally, the sulfur cathode with SP–PAA delivered the highest capacity and quite stable cycling performance compared with single soy protein or PAA binders as shown in Figure 13e. The average Coulombic efficiency was as high as 99.3%. The excellent battery performance was contributed by the multifunctionalities from SP–PAA binder as discussed above.

In addition to proteins, gums have also drawn considerable attention owing to their good mechanical properties and easy processability. For instance, Li et al.\cite{204} initially used GA as the binder for fabricating sulfur cathodes. The GA binder brought about good mechanical performance for buffering volume change and polar functional groups for physically and chemically confining polysulfides. As a result, long-lived Li–S batteries with a capacity of 841 mA h g$^{-1}$ for 500 cycles were demonstrated. Recently, Liu et al.\cite{192} reported a facile strategy based on intermolecular binding for fabricating a robust network biopolymer binder and demonstrated ultrahigh sulfur loading cathodes. In their work shown in Figure 13f–h, the researchers blended two types of biopolymers, xanthan gum (XG) and guar gum (GG), and the intermolecular binding effect gave rise to a robust network biopolymer binder (N-GG-XG). This robust network binder did not only provide strong mechanical support for the sulfur cathodes, but also presented great capability of preventing diffusion of polysulfides owing to its rich polar functional groups. The scratch track of the sulfur cathode with network biopolymer binder (S@N-GG-XG) was very smooth in Figure 13i, indicating that the N-GG-XG binder showed good ability to tolerate the volume change of sulfur AMs. Consequently, high loading S@N-GG-XG (S loading: 6.5 mg cm$^{-2}$) was achieved that delivered a quite stable cycling performance compared to other binder systems as shown in Figure 13j. The researchers further successfully fabricated ultrahigh loading sulfur cathodes (11.9 mg cm$^{-2}$) that demonstrated stable cycling performance with a capacity of about 800 mA h g$^{-1}$ corresponding to an excellent areal capacity of about 9 mA h cm$^{-2}$ in Figure 13k.
3.3. For High-Voltage Cathodes

High-voltage cathode materials such as spinel LiMn$_2$O$_4$ (LMO) and its derivatives LiNi$_x$Mn$_{2-x}$O$_4$ (LNMO, $x \leq 0.5$) deliver ordinary capacity of $\approx 148$ mA h g$^{-1}$,\textsuperscript{[27]} but their high working voltage of 4.0 and 4.8 V versus Li/Li$^+$ actually compensates the relatively low capacity. The high-voltage spinel cathodes usually present better rate capability because the transport of Li ions occur in 3D channels inside the spinel structure\textsuperscript{[15]} and they exhibit relatively high electrical conductivity.\textsuperscript{[206]} However, it is a critical challenge to maintain the stability of the electrolyte and electrode when being charged to high voltage, in which the

Figure 13. Biobased binders for sulfur cathodes. Protein-based ion-conductive and robust binder for sulfur cathodes. Reproduced with permission.\textsuperscript{[191]} Copyright 2018, Royal Society of Chemistry; a) Schematic illustration of the design concept for the protein-based multifunctional binder by blending two functional materials; b) SEM images of sulfur cathode with protein-based binder; c) Photograph of adsorption testing of polysulfides for different binder/carbon black composites; d) Adhesion strength and e) cycling performance of sulfur cathodes with different binders. Robust biopolymer network binder for high loading sulfur cathodes. Reproduced with permission.\textsuperscript{[192]} Copyright 2017, Royal Society of Chemistry: Chemical structures of f) xanthan gum (XG) and g) guar gum (GG); h) Schematic illustration of formation of the network biobinder by intermolecular binding; i) In situ 3D nanoscratch image of the sulfur cathode with the network biobinder; j) Cycling performance of sulfur cathodes with different binders; k) Cycling performance of high loading (11.9 mg cm$^{-2}$) sulfur cathode with XG-GG binder.
side reactions at the electrolyte/cathode interface will result in capacity fading. Meanwhile, the distortion and dissolution of Mn ions from Jahn-Teller effect will finally result in deposit of Mn on the anode surface and further deteriorate the electrochemical performance. Thus far, various biobased binders, e.g., CMC, guar gum, alginate, etc. have been adopted for fabricating spinel cathodes with aims to prevent the diffusion of Mn ions and stabilize the SEI layer. Recently, Tang et al. reported a profound study of using sericin protein with various functional groups as the binder for stabilizing the SEI layer for LNMO cathode (Figure 14(a)). The main idea was to create a highly ion-conductive protective layer with low Li-ion-migration barrier on the LNMO particle surface to avoid the direct contact between LNMO and liquid electrolytes.
Therefore, this layer was able to suppress the oxidation of electrolytes at high voltage and help to form stable SEI. It was found in their study that the viscosity of sericin solutions increased notably with the molecular weight of sericin, and 100 KDa sericin showed comparative viscosity with 534 KDa PVDF. The sericin film possessed an excellent elastic modulus of 8.66 GPa compared with PVDF of only 2.14 GPa. As indicated by the SEM images in Figure 14b,c, the electrode with sericin protein showed no cracks after cycling testing, in contrast to the one with PVDF. Moreover, it was noted that a thicker SEI layer grew on the LNMO particle for PVDF than that of the electrode with sericin protein. The evolution of resistances especially the resistance of SEI ($R_{SEI}$) upon cycling in Figure 14d suggested that the sericin protein system showed a result, the battery performance was substantially improved due to the self-discharge behavior in Figure 14f, due to the good surface coverage of sericin on the LNMO particles compared with poor coverage of PVDF, which prevented the electrolyte oxidation.

Ma et al.\cite{217} reported using lignin binder for preventing electrolyte oxidation and dissolution of Mn ions by scavenging free radicals. Specifically, in charging process once the carbonate solvent lost electrons, alkyl free radicals were generated and reacted with vicinal solvent molecules, resulting in polymerization of solvent and formation of cathode/electrolyte interphase (CEI). Therefore, capturing the radicals was effective for suppressing the continuous formation of unstable CEI and consumption of electrolytes. In Figure 14g,h based on the density functional theory (DFT) result (Figure 14i) that lignin exhibited much larger trapping energy (~3.37 eV) compared with PVDF (~0.29 eV), the researchers proposed mechanism models for lignin and PVDF regarding their ability for capturing radicals. It implied that lignin had good ability for scavenging radicals due to its abundant phenol structure groups, while PVDF did not. The TEM images in Figure 14j,k indicated that a thin and compact CEI layer was formed on LNMO surface when using lignin binder, but an uncompact and irregular CEI layer was observed for the PVDF system. This verified that lignin helped to form homogeneous and stable CEI layer, which protected the electrolyte from oxidation and decomposition. As a result, the lignin electrode delivered a higher capacity of 110.8 mA h g$^{-1}$ with a higher Coulombic efficiency of 99.5%, compared to the PVDF electrode with a capacity of 100 mA h g$^{-1}$ and a Coulombic efficiency of 99.0% in Figure 14l.

3.4. Summary

Previous studies have indicated that the diversity of structures and compositions of biomaterials brought about rich functional groups (polar and nonpolar groups). Meanwhile, complex intra-/inter-molecular interactions of biomaterials led to good mechanical properties. Thus, multiple advantages have been shown for biobased binders: 1) high adhesion strength, 2) robust mechanical properties, 3) good dispersing ability for AMs and conductive agents, 4) function of trapping electrochemical intermediates, 5) ability of stabilizing electrode/electrolyte interphase, 6) “green” processing in aqueous solvents. These characteristics of biobased binders made a great contribution to improving electrode microstructures (e.g., uniformity, interface quality, etc.) and thus structural stability of electrodes. More significantly, in addition to improving structural stability of electrodes, biobased binders have shown specific contributions to sulfur and high-voltage cathodes, via alleviating loss of active materials or preventing side reactions.

4. Electrolyte Engineering

Electrolytes as the only ion-conduction media play a pivotal role in ion-transport kinetics. Today’s Li-based batteries mainly use organic liquid electrolytes based on carbonate esters as the ion-conduction media, which poses safety concerns as the liquids are flammable to catch fire if battery overheating occurs.\cite{218,219} The growing demands on highly safe batteries have driven the development of solid-state or quasi-solid-state (e.g., gel-type) electrolytes for substituting currently used liquid electrolytes. The employment of these two types of electrolytes not only enhances the battery safety, but also potentially boosts the electrochemical performance via avoiding the use of a separator. In this section, we cover recent significant advancements of applying biomaterials for solid-state and gel electrolytes for advanced Li-based batteries.

4.1. Biomaterials for Solid Electrolytes

4.1.1. Biomaterials as Electrolyte Hosts

Biopolymers such as proteins and polysaccharides that possess good solubility of Li salts have been demonstrated to be attractive solid electrolyte hosts.\cite{220,221} Thus far, intensive studies have reported various types of biobased solid electrolytes based on chitosan and its derivatives,\cite{222–225} proteins,\cite{226,227} starch,\cite{221,228–230} agar,\cite{231} and so on. The strategies for fabrication of biobased electrolytes follow the ones for conventional synthetic solid polymer electrolytes, in which the electrolyte hosts are doped with different kinds of Li salts. Possibly due to the limited understanding of the interactions between the ions (i.e., Li ions, counterpart anions) and biopolymers, as well as the complex structures of biopolymers, the studies on biobased solid electrolytes have been retarded and the ionic conductivity has been bounded to be below 10$^{-5}$ S cm$^{-1}$. Recently, Fu et al.\cite{220} reported an interesting study of a high-performance protein-based solid electrolyte and systematically studied the ion-transport mechanism. In Figure 15a, the researchers developed a bioapproach to subtly control the structures of protein-ion complex through varying the Li salt loading and formation temperature. They found that the two parameters even affected the ionic conductivity as shown in Figure 15b, that higher formation temperatures improved the ionic conductivity by several orders of magnitude, and the optimal ionic conductivity was ~10$^{-3}$ S cm$^{-1}$. It was surprisingly found that the protein...
solid electrolyte showed an extremely high modulus (∼1 GPa) and Li-ion transference number (0.93), which greatly exceeded the values of a conventional PEO solid electrolyte as shown in Figure 15c. Meanwhile, the protein electrolyte exhibited a good thermal stability and decomposed at about 260 °C by TGA analysis. They proposed a decoupled ion-transport mechanism for this protein solid electrolyte that the transport of Li ions was dependent on the oxygen atoms in the protein backbones and the anion clusters “locked” by the positively charged amino acids.

A majority of studies of biobased electrolytes have rested on the materials level, and the proof-of-concept demonstration in real battery devices has been rarely found. A breakthrough study by Lin et al.\(^{[221]}\) reported using starch solid electrolytes for fabricating all-solid-state Li–S batteries. As shown in Figure 15d, the researchers cross-linked corn starch to be used as the electrolyte host exhibiting good mechanical flexibility. After mixing with Li salt, LiTFSI, the starch solid electrolyte presented a much higher ionic conductivity of \(3.39 \times 10^{-4} \text{ S cm}^{-1}\) at room temperature compared with a PEO electrolyte in Figure 15e. It was believed that the -C-O-C- backbone of starch that was similar with the PEO structure and the high electric constant of starch (ten times of PEO) were responsible for the high ionic conductivity. The starch solid electrolyte was thermally stable up to 150 °C as indicated by the TGA curves in Figure 15f. At the same time, the starch electrolyte presented a very high Li-ion transference number of ∼0.8. The researchers further demonstrated the use of this starch solid electrolyte in Li–S batteries and inspiring results were acquired. As shown in Figure 15g, the all-solid-state Li–S batteries delivered average capacities of ∼864 mA h g\(^{-1}\) in 100 cycles at room temperature, which indicated that the starch solid electrolyte was able to act as both an ion conductor and a separator.

4.1.2. Biomaterial-Enhanced Composite Solid Electrolytes

In comparison of direct employment of biomaterials as electrolyte hosts, incorporating biomaterials into conventional solid polymer electrolytes have been more intensively studied. This is because biomaterials especially biopolymers usually possess good mechanical strength and good compatibility

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**Figure 15.** Biobased solid electrolytes. Soy protein-based solid electrolyte with high ionic conductivity and high mechanical properties. Reproduced with permission.\(^{[220]}\) Copyright 2016, American Chemical Society: a) Schematic illustration of controlling the protein-ion complex structures by adjusting protein/ion ratio and complex formation temperature; b) Effects of complex formation temperature and Li salt loading on the ionic conductivity of protein-based solid electrolytes; c) Storage modulus and Li-ion transference number of protein-based solid electrolytes. Starch solid electrolyte for Li–S batteries. Reproduced with permission.\(^{[221]}\) Copyright 2016, Royal Society of Chemistry: d) Schematic illustration of starch structure and synthesis strategy; e) Temperature dependence of ionic conductivities of starch solid electrolytes; f) Thermal stability of the starch solid electrolyte; g) Cycling performance of all-solid-state Li–S batteries using starch solid electrolytes.
with many synthetic polymers owing to the abundant polar groups.[232–234] Therefore, introducing biopolymers into conventional solid polymer electrolytes can effectively reinforce the overall mechanical properties. In this strategy, cellulose and its derivatives,[233,235–237] proteins,[238,239] etc. have been adopted as reinforcement agents. Specifically, owing to the good affinity with other polymers and unique structures, e.g., robust networked fibrous structure, cellulose and its derivatives have been widely studied as a type of supporting frameworks. For instance, Zhang et al.[232] reported a poly(propylene carbonate) (PPC) electrolyte supported by cellulose nonwoven, which exhibited high ionic conductivity and enhanced safety. The researchers used a facile solution-casting method via pouring electrolyte solutions on the cellulose nonwoven to result in the final cellulose-supported PPC solid polymer electrolyte (CPPC-SPE). The researchers surprisingly found that the ionic conductivity of CPPC-SPE was much higher than that of PEO electrolyte throughout all temperature range. The ionic conductivity of CPPC-SPE was 3.0 \times 10^{-4} \text{ S cm}^{-1} at 20 \degree \text{C}, which was much higher than that of PEO electrolyte (2.1 \times 10^{-6} \text{ S cm}^{-1}). Meanwhile, the CPPC-SPE presented a good electrochemical stability up to 4.6 \text{ V}. As shown in Figure 16a, the cells worked very well at room temperature and delivered exceptional rate capability benefiting from the high ionic conductivity and good interfacial properties. The researchers examined the safety merits of CPPC-SPE by cutting away the soft-package cells in Figure 16b and observed that the LED bulb was still lighted up. Another study by Zhang et al.[233] reported a type of copolymer-based solid electrolyte, poly(ethylene glycol) methyl ether methacrylate-co-steryl methacrylate (PEGMEM-co-SMA), which was supported by cellulose. The resulting composite electrolyte exhibited an optimal ionic conductivity of 2.54 \times 10^{-3} \text{ S cm}^{-1} as shown in Figure 16c. When the PEGMEM-SMA composite electrolytes were added into half cells, the cell only presented a capacity of 70–80 mA h g^{-1} at 1 C; however, when elevating the temperature above the melting point of the copolymer, much higher capacities (=160 mA h g^{-1}) were delivered (Figure 16d).

The above discussion has outlined the use of cellulose as a type of framework for reinforcing the mechanical and interfacial properties for solid electrolytes. In these studies, cellulose has no significant impact on ionic conductivity. Here, another important contribution from biomaterials for enhancing solid electrolytes, that is, the contribution to ionic conductivity, is discussed. Ji et al.[238] reported a fully amorphous PEO-based solid electrolyte achieved by incorporating PEO with soy protein isolate (SPI). The good miscibility between PEO and SPI effectively suppressed the crystallization of PEO to generate a fully amorphous PEO/SPI composite electrolyte. This amorphous structure significantly improved the ionic conductivity of PEO/SPI compared to pure PEO electrolytes. Recently, Fu et al.[239] reported a novel study of manipulating protein configuration for enhancing performance of PEO electrolytes. In their work, the researchers adopted a biotechnology to adjust the structures of soy protein (SP) and then fabricated two types of hybrid nanoparticles based on TiO_{2} and SP: TiO_{2}/(SP-open) and TiO_{2}/(SP-close) hybrids (“open” and “close” indicated the corresponding protein structures). They revealed that with an open protein structure, fast ion-conduction channels were formed on the TiO_{2} nanoparticle surface. As a result, the composite polymer electrolyte (CPE) with the TiO_{2}/(SP-open) nanoparticles showed significantly higher ionic conductivity (=6 \times 10^{-5} \text{ S cm}^{-1}) compared with the TiO_{2}/(SP-close) case (=2 \times 10^{-5} \text{ S cm}^{-1}). This proved that the protein structure strongly affected the ion-conduction and interfaces between the PEO host and nanofillers, and the open protein structure benefited these two properties. The research group further fabricated core–shell structured hybrid nanowires (NWs) of SP and TiO_{2} (SP@TiO_{2} NWs) for further enhancing the properties of PEO electrolytes, because 1D NWs helped to build more continuous ion-conduction pathways (Figure 16e).[240] The researchers electrosynthesized TiO_{2} nanofibers and subsequently calculated the nanofibers to finally obtain TiO_{2} NWs. Then they then in situ grew SP on TiO_{2} NWs via denaturation of SP. As shown in Figure 16f, there was a very thin layer of SP on the TiO_{2} NW surface, proving the core–shell structure. Benefiting from the 1D morphology and promoted ion conduction by SP, the ionic conductivity and modulus of the CPE were further improved compared with the 0D hybrid nanoparticle case as shown in Figure 16g,h. The ionic conductivity of the CPE with SP@TiO_{2} NWs was as high as =10^{-4} \text{ S cm}^{-1} at room temperature, which was obviously higher than that of the CPE with SP@TiO_{2} nanoparticles (=6 \times 10^{-5} \text{ S cm}^{-1}). The half cells with the CPE with SP@TiO_{2} NWs demonstrated stable cycling performance at 65 \degree \text{C} with a capacity of about 130 mA h g^{-1} as shown in Figure 16i, which resulted from the high ionic conductivity and good mechanical/interfacial properties of the CPE.

4.1.3. Molecular Dynamic (MD) Simulation Studies of Ion-Conduction Mechanisms

State-of-the-art biobased solid electrolytes have shown ionic conductivities below 10^{-5} \text{ S cm}^{-1} in most studies, which fail to satisfy the practical needs. This possibly results from the lack of understanding of the specific interactions between ions and biomaterials. Well studied synthetic polymer-based electrolytes such as PEO exhibit a coupled ion-conduction behavior,[240,241] where Li ions complex with polymers and then are transported via ion-hopping process.[242,243] By contrast, biomaterials having more complex structures and compositions may bring about complicated interactions with ions and thus present different ion-conduction behavior. Therefore, a critical understanding of biomaterial-ion interactions is in high demand, which is conducive to rationally design and fabricate high-performance biobased solid electrolytes and even biomaterial-enhanced composite electrolytes.

As an attempt to achieve the above goal, recently, Fu et al.[220] used MD simulations to study the ion-conduction behavior of SP-based electrolytes. In their studies, the researchers explored an interesting phenomenon that at higher formation temperature (e.g., 40 \degree \text{C}) of protein-ion complex (i.e., SP-based solid electrolyte), the ionic conductivity was dramatically improved by several orders of magnitude. They calculated the number of anions (ClO_{4}^{-}) that were adsorbed by SP at different formation temperatures in Figure 17a, which was revealed to increase with the formation temperature and 50 \degree \text{C} resulted in the highest number. The number of ClO_{4}^{-} that were adsorbed by SP with varying loadings of Li salt was also calculated in Figure 17b,
Figure 16. Biomaterials for enhancing properties of conventional solid polymer electrolytes. Safety-reinforced poly(propylene carbonate) (PPC) solid electrolyte supported by cellulose. Reproduced with permission.\textsuperscript{[232]} Copyright 2015, Wiley-VCH: a) Rate performance of CPPC-SPE at 20 °C; b) Photographs of soft-package cells being cut away for powering LED bulbs. Composite electrolyte membrane supported by cellulose. Reproduced with permission.\textsuperscript{[233]} Copyright 2016, Elsevier: c) Temperature dependence of ionic conductivity of composite electrolyte membrane; d) Cycling performance of composite electrolyte membrane at various temperatures. Core–shell hybrid protein/TiO\textsubscript{2} nanowires (SP@TiO\textsubscript{2} NWs) for improving ionic conductivity of PEO electrolytes. Reproduced with permission.\textsuperscript{[234]} Copyright 2018, Wiley-VCH: e) Schematic illustration of fabrication of SP@TiO\textsubscript{2} NWs; f) TEM images of SP@TiO\textsubscript{2} NWs; g) Temperature dependence of ionic conductivity of composite polymer electrolyte (CPE) with SP@TiO\textsubscript{2} NWs; h) Summary of ionic conductivity and storage modulus of various CPEs; i) Cycling performance of various CPEs.
Figure 17. Simulation studies for understanding of ion-conduction mechanisms for biobased or biomaterial-enhanced solid electrolytes. Molecular dynamic (MD) simulations of soy protein (SP)-based solid electrolyte. Reproduced with permission.[220] Copyright 2016, American Chemical Society: Variation of number of ClO$_4^-$ ($N_{ClO_4^-$}) a) as a function of evaporation temperature and b) as a function of Li salt loading at 50 °C. The experimental results of ionic conductivities are shown by green circles for comparison; c,d) Snapshots of the protein-ClO$_4^-$ complex at c) 25 °C and d) 50 °C; e) Schematic illustration of decoupled ion transport for SP-based solid electrolyte. MD simulations of manipulation of SP configuration for building fast ion-conduction pathways. Reproduced with permission.[239] Copyright 2018, American Chemical Society: f) Snapshots of the final state of denatured SP in mixture solvent (acetic acid (AA) and water) under two conditions: w/o and w/TiO$_2$ (shown as plate); g) Time evolution of the radius of gyration ($R_g$) of denatured SP under the two different conditions; h) Adsorption of acid molecules on TiO$_2$ surface and number density of AA (oxygen atom on hydroxyl group) and water (oxygen atom) molecules along the $Z$ direction; i) Schematic of protein ion-conduction channel on TiO$_2$ surface.
structures to ion-conduction behavior. The results indicated that a proper way for manipulating protein structures led to high-performance solid electrolytes. These pioneering studies are instructive for mechanism analysis of bio-based or biomaterial-enhanced electrolytes and promote the development of advanced and new bioelectrolytes.

4.2. Biomaterials for Gel Electrolytes

Biobased gel electrolytes have been of increasing interest, because they present much higher ionic conductivity boosted by the liquid component, as compared with solid electrolytes. With a liquid component, the ionic conductivity of biobased gel electrolytes can be improved to the order of magnitude of 10^{-3} \text{ S cm}^{-1}, which is comparable to liquid electrolytes. The efforts for developing biobased gel electrolytes have mainly focused on cellulose and its derivatives because of their remarkable thermal stability and affinity with liquid electrolytes.\textsuperscript{244-245} Thus far, cellulose,\textsuperscript{246,247} hydroxyethyl cellulose (HEC),\textsuperscript{244,248} cyanomethyl cellulose derivative,\textsuperscript{245} methyl cellulose (MC),\textsuperscript{249} CMC,\textsuperscript{250} bacterial cellulose (BC),\textsuperscript{251,252} lignocellulose\textsuperscript{253,254} etc. have been the commonly used biomaterials as gel electrolyte hosts.

Zhu et al.\textsuperscript{250} fabricated a porous CMC membrane as the gel electrolyte skeleton. It was found that the high porosity (62.5\%) of the CMC membrane led to a high liquid electrolyte uptake of 75.9\% and thereof a high ionic conductivity of 4.8 \times 10^{-4} \text{ S cm}^{-1}. Li et al.\textsuperscript{244} reported a nonporous HEC-based gel electrolyte different from conventional porous gel electrolytes, which presented an ionic conductivity of 1.8 \times 10^{-4} \text{ S cm}^{-1} at room temperature and a good thermal stability up to 280 °C. The nonporous structure helped to prevent the short-circuit, but the HEC film still exhibited a decent electrolyte uptake of 78.3 wt\% due to the strong interactions between -OH groups of HEC and carbonate electrolyte solvents. It is noted that these cellulose-based gel electrolytes show relatively poor mechanical properties, the tensile strength of which were lower than 20 MPa. Xu et al.\textsuperscript{251} prepared a high-strength cross-linked BC network as the gel electrolyte matrix, the tensile strength of which was up to about 49 MPa. Benefiting from the good porosity of the BC aerogel, the liquid electrolyte uptake was as high as 93.32\%, giving rise to an extremely high ionic conductivity of 2.48 \times 10^{-3} \text{ S cm}^{-1}. Recently, Wan et al.\textsuperscript{246} reported a cellulose aerogel-based gel electrolyte with tunable nanoporous networks. It was found in their work that the initial concentration of cellulose played an important role in modulating the microstructures of cellulose aerogel membranes (CAMs). At an optimal concentration (4\%), the resulting CAM-4 exhibited loosely packed nanofibrils to form highly porous networks with a high porosity of 79.4\%. This good nanoporous structure led to a much higher ionic conductivity than Celgard separator. The CAM also demonstrated excellent thermal stability that it maintained its structures even at 150 °C, while Celgard separator exhibited an obvious thermal shrinkage of \approx 40\%. At the same time, the CAM widened the operation potential window to about 4.6 V that was greater than that of a Celgard separator (4.2 V). The CAM gel electrolyte enhanced the rate performance that especially at high current densities.
(4 C, 8 C), the capacities were obviously higher than that of Celgard separator. Song et al.\[254\] studied a novel gel electrolyte based on lignocellulose (LC), a kind of biomass consisting of cellulose, hemicellulose and lignin. The rich intermolecular hydrogen bonding among these three components and functional groups (hydroxyl, carboxyl groups, etc.) resulted in high mechanical strength and exceptional affinity with electrolytes. The researchers composited polyethylene glycol (PEG) with LC as the matrix and revealed that the PEG-LC composite exhibited much higher tensile strength of 4.42 MPa than that of LC (1.21 MPa). Owing to the good affinity with liquid electrolytes from LC, a very high electrolyte uptake of 267 wt% was achieved, which gave rise to a high room temperature ionic conductivity of $3.22 \times 10^{-3}$ S cm$^{-1}$. Using the gel electrolytes, the battery performance was greatly improved benefiting from the remarkable electrolyte properties (e.g., high ionic conductivity). The PEG-LC composite gel electrolyte delivered quite stable cycling performance with a capacity of about 164.4 mA h g$^{-1}$ at 0.2 C with a capacity retention of 99.4%.

In addition, some other biopolymers such as chitosan,\[255,256\] starch,\[257–262\] proteins,\[263,264\] etc. have also been widely investigated. For instance, Zhu et al.\[264\] first reported fabrication of composite nanofibers, soy protein/poly(vinyl alcohol) (SPI/PVA), as skeletons for gel electrolytes. As shown in Figure 18a, the SPI/PVA exhibited a randomly interconnected 3D networked structure with an average fiber diameter of about 120 nm. Such a fibrous structure gave rise to a high porosity of $\approx 89\%$ and an electrolyte uptake of 700%. This made the SPI/PVA gel electrolyte present a much lower ion-transport resistance than that of Celgard separator. The researchers studied...
the degradation behavior of SPI/PVA nanofibers in Figure 18b and discovered that SPI completely degraded in about 40 days and the degradation rate of SPI/PVA nanofibers was affected by the SPI content. The cell with SPI/PVA gel electrolyte showed a higher capacity of about 118.2 mA h g⁻¹ than that of the cell with Celgard separator (103.9 mA h g⁻¹), due to the much higher electrolyte uptake and better interfacial stability. The research group then developed a novel composite gel electrolyte based on this SPI/PVA skeleton for addressing the issues of LiMn₂O₄ (LMO) cathodes (diffusion of Mn ions). Basically, they sandwiched a layer of polydopamine spheres (PDSs) between two layers of SPI/PVA nanofibers, and then loaded a layer of carbonized PDSs (CPDSs) on the top of the sandwiched configuration as shown in Figure 18d. The mesoporous PDSs and CPDSs had uniform sizes with an average diameter of about 210 nm. Here, the layer of CPDSs offered good mechanical strength for suppressing Li dendrites and the layer of PDSs captured Mn ions and acted as an additional protective layer for blocking Li dendrites. To prove PDSs were capable of trapping Mn ions, the researchers soaked PDSs in an electrolyte solution of Mn(ClO₄)₂ and Mn(CH₃COOH)₃ in Figure 18e. It was revealed that PDSs could chelate 40.8 (mg per mg PDSs) Mn ions by hydroxyl and amine groups. Moreover, the composite SPI/PVA gel electrolyte (designated as c-GPE) effectively suppressed the growth of Li dendrites as shown in Figure 18f–i. For Li anodes with Celgard separator and neat SPI/PVA gel electrolyte (n-GPE), there exhibited many irregular Li dendrites on the surface, but the surface was still smooth for c-GPE system. These good properties also contributed to the battery performance that the rate capability of c-GPE was substantially better than that of Celgard separator and n-GPE even at high rates of 1 C or 2 C in Figure 18j. The good battery performance resulted from the high ionic conductivity (2.2 × 10⁻³ S cm⁻¹), suppressed Li dendrite growth and effective Mn ion capturing from the high-performance c-GPE. After cycling testing, the interfacial resistance of the cell with c-GPE only showed small change indicating stable formation of SEI in Figure 18k.

4.3. Summary

Biomaterials have been studied as electrolyte hosts or additives for fabricating composite electrolytes. Specific conclusions are drawn from the above discussion: 1) Development of biobased solid electrolytes has been sluggish. State-of-the-art biobased solid electrolytes usually exhibited unsatisfactory ionic conductivity (<10⁻⁵ S cm⁻¹), possibly because of a lack of fundamental understanding of their ion-conduction mechanisms. Recently, there has emerged breakthrough studies reporting biobased electrolytes with high ionic conductivity >10⁻³ S cm⁻¹ via tuning structures of biomaterials. Critical methods such as MD simulations were adopted to gain fundamental understanding of the ion-conduction mechanisms of biobased solid electrolytes. 2) Adding robust biomaterials into conventional solid polymer electrolytes has been more intensively studied, which was effective for reinforcing overall mechanical properties and even ionic conductivity. Ion-conductive biomaterials when used as fillers notably increased the ionic conductivity. 3) Biomaterials have also been used as gel electrolyte skeletons and reinforcement additives for conventional gel electrolytes. Biobased or biomaterial-enhanced gel electrolytes exhibited improved mechanical properties and decent ionic conductivity (>10⁻³ S cm⁻¹). Recent studies have indicated that specific biobased gel electrolytes with heteroatoms and unique configurations were even able to trap electrochemical intermediates and suppress the Li dendrites.

5. Separator Engineering

Fabrication of high-performance separators should take several factors into consideration, including porosity, mechanical properties (e.g., puncture strength, tensile strength), thermal/electrochemical stability, wettability, etc. Existing batteries mainly use polypropylene (PP), polyethylene (PE) or their copolymers as the separator materials. These separators show significant advantages in chemical stability and thermal shut-down function. However, they suffer from relatively low mechanical strength and notable thermal shrinkage at a relatively high temperature >100 °C.[266,267] At the same time, the low porosity and hydrophobicity of polyolefin separators result in poor wettability with liquid electrolytes, reducing the ion-conduction efficiency.[268,269] Therefore, development of new separator alternatives is in critical need. Biomaterials as discussed above present good mechanical properties and many polar groups endowing them with good affinity with liquid electrolytes, which make biomaterials suitable separator alternatives. Moreover, there emerges a great number of studies on modifying separators, e.g., creating separator coatings by biomaterials, for advanced Li metal batteries. In this section, the development of biobased separators and strategies of using biomaterials for modifying conventional separators are discussed.

5.1. Biobased Separators

The main efforts for biobased separators have concentrated on cellulose and cellulose-derived materials. This is because cellulose and its derivatives exhibit rich polar functional groups (carboxyl, hydroxyl groups), resulting in good wettability with liquid electrolytes. At the same time, cellulose fibrils tend to form porous network structure for conserving a large amount of liquid electrolytes. In this section, some representative work about cellulose-based separators is reviewed, and the readers are encouraged to refer some comprehensive reviews[266,270,271] for more detailed information. Basically, cellulose-based separators usually possess higher electrolyte uptake and better thermal stability compared with conventional polyolefin separators. In this regard, numerous studies on cellulose-related separators have mainly focused on cellulose,[272–276] CMC,[277,278] carboxylated cellulose,[279] bacterial cellulose,[280] and even commercial paper.[281,282] For example, Zhang et al.[276] used cellulose pulp as the raw material and applied a papermaking method via mixing cellulose pulp, flame retardant and silica to fabricate a composite cellulose nonwoven with flame resistivity (FCCN). As displayed in Figure 19a, the microfibers of cellulose nonwoven (CN) randomly interconnected and showed numerous micropores (>4 µm), making the cellulose...
nonwoven vulnerable to internal short-circuit. Figure 19b indicated that the FCCN exhibited a porous structure with pore diameter of 100–200 nm due to the flame retardant and silica. This nanoporous structure helped to prevent internal short-circuit. Figure 19c proved that the FCCN (on the right) had a good flame-retardant property, while the Celgard separator (on the left) caught fire immediately. They also found that the FCCN nonwoven presented a good wettability with liquid electrolytes, the contact angle of which was only 15°, compared to the Celgard separator (84°). Benefiting from the high ionic conductivity (2.0 × 10⁻³ S cm⁻¹) and improved interfacial contact, the cell with FNNC delivered much higher capacities than that of a Celgard separator throughout all tested current rates in Figure 19d.

Xu et al. [273] reported a high-performance separator based on cellulose/polysulfonamide (PSA) composite membrane. In their study, they mixed cellulose pulp with PSA and then added the homogeneous slurry into a papermaking machine. The final cellulose/PSA composite nonwoven membrane was obtained after applying calendaring at 20 MPa. The calendaring process played a critical role in generating tortuous nanopores that were essential for preventing short-circuit and self-discharge. As indicated by the SEM images, the as-prepared composite nonwoven presented large-sized and irregular pores in Figure 19e; however, the calendaring pressure led to much smaller and torturous nanosized pores between the compact nanofibers in Figure 19f. The thermal stability of the cellulose/PSA was exceptional that the membrane was stable without shrinkage even after exposure to 200 °C, in contrast to Celgard separator that severely shrunk in Figure 19g,h. The tensile strength of the cellulose/PSA membrane was 17 MPa, because the cellulose skeleton was well bonded with PSA for improving the mechanical properties (Figure 19i). A good interfacial compatibility between the separator and Li metal was also achieved as shown in Figure 19j, which displayed that the interfacial resistance of cellulose/PSA separator was only 200 Ω compared with Celgard separator (340 Ω). As a result, the cycling performance was much improved by the cellulose/PSA separator as compared to Celgard separator in Figure 19k.

Interestingly, commercial paper made of cellulose has also been used as the battery separator. Zhang et al. [281] reported the use of rice paper (RP) for the battery separator for the first time. The RP consisted of tortuous cellulose fibers with diameter range of 5–40 μm. They explored that RP exhibited much better
thermal stability than Celgard separator. At high temperature, RP only shrunk about \(-0.26\%\) while the shrink rate of Celgard separator was \(-0.5\%\). The researchers also explored that RP presented an electrochemical stability window of about 4.5 V and tested the compatibility of RP in several battery systems. In graphite/Li and LiCoO2/Li cells, the capacities for RP and Celgard separator were both comparative, which implied that RP was a promising separator candidate.

5.2. Biomaterials for Li–S Battery Interlayers

Separator coatings or interlayers are believed to be effective components for solving the diffusion of polysulfides and shuttle effect issues of Li–S batteries. This is because the interlayers inserted between the sulfur cathode and the original separator serve as barriers for capturing polysulfides. The interlayers are fabricated in the form of free-standing films or separator coatings that intimately contact with separators. In most cases, the interlayers are electrically conductive for providing electrons for converting trapped polysulfides\(^{[283]}\) and acting as “upper current collectors” that increase the conductive areas\(^{[284,285]}\). Therefore, biomaterials are appropriate carbon source for fabricating conductive carbon-based interlayers. In addition, for maximizing the function of trapping polysulfides, it is believed that high surface area from unique nanostructure is helpful for accommodating polysulfides. In such a way, specific biomaterials that can generate porous structure, networked structure, etc. have been of great interest. Thus far, cellulose paper\(^{[286,287]}\), leaf\(^{[288]}\), eggshell membrane\(^{[289]}\), bacterial cellulose\(^{[290]}\), cassava\(^{[291]}\), fungus\(^{[292,293]}\), bamboo\(^{[294]}\) etc. have been reported to be used as the carbon source. These materials when being fabricated into interlayers significantly enhance the performance of resulting Li–S batteries.

Chung et al.\(^{[288]}\) were inspired by the unique hierarchical structure of a leaf and fabricated an interlayer based on a carbonized leaf (CL) as illustrated in Figure 20a. They explored that the CL showed an integral carbon framework and hierarchical pore structures including micro-/meso-pores and even macropores. The pores and stomata of the lower epidermis

![Figure 20. Biomaterials as carbon source for separator coatings/interlayers for advanced Li–S batteries. An interlayer based on a carbonized leaf (CL). Reproduced with permission.\(^{[288]}\) Copyright 2014, Wiley-VCH: a) Schematic illustration and photographs of CL; b) SEM image and EDS mapping of CL disassembled from cycled Li–S batteries; c) Nyquist plots and d) cycling performance of Li–S batteries with CL as the interlayer. An interlayer based on carbonized interwoven bamboo carbon fiber (BCF). Reproduced with permission.\(^{[294]}\) Copyright 2015, Royal Society of Chemistry: e) Schematic illustration of Li–S batteries with BCF as the interlayer; f,g) SEM and TEM images of BCF, respectively. An interlayer based on porous carbonized fungus film. Reproduced with permission.\(^{[293]}\) Copyright 2015, Elsevier: h) Schematic illustration of fabrication process; i) Rate performance of Li–S batteries.](image-url)
originally acted as reservoirs in the plant, and then presented the same function in the battery for preserving liquid electrolytes. The SEM image and EDS mapping of the CL interlayer dissembled from cycled Li-S batteries clearly indicated the presence of sulfur element, which was a proof that polysulfides were trapped by the CL interlayer as shown in Figure 20b. At the same time, the still strong carbon signal indicated that the trapped polysulfides did not totally cover the CL interlayer. The Nyquist plots in Figure 20c suggested that CL interlayer reduced the charge-transfer resistance from 500 to 40 Ω, because the conductive CL interlayer increased the surface area for electron conduction and thereby the electrical conductivity of the sulfur cathodes. Equipped with this CL interlayer, the Li–S cell exhibited an exceptional cycling performance in Figure 20d with a much higher initial capacity of 1320 mA h g⁻¹ than that of the cell with a bare separator (845 mA h g⁻¹). The capacities of the CL interlayer cell were significantly higher than that of the bare separator cell at all current rates within 100 cycles. Gu et al. reported an interlayer based on carbonized bamboo carbon fiber (BCF) in Figure 20e. It was found in their study that the BCF possessed microfibers with hollow structure (Figure 20f) and meanwhile, numerous micropores were observed in Figure 20g. This hollow microporous structure benefited infiltrating electrolytes and capturing polysulfides. As a result, the BCF interlayer enhanced the reversible capacity from ~200 mA h g⁻¹ to ~600 mA h g⁻¹ and delivered a high Coulombic efficiency of 98%. Another interesting work by Chai et al. demonstrated a porous carbonized graphene-embedded fungus carbon fiber (GFC) as an interlayer illustrated in Figure 20h. They blended fungus and graphene together, in which fungus acted as a binder. Then the mixture was carbonized to generate a porous structure with graphene nanosheets embedded in fungus carbon fibers. Importantly, the fungus also served as heteroatom sources to result in N-doping and O-doping for the final GFC. The N-/O-doped carbonaceous materials show chemical adsorption of polysulfides. Previous studies have verified that strong binding could be formed between the heteroatoms of the carbonaceous materials and polysulfides, and the heteroatoms could directly participate in chemisorption of polysulfides. Therefore, the affinity with polysulfides was improved in addition to the electrical conductivity. Consequently, the battery performance such as rate performance was notably enhanced by the GFC interlayer, that the capacities of the cell with GFC were much higher than that of the cell with a bare separator at all current densities in Figure 20i. At the same time, the GFC interlayer decreased the interfacial resistance from 8 to 2 Ω and charge-transfer resistance from 19 to 4 Ω, due to the fact that the GFC interlayer enhanced the wettability and provided larger electrochemical reaction surface area.

The above discussion has introduced the studies of using biobased materials as the carbon source for preparing conductive separator coatings/interlayers. Very recently, there has emerged some work using biomaterials directly as the polysulfide immobilizers, different from the strategy of carbonizing these materials. The basic rationale is that biomaterials themselves possess oxygen-/nitrogen-containing groups making them good adsorbents for polysulfides. In this way, directly applying proper biomaterials by adding them with conductive fillers has great potential to provide both chemical and physical blocking functions. For instance, Tu et al. introduced GA into carbon nanofiber (CNF) via solution-casting and used this CNF-GA composite as an interlayer in Figure 21a. GA, as a kind of branched polysaccharides, consisted four types of side chains: galactose, arabinose, rhamnose, and hydroxyproline. The researchers speculated that these side chains offered strong binding with polysulfides and performed DFT calculations on the binding energies. As shown in Figure 21b, these four side chains all presented much higher binding energies compared with graphene, because the electron-rich groups in GA, such as hydroxyl and ketone groups as well as cyclic oxygen, acted as the Lewis base to form a strong lithium bond with polysulfides. When putting the various separators in the polysulfide solution as indicated by the inset photograph in Figure 21c, it was evidently found that the color of the solution with CNF-GA disappeared, but no obvious color change occurred for base separator and CNF. The UV–vis spectra were also consistent with the photographs. These results confirmed that GA played a critical role in adsorbing polysulfides. Figure 21d is the SEM image of the CNF-GA interlayer after cycling testing and there were many polysulfides adsorbed by GA. Benefiting from the effectiveness for trapping polysulfides by CNF-GA, the self-discharge was suppressed that the open-circuit voltage (OCV) was very stable and only slightly decreased from 2.4 to 2.35 V. By contrast, the OCVs of bare separator and CNF were decreased from 2.4 V to 2.13 and 2.23 V, respectively (Figure 21e). Regarding the cycling performance in Figure 21f, CNF-GA showed the highest capacity of 880 mA h g⁻¹ and remained this advantage throughout 250 cycles, as compared with the bare separator and untreated CNF interlayer. The improved electrochemical performance was owing to the effects of CNF-GA for immobilizing polysulfides.

Fu et al. reported a polysulfide nanofilter (PSNF) based on gelatin protein in Figure 21g, via surface treatment of CB by gelatin. The researchers surprisingly found that gelatin protein could drive a unique self-assembly of CB particles, which finally resulted in a 3D porous structure. The gelatin dissolved in water gelled due to poor denaturation, while the acetic acid solution helped break down the inter-/intra-chain interactions of gelatin and then prevented the gelation of gelatin. Based on the adsorption testing in Figure 21h,i, the protein PNSF showed obvious effect of preventing the diffusion of polysulfides through the separator as compared with the bare separator. To reveal how the protein PNSF contributed to the polysulfide trapping, the researchers conducted MD simulations as illustrated in Figure 21j. There were strong interactions between gelatin and polysulfides. Specifically, the backbone oxygen atoms and carboxyl groups from the end chains showed notable electrostatic interactions with Li ions in polysulfides. When compared with a conventional interlayer, PVDF/CB, the protein PSNF showed significant advantages in improving the battery performance such as cycling performance in Figure 21k. One found that the capacity of the cell with PSNF was much higher than that of the control cells with bare separator and PVDF/CB interlayer. This was due to the fact that such PSNF not only strongly captured polysulfides by the excellent trapping ability by gelatin, but also effectively promoted the ion transport by its rational porous structure. The inset SEM images in Figure 21k also confirmed that the PSNF after
undergoing 200 cycles actually captured numerous polysulfides compared with the clean morphology for the as-prepared PSNF without cycling. Chen et al.[301] used chitosan as the functional additive for fabricating conductive separator coating. Chitosan that possessed many carboxyl and amine groups proved to be polysulfide trapping agent. They also added chitosan in the sulfur cathode to further improve the polysulfide-adsorption ability. As a result, the Li–S battery with chitosan showed a higher reversibly capacity of 680 mA h g⁻¹ compared with the chitosan-free battery (508 mA h g⁻¹).

5.3. Summary

Thus far, reported studies on separator engineering have focused on development of innovative separator alternatives or creation of separator coatings. Regarding separator alternatives, cellulose-based materials exhibited good affinity with liquid electrolytes and good thermal stability compared with classic polyolefin separators. To improve the separator properties, people have made numerous efforts to fabricate highly-porous and robust cellulose-based materials via freeze-drying, polymer
blending, etc. In addition, biomaterials have been widely used as separator coatings/interlayers of Li–S batteries with the aim of blocking polysulfides. In this strategy, biomaterials have been employed as carbonaceous materials or polysulfide immobilizers for fabricating conductive interlayers. It has been widely reported that carbonaceous materials derived from biomaterials solely acted as conductive interlayers or were glued by polymer binders to generate conductive interlayers. Furthermore, heteroatom-rich biomaterials served as exceptional polysulfide immobilizers and the resulting conductive interlayers also presented excellent capturing ability for polysulfides when they were doped with conductive fillers.

6. Concluding Remarks
6.1. Conclusions and Challenges

High-energy Li-based batteries are of great interest for implementation in advanced consumable electronics, long-range electric vehicles, etc. However, the widespread applications of them are still sluggish today, mainly due to the limited properties of key battery components (e.g., electrode, electrolyte, separator) and potential safety concerns. Biomaterials featuring diverse chemistries and functionalities, vast resources and low cost, not only contribute to improving battery material properties and thus device performance, but also benefit sustainable and cost-efficient energy storage. In this review, recent advancements of exploiting biomaterials for achieving high-energy Li-based batteries with a focus on fulfilling three critical targets are discussed: 1) stabilizing electrode structures; 2) capturing electrochemical intermediates; 3) protecting Li metal anode/enhancing safety. As battery performance is an outcome of the “teamwork” of various battery components, the primary strategies of using biomaterials for engineering of electrodes, electrolytes and separators are summarized. Nature is like “sea of inspirations” such that numerous biomaterials have been demonstrated to be effective for boosting high-energy Li-based batteries.

Although employment of biomaterials is becoming the mainstream for development of inexpensive, sustainable and high-performance Li-based batteries, further improvement is critically needed, particularly from perspectives of energy density and manufacturing cost. The strategies of applying biomaterials in electrode, electrolyte and separator engineering as discussed in this review, make a great leap toward realization of advanced high-energy Li-based batteries at materials level. However, challenges in further enhancement of material properties and in improvement of energy density and manufacturing cost-effectiveness still remain to be solved. Table 2 summarizes the typical biomaterials and contributions from each engineering strategy as well as the corresponding challenges: 1) AM structure design (core–shell, porous structures, etc.) is the most important strategy for stabilizing the high-capacity electrode structures, which are characterized with good controllability of AM structures, fast ionic/electronic-conduction and even ability of trapping electrochemical intermediates. AM structure design improves the power density by the fast charge-transfer, but unfortunately, porous AM structure greatly sacrifices the energy density especially volumetric energy density. Meanwhile, fabrication of rational AM structures usually involves multiple steps and complicated technologies, resulting

| Table 2. Summary of the contributions and challenges of the main engineering strategies via adopting biomaterials. |
|---|---|---|---|
| Strategy | Typical biomaterials | Contribution | Disadvantage |
| Electrode engineering | AM structure design | Monosaccharides (glucose, xylose), proteins, fungus, agricultural byproducts | Stabilized structure, good ionic/electronic-conduction, good controllability, intermediate trapping, high power density | Poor scalability, high manufacturing cost, sacrificing energy density |
| Electrode framework | Cotton fibers, cellulose-related species, alginates | Stabilized structure, mechanical flexibility, good ionic/electronic-conduction, high energy/power densities | Increasing manufacturing cost |
| Electrode channel | Woods, animal shells | Structural integrity, fast and controllable ionic/electronic-conduction, high energy/power densities | High manufacturing cost |
| Binder engineering | Oligo-/poly-saccharides (gums, cellulose-related species, alginates), proteins, lignin | Stabilized structure, intermediate trapping | Inactive, sacrificing energy density |
| Electrolyte engineering | Cellulose-related species, proteins (soy protein, gelatin), starches, chitosan | High safety, intermediate trapping, Li metal protection | Low ionic conductivity, poor interfacial properties |
| Separator engineering | Separator alternative | Cellulose-related species, commercial paper | High thermal stability, high modulus, high ionic conduction | Poor controllability, low puncture strength, increasing manufacturing cost |
| Separator coating | Gums, proteins, chitosan | Improving interface, intermediate trapping, Li metal protection | Sacrificing energy density, high manufacturing cost |
in high manufacturing cost. 2) Electrode framework and electrode channel strategies are able to improve the overall mechanical flexibility or integrity of the electrodes as well as provide fast conduction of ions/electrons. Owing to the relatively low bulk density of biomaterials such as cellulose and wood compared with metallic electrode frameworks/channels, these two strategies help to achieve relatively high power/energy densities. However, they also suffer from high manufacturing cost. 3) Binder engineering is a rather cost-efficient strategy for stabilizing the electrode structures and even trapping electrochemical intermediates. Nonetheless, biobased binders are usually not electrically conductive, and the inactive nature inevitably sacrifices the energy density. 4) Electrolyte engineering using biomaterials mainly focuses on development of solid and gel electrolytes, which warrants the safety of batteries. This strategy enables the trapping of intermediates that protects cathodes and Li metal anodes. The issues for electrolyte engineering mainly stem from the limited material performance. The low ionic conductivity and poor interfacial properties remain the most critical challenges. 5) Replacing current separators by biomaterials provides several advantages such as fast ion-conduction by higher electrolyte uptake, good thermal stability and higher modulus, etc. The disadvantages for the biobased separators are the poor controllability of porosity, insufficient puncture strength and increasing manufacturing cost. Separator coating is an important strategy for Li–S batteries. The coatings play an intriguing role in modifying the interfaces between electrodes and separators, trapping electrochemical intermediates and then protecting Li metal anodes. However, the coatings as additional layers reduce the energy density and fabrication of separator coatings is of high manufacturing costs.

6.2. Perspectives

Based on the progresses and challenges of using biomaterials for advanced Li-based batteries as discussed in above sections, the future research directions and forthcoming opportunities are summarized as follows:

1) For design of AM structures and electrode architectures: Utilizing biomaterials for designing rational AM structures and building unique electrode architectures may still follow the route of generating biomaterial-derived carbonaceous materials. In the case of AM structure design, careful manipulation of final AM structures is critically needed via establishment of structure-property-performance relationships for different biomaterial precursors. A fundamental understanding of effects of surface/bulk properties on electrochemical performance will help rational and more controllable design of AM structures. The porosity and pore size are important factors for design of porous AM structures, which affect the AM loading level and charge-transfer kinetics. For core–shell structured AMs, creating robust shell and controllable shell thickness is critical. Employing proper biomaterials that can uniformly bind with AMs and experience less decomposition intensity in carbonization process are expected to help form rational core–shell structures. Meanwhile, an optimal balance between buffering volume expansion and providing fast electron conduction should be found, and real-time characterization tools such as in situ microscopy in electrochemical reactions will help to identify this balance point. Furthermore, it is suggested searching for biomaterials with high percentage of heteroatoms to generate high doping rate of heteroatoms for carbonaceous materials to further enhance the electrochemical performance. On the strategies of electrode frameworks/channels, fabricating thick electrodes and binder-free or binder-less electrodes are promising for further increasing energy density. For electrode frameworks, layer-by-layer configuration of electrodes has great potential for realizing thick electrodes. Meanwhile, biomaterials with hierarchical structures may help to anchor AMs, form efficient conduction networks inside electrodes, and finally achieve binder-less/binder-free electrodes. Regarding electrode channel strategy, biomaterials with well-defined microstructures are potential electrode channel candidates. For this strategy, controlling the tortuosity and porosity as well as exploiting the methods for more efficiently loading AMs into the channels are the main tasks.

2) For binder engineering: There is a strong demand for developing mechanically stronger, more adhesive and multifunctional biobased binders and reducing the fraction of binders in electrodes. High robustness and strong adhesion of biobased binders will facilitate the fulfilment of binder-less electrodes. Basically, biomaterials possessing strong inter-/intra-molecular interactions and relatively high molecular weight will have high mechanical robustness, and the ones with a variety of functional groups will lead to higher adhesion strength. It will be significant to correlate the molecular structures of the biobased binders to the physicochemical/electrochemical properties. Generally, biobinders with a number of branches show stronger adhesion strength compared with linear ones, because more adhesion sites are offered. For example, Jeong et al. systematically investigated several types of polysaccharide binders for Si anodes and concluded that Xanthan gum with helical superstructures with side chains and ion-dipole interactions led to the best comprehensive performance (e.g., adhesion strength, mechanical properties, etc.). Blending and cross-linking are two effective ways for reinforcing the mechanical robustness of the biobased binders, which potentially lead to self-healing properties and are cost-effective as well. In addition, exploration of new biobased binders should be considered with respect to specific electrodes. For instance, hydroxyl group-rich biomaterials are appropriate for silicon anodes because hydrogen bonding can be formed between the biomaterials and silicon anodes. Heteroatom-rich biomaterials such as the ones having N-/S-containing groups, are suitable binders for sulfur cathodes, which have great potential to strongly bind polysulfides. For high-voltage cathodes, biomaterials enabling to form good coating layer on the AM surface will be attractive binders. It is also critically important for sulfur and high-voltage cathodes to uncover the mechanisms of how biobased binders contribute to trapping intermediates or stabilizing electrode/electrolyte interphase. In situ characterization techniques, such as in situ X-ray photoelectron spectroscopy and in situ X-ray diffraction, may help to analyze the interactions between biobased binders and intermediates, as
well as structure evolution of AMs, binders, etc. Endowing conductivities to biobased binders may compensate the sacrificed energy density by the binders. To this end, applying ion-conductive biomaterials as the binder will be a feasible strategy to improving ion-transport kinetics, while incorporating biobased binders with conductive polymers will give rise to electrically conductive biobased binders.

3) For electrolyte engineering: Electrolyte engineering may primarily focus on improving the ionic conductivity for solid-state electrolytes and reinforcing mechanical properties for gel electrolytes. For crystalline or semi-crystalline biomaterials, chemical modifications, addition of nanofillers, cross-linking, etc. are useful routes for reducing crystallinity and thus increasing ionic conductivity. Meanwhile, introducing inorganic electrolyte nanoparticles to the biobased electrolytes might be a promising strategy for further improving ionic conductivity. Importantly, in-depth understanding of the ion-conduction mechanisms for biobased electrolytes is in critical need. It is expected that the different molecular structures of the bioelectrolytes are crucial factors affecting the ion-conduction process. For example, for protein solid electrolytes, it is critical to uncover the contributions from the protein configurations (e.g., polypeptide chain folding structures) to the ion-conduction behavior. Therefore, MD simulations or DFT calculations along with nuclear magnetic resonance may make great contributions. Learning the ion-conduction mechanisms will help to improve the ionic conductivity by purposefully designing desired compositions or structures that are beneficial for ion-conduction. Regarding biobased gel electrolytes, adding ion-conductive biomaterials as fillers might be effective for improving ionic conductivity and reinforcing mechanical properties simultaneously for conventional gel electrolytes. Fabrication of biobased nanofibers as gel electrolyte skeletons is of great interest, which enable to adsorb a large quantity of liquid electrolytes. In this regard, tuning the morphologies of nanofibers and balancing the mechanical properties and liquid electrolyte uptake will be important tasks. There is also a strong need for finding biomaterials that can be plasticized by liquid electrolytes or ionic liquids for fabricating biobased gel electrolytes using biomaterials as the hosts.

4) For separator engineering: Development of biobased separator alternatives is suggested exploring critical methods for realizing effective control of porosity. Meanwhile, improving the puncture strength is strongly demanded, and ceramic coating, polymer blending, etc. will be proper approaches. It is also important to solve the flammable issue of biobased separators. In this regard, creating thin ceramic coatings on the separator surface will make significant contributions. In addition, for separator coating studies in Li–S battery community, reducing the coating thickness by such as solution-casting, spin coating, vacuum filtration, etc. will be a big challenge for increasing the energy density of the batteries. However, there is a conflict between reducing the thickness of separator coating and increasing the capacity of the coating for storing polysulfides. Therefore, it will be significant to estimate the capacity of the separator coating for accommodating polysulfides and establish the relationship between the separator thickness/mass and the capacity for trapping polysulfides. Based on these considerations, it will be equally critical to improve the capability of the separator coatings for trapping polysulfides. Employment of biomaterials that have stronger interactions with polysulfides as the binder to glue conductive fillers will be an attractive solution. In this scenario, biomaterials with rich polar functional groups present chemisorption of polysulfides. Meanwhile, it will be important to recognize the proper type of biomaterials with greater capability for capturing polysulfides. For instance, regarding the biomaterials such as proteins or gums as promising polysulfide immobilizers, simple chain structures or short side chains may help expose the functional groups for adsorbing polysulfides. At the same time, N, O, S-doped carbonaceous materials with porous, fibrous and hollow structures derived from biomaterials are of significant interest, which show great potential of strongly binding polysulfides. Naturally, combination of the abovementioned two routes seem to be viable. Furthermore, producing “Janus” separators with abilities of trapping polysulfides and stabilizing Li metal anodes is promising for addressing the two critical issues of Li–S batteries. For this strategy, it seems that combining biobased conductive coatings and biobased separators holds great promise for realizing this goal.

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Conflict of Interest

The authors declare no conflict of interest.

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biomaterials, high-voltage cathodes, lithium–sulfur batteries, silicon anodes, solid electrolytes

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