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2021

Jin, C., Nai, J., Sheng, O., Yuan, H., Zhang, W., Tao, X. & Lou, D. X. W. (2021).
Biomass-based materials for green lithium secondary batteries. *Energy & Environmental
Science*, 14(3), 1326-1379. <https://dx.doi.org/10.1039/D0EE02848G>

<https://hdl.handle.net/10356/147398>

<https://doi.org/10.1039/D0EE02848G>

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Biomass-based materials for green lithium secondary batteries

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Abstract

The advances in process engineering, nanotechnology, and materials science gradually enable the potential applications of biomass in novel energy storage technologies such as lithium secondary batteries (LSBs). Of note, biomass-derived materials that range from inorganic multi-dimensional carbons to renewable organic biomolecules or biopolymers can contribute towards “green battery” systems, serving as the sustainable battery components. This review offers a comprehensive overview of the fabrication and application of both biomass and biomass-derived materials in LSBs. First, the processing routes of biomass towards different products are considered and described. The corresponding mechanistic understanding of biomass processing is particularly underscored. Classified by the battery components, focused discussions on biomass applied as electrode scaffolds, active cathode/anode materials, binders/additives, and separators/solid-state electrolyte layers in LSBs are systematically provided. The insights from this review demonstrate that biomass has significant potential for the development of high-performance “green battery” systems, which to different extent employ sustainable and green biomass-derived battery components. To accelerate its industrialization, specific attention should be paid to upgrading the processing technologies to maximize biomass utilization with high efficiency and low cost. Meanwhile, we summarize the present limitations over the application of biomass in LSBs and propose the potential strategies for revolution. Additionally, we foresee further usage of biomaterials to advance LSBs and other alkali-

1 metal secondary batteries. This review comprehensively describes the significance of biomass and
 2 biomass-derived materials that have already received some attention and will bring numerous
 3 breakthroughs in the battery community. It is intended to arouse the broad attention of scientists for
 4 this prospective trend of development in “green batteries”.

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1. Introduction

Biomass is undoubtedly the most abundant, inexhaustible, and greenest energy source on the planet, which has attracted significant attention from scientists. Instead of the original utilization of biomass (*e.g.*, simple burning, ferment), which cannot meet today's demand for both high efficiency and powerful energy, processing and transformation techniques for biomass play significant roles and must be improved. As assisted by the booming advances in nanotechnology, catalysis design, material science, *etc.*, the exploitation of biomass has experienced significant revolutions and breakthroughs.¹⁻⁴ Bioelectrogenesis, biodiesel, biocatalyst, and various nano-energy biomaterials have been found and produced.⁵⁻¹⁰ Biomass has attracted the attention of material scientists and countless interesting biomaterials for different kinds of research fields have been developed. Among these potential applications, this review is focused on its employment as advanced battery materials for lithium secondary batteries (LSBs), since this green material has huge potential to be transformed and deployed in any component of a battery.

LSBs have been regarded as promising green energy devices for modern society.¹¹⁻¹³ Given the advantages like light-weight, high-efficiency, portability, and high performance, LSBs have been widely commercialized over recent decades and have even become ubiquitous in more recent years. And LSBs have already been one of the core solutions to the environmental issues caused by the consumption of non-renewable energy resources. Over the last 30 years, LSBs have undergone significant revolutions that have caused an explosive increase of interest in their further development.¹⁴⁻²² When pursuing batteries with higher energy and power densities, and better safety, maintaining their sustainability (replacement of non-sustainable battery components) has also been raised as a key point that may be a great challenge to researchers.^{15,23-26} As is well-known, LSBs are mainly composed of anodes, cathodes, separators, electrolytes, binders, and additives, which dictate the battery performance. The current bottleneck for each of these components can be described as follows.

(1) Electrode materials: For the cathode, the state-of-the-art commercial materials are mainly lithium (Li) metal oxides, which deliver energy through the intercalation/de-intercalation reaction.^{21,27-29} The primary limitation of Li-metal oxide cathodes comes from their low theoretical capacity of less than 300 mAh g⁻¹. This in addition to high costs, possible environmental contamination, structural instability at high operation voltages, and catalysis for electrolyte

1 decomposition is another great obstacle for constructing batteries with both high-energy and high-
2 power densities. As for the anode, graphite is the most widely used material, which also faces the
3 issue of low specific capacity.³⁰⁻³² Consequently, the conventional LSBs comprised of graphite anode
4 and Li-metal oxide cathode face great challenges of low battery energy density. Instead, the
5 employment of anodes like Li metal and lithium alloys (*e.g.*, lithiated silicon, lithium-boron alloy,
6 lithium-tin alloy) with much higher capacities are believed to make great differences,³³⁻³⁶ since they
7 can be paired with novel cathodes (*e.g.*, sulfur, transition metal fluorides) with features like ultrahigh
8 capacities, environment friendliness, and low cost.²⁶ However, those next-generation electrode
9 materials with high performances also face some great challenges, resulting from limited battery
10 chemistries and material chemistries. For instance, the Li-metal anode is challenged by the destructive
11 volumetric effect (hostless nature),³⁷ uncontrollable dendrite growth and unstable solid-electrolyte
12 interphase (SEI) formation,^{38,39} while the application of sulfur cathode is inhibited due to the poor
13 electronic conductivity, infinite volume change, and serious dissolution/shuttle of electrochemical
14 intermediates (Li polysulfides).⁴⁰ These dilemmas appeal to the considerations of stabilizing both the
15 cathode and anode by constructing three-dimensional (3D) conductive scaffolds, regulating the
16 electrochemical behaviors of active materials (*e.g.*, the deposition/dissolution of Li metal),^{41,42} and
17 developing stable electrode/electrolyte interface.

18 (2) Electrode additive: To obtain a high-performance electrode, electronically conductive additive
19 and polymer binders are of great importance.⁴³⁻⁴⁶ These indispensable additives are generally used to
20 bind active materials and offer an electronically conductive network for electrodes. However, these
21 functions are usually achieved at the expense of increasing the weight of a battery. Since these
22 additives are in general electrochemically inert, they will largely reduce the energy density of batteries.
23 It seems simple to resolve this issue by minimizing or even avoiding the employment of electrode
24 additives, such as the construction of 3D highly connected conductive electrodes (carbon-less and
25 binder-free),^{47,48} but this is indeed a significant challenge.

26 (3) Electrolytes and electrolyte additives: Various ester- and ether-based electrolytes containing
27 different Li salts in a liquid state impact the market of commercial LSBs.⁴⁹ The inherit inflammability
28 of these materials causes LSBs to face significant challenges from catching fire and even exploding.
29 Moreover, liquid electrolytes are poisonous and not considered to be green. The electrolyte additives
30 are an important part of the electrolyte, which are generally used to shape the growth patterns of

active materials during the electrochemical process, to control the distribution of ions, and to induce the SEI with specific structures and components. Current limitations of electrolytes at the cathode side are mainly from their decomposition at high operation voltages,⁵⁰⁻⁵³ which cause continuous performance degradations and can even trigger safety hazards. For the anode side, the uncontrollable reactions between the electrolyte (both the solvents and Li salts) and anode materials, as well as dendrite growth will lead to active material loss and unstable electrolyte/anode interfaces,⁵⁴⁻⁵⁸ which will lead to performance degradation and rapid battery failure.

(4) Separator: The separator plays a vital role in isolating the anode and cathode from a short circuit, guaranteeing a high ion migration rate while resisting the dendrite growth of the anode.⁵⁹⁻⁶⁵ Most widely-commercialized separators are made of polypropylene (PP) and polyethylene (PE) polymers, which are often light, thin, and porous but suffer from unsatisfactory mechanical properties and insufficient thermal stabilities.^{56,60,66-69} Moreover, as an organic polymer, the safety hazards of combustion and environmental pollution are also inevitable. Therefore, the design of next-generation separators with sustainable, green, cheap, and safe properties should not be overlooked.

Numerous works have explored advanced battery materials to address these material- and chemistry-related issues. The solutions have included constructing high-performance electrode materials, fabricating high safety electrolytes, introducing functionalized electrolyte additives, designing tough separators, and others. In these pursuits, biomass has been found useful in LSBs, as it can contribute to any component of the battery with better performance and higher sustainability (Fig. 1).⁷⁰⁻⁸² In short, biomass can be transformed into functionalized scaffolds for optimizing cathode/anode materials or itself function as the active material. Moreover, there have been mature procedures to extract natural chemicals [carbohydrates (starches, terpenes, low-molecular sugars), celluloses, hemicelluloses, lignins, uronic acids, oil, proteins, *etc.*], which could be further processed into various designed chemical products [*e.g.*, polylactide (PLA), poly(ethylene furanoate) (PEF), poly(ethylene terephthalate) (PET), PE, polymer resins/elastomers].^{2,4,83} Among these chemicals, some sustainable biomolecules/biopolymers (*e.g.*, starch, cellulose, lignin, natural gums, proteins, furfural) can be regenerated and employed to fabricate functionalized binders, separators, and solid-state electrolytes,^{60,84-86} while other natural chemicals can be modified to serve as electrolyte additives to efficiently improve the battery performance. Due to their features like being sustainable, inexpensive and abundant, biomass materials are greatly competitive for use in establishing green

1 and high-performance LSBs.⁸⁷⁻⁸⁹ In this contribution, we emphasize the processing of biomass and
2 the applications of these materials in LSBs.

3 **2. Processing of biomass**

4 The overall biomass (*e.g.*, plants, bacteria, fungi, animals) in the biosphere of our planet delivers a
5 content of ~550 gigatons of carbon (Gt C) and the total annual primary production of biomass is over
6 100 billion tonnes of carbon per year.⁹⁰⁻⁹² Meanwhile, land plants with a carbon mass content of
7 almost 80% (450 Gt C) are the most abundant biomasses. Additionally, a census of ~140 Gt per year
8 of the global biomass waste will be produced. All in all, under the reasonable application and
9 advanced recycle techniques, the biomass (including the natural biomass, the energy crops, and bio-
10 wastes) for battery production is inexhaustible in supply and always available for use.

11 To further extend this success to battery chemistries, the progressive and modern processing
12 techniques of transforming biomass into battery materials are of great significance, which are
13 particularly supposed to purify the quantity of the variable biomass materials and achieve high
14 efficiencies and yields at low cost and minimum environmental concerns. Moreover, the hierarchical
15 and delicate applications of biomass ranging from the natural structures/chemical components to the
16 biological/biochemical/biophysical properties should be comprehensively understood. Since the
17 natural structures of biomass usually show effectively optimized mechanical properties (stiffness,
18 strength, and toughness) and are closely related to the molecule/ion transfer/transformation at the
19 interfaces,⁹³⁻⁹⁵ which may be ideal architectures for building high-performance LSB components and
20 can shed lights on the development of the interface chemistry, that is, the core of battery chemistries.
21 The above overall assumption and prospects largely depend on the successful and highly-efficient
22 processing of biomass.

23 In general, biomass materials are naturally shaped with hierarchical structures at different scales
24 (Fig. 2), which are usually composed of repetitive sequences and designed to provide mechanical
25 strength and structural scaffolds. For instance, the three typical structural motifs of biomass (protein,
26 cellulose, and chitin) are consisting of amino acids (Fig. 2a), β -(1,4)-linked D-glucose units (Fig. 2b),
27 and (1,4)- β -N-acetylglucosamine (a long-chain polymer as a derivate of glucose) (Fig. 2c),
28 respectively. These biopolymers can be assembled into semi-crystalline structures (nanocrystal
29 components embedded in the amorphous region *via* hydrogen bonds and *van der Waals* forces) and

1 further organized into nanofibrils. With the further multi-dimensional bundling and stacking of the
2 nanofibrils on selective orientation, 3D hierarchically structured products of silk fiber, wood wall,
3 and arthropod exoskeleton are obtained. To maintain and homogenize the advanced natural structures
4 and chemical components of biomass as well as to promote its further processing and applications,
5 the corresponding chemical/physical pretreatments, carbonization, and activation processes are often
6 needed. These treatments guarantee the successful fabrication of chemicals with various compositions
7 and structures, including organic biomolecules/biopolymers [sucrose, starch, poly(limonene
8 carbonate), long-chain aliphatic polyesters, polylactic acid, *etc.*], and carbon materials [activated
9 carbons (ACs), carbon fibers (CFs), carbon nanosheets (CNSs), carbon spheres (CSs), *etc.*], which
10 can be employed to produce various battery products (cathode, anode, scaffold, binder, electrolyte,
11 and separator) with superior electrochemical performances (Table 1).⁹⁶⁻¹⁰⁵ Celluloses and proteins are
12 the major components in plant and animal biomasses, respectively, and are often dissolved and
13 separated into the basic segments, allowing for regeneration according to the desirable designs (multi-
14 dimensional structures and specific chemical components) and large-scale production. This indicates
15 the respective potential of preparing free-standing electrodes, high-performance separators, and a
16 protective layer coupling hardness and softness for advanced LSBs. In this contribution, we will focus
17 on the discussion towards the processing of cellulose- and protein-based biomasses that have huge
18 potential in mass production for battery materials (3D skeletons, separators, polymer electrolytes,
19 *etc.*).

20 **2.1 Chemical and physical treatments**

21 Appropriate treatments by using certain chemicals or physical processing (solvent dissolution, pre-
22 carbonization, solidification, *etc.*) could primarily achieve the change and transformation for
23 microstructures and components of biomass materials (selectively maintaining the specific structures
24 and purifying the chemical components). After that, the biomass materials with higher quality and
25 purity will be more accessible for further processing or relevant direct applications.

26 **2.1.1 Dissolution and regeneration**

27 In general, cellulose is produced by plants at billions of tons per year, which makes it the largest
28 organic carbon reservoir. And cellulose is a polysaccharide composed of repeated D-glucose units
29 [anhydroglucose rings, (C₆H₁₀O₅)_n], linked together *via* the so-called β-1,4-glycosidic bonds. This

accounts for the micro- and nano-fiber composition of the natural cellulose with excellent mechanical properties. In addition, due to its properties of abundant storage, low-cost, biodegradation, environment friendliness, and thermal/chemical stability, it has drawn attention as a natural renewable polymer material for battery materials. In fact, the commercial cellulose-based non-woven separator has already been produced for LSBs. Generally, cellulose coated with hemicelluloses is tightly combined due to the strong binding effect from natural binder lignin and abundant hydrogen bonds. Therefore, cellulose plants usually do not exhibit obvious microfiber structure, with nanofibers being even rarer. Therefore, the pretreatment, separation, and functionalization of cellulose have become important topics in the fields of biomaterials and organic chemistry.

In recent years, numerous strategies from more sustainable perspectives have been developed to dissolve, separate, and regenerate cellulose, replacing the traditional but exclusively used viscose route with high costs, complex processing, and harmful byproducts.¹⁰⁶ In contrast to mechanical separation (*e.g.*, high-pressure homogenization, high-speed agitation, and ultrasonic treatment), dissolving and separating cellulose with green solvents is thought to be a more efficient and facile approach. N-methylmorpholine-oxide (NMMO) is one such typical green solvents to directly dissolve cellulose *via* physical procedures to harvest man-made cellulose products (Lyocell, *etc.*).¹⁰⁷ However, drawbacks include unsatisfactory thermal stability, high-energy requirements, and ease of fibrillation, which make this environment-friendly method also facing great resistance as a replacement to the ubiquitous viscose method.

To solve these challenges, numerous novel green solvents have been investigated and enriched for the successful utilization of cellulose. In this process, a variety of cellulose and cellulose composite architectures can be harvested by controlling the regeneration parameters. In recent decades, green solvents, such as ionic liquids (ILs), LiCl/N,N-dimethylacetamide (LiCl/DMAc), NaOH aqueous solutions, alkali/urea/thiourea aqueous solutions, tetra butyl ammonium fluoride/dimethyl sulfoxide, metal complex solutions, and molten inorganic salt hydrates, have been proposed to dissolve and regenerate cellulose.^{106,108-111} Cellulose-based powders, fibers, films, membranes, hydrogels, and aerogels can be collected and used directly to fabricate the separator of LSBs or can be transformed into free-standing scaffolds/electrode/protective layer using carbonization and activation treatments.

One of the most promising systems that comprises a green solvent of alkali solution (sodium

hydroxide/lithium hydroxide, NaOH/LiOH; urea) and a low-temperature pretreatment for dissolving and processing native cellulose (Fig. 3a) was proposed by Zhang and coworkers.¹¹² Compared to the organic solvents and ILs, the alkali aqueous solution systems are more cost-effective, energy-saving, and non-toxic, which will not produce environmental pollution and are promising for mass production. Figure 3b presents a schematic illustration for the cellulose dissolution process in such an alkali/urea aqueous solution. When the native cellulose is immersed into an alkali/urea solution at a low temperature (*e.g.*, $-10\text{ }^{\circ}\text{C}$), it is surrounded by free water molecules as well as alkali and urea hydrates (Fig. 3b, first panel), which gradually penetrates the cellulose and destroys the hydrogen bonds among its fibrils (Fig. 3b, second panel). As a result, the cellulose is solvated with the alkali and urea hydrates absorbed onto the surface, leading to its expansion in the form of a swollen gel (Fig. 3b, third panel). During this process, the cellulose is coated with sheath-free water, alkali and urea hydrates, which completely separates the cellulose to provide the dissolved cellulose aqueous solution (Fig. 3b, fourth panel). With the adoptable green strategy for harvesting the dissolved cellulose solution,¹¹³ regeneration and fabrication of various kinds of cellulose fiber fabric (*e.g.*, cellulose multifilaments, Fig. 3c, d) may be easily designed and produced on an industrial scale together with a simple wet-spinning method and a pilot machine. This advance provides a reasonable prospect for the revolution of battery separators with highly-processable cellulose. Moreover, with the dissolved cellulose solution and many available processing techniques (*e.g.*, electrospinning, self-assembling, freeze-drying, and doping), it is of great interest to blend cellulose with functional additives to harvest tremendous cellulose-based materials for battery chemistries. As an extension of the alkali-dissolving cellulose strategy, Xu *et al.* successfully prepared the cellulose-based spherical droplets with the dissolved cellulose and polyaniline (PANI) *via* an emulsion separation process (Fig. 3e).¹¹⁴ This cellulose composite material can be carbonized into heteroatom-doped porous carbon microspheres, which can be deployed in LSBs,¹¹⁴ such as the carbon host for the sulfur cathode or a high-performance carbon anode.

All in all, developing green solvents that can dissolve cellulose-containing plant biomass for large-scale production at low cost and without the emissions of toxic byproduct is highly promising and already industrialized. Moreover, with the mature material processing techniques, it is easy to use cellulose solution to produce various functionalized battery materials with distinguished structures and morphologies at the nano-/micro scale. Of note, this strategy is especially adaptable for the

1 fabrication of high-performance separators (*e.g.*, cellulose-based non-woven separator with high
2 ionic conductivity, thermal stability, electrolyte uptake, and mechanical strength) and the construction
3 of 3D bipolar conductive carbon scaffolds (*e.g.*, scaffold for sulfur cathode or Li-metal anode).

4 Protein, as an abundant biopolymer in the animal biomass, is the key basis of organisms and the
5 main carrier of biologic processes in all living things.¹¹⁵ Generally, proteins are composed of various
6 types of amino acids in different arrangements and play specific roles in living organisms. There are
7 numerous categories of proteins, such as fibrin, globulin, keratin, collagen, chaperone, myoglobin,
8 and hemoglobin. Among these, fibrous protein is a 1D material (*e.g.*, silk from silkworms like *Bombyx*
9 *mori* and orb-weaving spiders like *Nephila clavipes*) with impressive mechanical properties,
10 environmental tolerance, biodegradability and flexibility, which has been used in daily life since
11 ancient times.¹¹⁶⁻¹¹⁹ It is found that silk shows a complex and hierarchical structure, ranging from the
12 macroscale to the nanoscale (Fig. 4a).¹²⁰ Generally, fibers of cultured silkworm silk fibroin are around
13 0.25–10 μm in diameter and are composed of two kinds of proteins (a light chain protein and a heavy
14 chain protein) connected by a single disulfide bond.¹²¹ Meanwhile, such fibroin is mainly composed
15 of glycine (Gly, 43 wt%), alanine (Ala) (30 wt%) and serine (Ser) (12 wt%). Similar to cellulose,
16 such silk fibers are bonded tightly by a natural binder (sericin) to assembly into rough fibers and
17 hierarchical structures. Considering the hierarchical structures and special biophysical/biochemical
18 properties of protein, it shows attractive advantages for fabricating battery materials like highly ionic-
19 conducting separators, 3D porous carbon network, functional buffering interlayers. Consequently, the
20 collection of the dissolved and regenerated protein with high processability and purity is of great
21 importance for the large-scale reassembling and production of battery materials.

22 Following a similar route of dissolving cellulose, Niu *et al.* proposed a method for achieving the
23 green exfoliation of silk fibers using the aqueous NaOH/urea system and several mechanical
24 treatments (*e.g.*, freezing, dialysis, sonication, centrifugation),¹²⁰ which enabled the collection of
25 uniform and high-purity silk nanoribbons (SNRs) with an average thickness of 0.4 nm. With a similar
26 green strategy associated with chemical-dissolution and physical-separation processes, Ling *et al.*
27 developed a liquid exfoliation method in another work,¹²² claiming that this method was inspired by
28 the liquid exfoliation of graphite (Fig. 4b). The proposed method exfoliates silk fibers *via* the
29 incorporation of organic solvents and ultrasonication to finally harvest the separated natural silk
30 nanofibrils. On the basis of this strategy, they successfully prepared ultra-thin silk nanofibril

1 membranes from commercial *Bombyx mori* silk fibers (Fig. 4c).¹²³ In this work, they first used
2 hexafluoroisopropanol (HFIP) to partially dissolve the silk cocoon debris under vortexing, after which
3 physical separating treatments including suspension-shaking/stirring, sonication, and centrifugation
4 at high speeds were carried out to finally collect the high-quality and uniform silk nanofibril
5 suspension. , The exfoliated silk nanofibrils are verified to have a homogeneous diameter of
6 approximately 20 nm and a length in the range of 300–500 nm, which could be assembled into
7 membranes using a simple vacuum filtration method (Fig. 4d).

8 These mentioned methods for fabrication of purified silk nanofibrils are easy, effective and
9 repeatable, which enables the deployments of the extracted silk fibroin to fabricate various types of
10 materials, including fibers, non-woven fibroin mats, fibroin films, fibroin hydrogels, and fibroin
11 porous sponges.¹²⁰⁻¹²³ The freestanding silk membranes can be applied to LSBs as either separators
12 or a protective layer between the electrode and electrolyte. Meanwhile, these materials can be further
13 carbonized and activated to serve as electrode materials or scaffolds in LSBs. Moreover, while
14 fabricating and processing silk fibroin, numerous chemical compounds can be easily introduced into
15 the silk to obtain specifically functionalized composites for more diverse applications.

16 **2.1.2 Stabilization**

17 Biomass materials are often naturally shaped and contain various interesting microstructures that are
18 ideal for constructing battery materials. For instance, wood livestock presents a channel structure
19 along its growth direction. Pollens from rape flower, lotus, pine, *etc.*, show capsule-like hollow
20 structures, while *Malvales* plants, like *Bombax malabaricum* and *Gossypium spp*, can produce cotton
21 fibers in tubular structures. However, these natural structures suffer from collapse due to various
22 processing conditions. Necessary strategies are needed to maintain these natural structures of
23 biomasses, which are important for improving structure-dependent properties towards future uses as
24 battery materials. A simple method is to pre-carbonize the biomass at a relatively low temperature
25 (below 500 °C) with or without an inert atmosphere that can also to some extent purify the chemical
26 composition of biomass.¹²⁴ Meanwhile, strongly oxidizing chemicals, such as hot concentrated
27 sulphuric acid and potassium permanganate (KMnO₄), could also pre-carbonize biomass, fix the
28 native morphologies via dehydration reactions at a low temperature (below 100 °C) and achieve the
29 removal of some contamination (*e.g.*, mineral). However, as the reactions between these chemicals
30 and biomass are often relatively aggressive, the morphology of biomass will be destroyed to some

1 extent, resulting in a porous and rough surface. Besides direct pre-carbonization, solidification is a
2 milder and widely used approach, which is achieved by applying solidifying agents like formaldehyde
3 (CH_2O). As is well-known, CH_2O is a common preservative that fixes organism structures, which
4 could react with amines and amino acids in the biomass (*e.g.*, biogenic amines and protein) *via*
5 Eschweiler-Clarke reactions.¹²⁵ To perform this solidification process, biomass is usually added to a
6 mixture of ethanol and CH_2O under violent stirring to allow the liquid to penetrate the entire structure,
7 meanwhile dissolving and removing some organic contamination. Additionally, the morphology of
8 the biomass can also be maintained and stabilized using a surface coating polymer, which serves as a
9 protective layer for the biomass structure during carbonization and activation processes. Among all
10 those strategies, direct pre-carbonization of biomass at low temperatures is facile and simple, while
11 the emissions of byproducts will lead to the low yield, insufficient utilization, and environmental
12 concerns. These raise the considerations of the collection and appropriate applications of the
13 byproducts to render the entire sustainability during biomass processing. As for the employment of
14 reactive chemicals, it enables the stabilized biomass to have more hierarchical porous structures, but
15 its large-scale production faces several difficulties in separating the stabilized biomass (processing
16 concern), recycling the chemicals (sustainability concern) and reducing the emissions of toxic wastes
17 (environment concern). Solidification seems to be a promising approach to be used in practical
18 production, in terms of low emissions of wastes, easy recyclability of solidifying agents, and facile
19 separation of the products. However, to achieve the desired stabilization of biomass, a combination
20 and synergy of these methods should be considered.

21 Microalgae are ideal templates for designing hollow and core-shell structured materials. For
22 instance, *Nannochloropsis oculata* cells (abbreviated as *N. oculata*) are spherically-shaped
23 microalgae with an average diameter of 2 μm (Fig. 5a). To maintain their natural structure, Xia *et al.*
24 used a $\text{KMnO}_4/\text{Na}_2\text{SO}_4$ aqueous solution both as the stabilization agent and a precursor to prepare the
25 composite material (Fig. 5b).¹²⁶ Due to the strongly oxidizing capability of KMnO_4 and the etching
26 of Na_2SO_4 , the *N. oculata* gradually solidify to form hollow spheres that are loaded with Mn-
27 containing particles (Fig. 5c). Subsequently, polystyrene (PS), as an inexpensive and common
28 polymer, is used to retain the structure of biomass during carbonization. With a similar stabilization
29 process, Xia *et al.* maintained the naturally shaped capsule-like structure of pollens, which can further
30 be transformed into hollow scaffolds for electrode materials.¹²⁷ Figure 5d shows a photograph of the

1 starting materials of the lotus flowers carried pollens, which own natural hollow structures composed
2 of a soft core (proteins, amino acids, and nucleic acids) and a hard exine (cellulose, hemicelluloses,
3 and lignin). To stabilize and enrich the pore structures of pollens, the raw material was firstly purified
4 and initially fixed with the solidifying agent, followed by further pre-carbonization with reactive
5 chemicals (Fig. 5e). After the preservation of the natural morphology, electrode materials can then be
6 easily introduced into the biomass (*e.g.*, chemical bath deposition) without the risk of destroying the
7 native biomass morphology. The carbonized pollen/nickel oxide composite successfully inherited the
8 original capsule-like structure of pollen (Fig. 5f) and delivered remarkable rate performances
9 comparable to many recent results with graphene and heteroatom doped carbon (Fig. 5g),^{128,129}
10 confirming the significance of natural hierarchical structures towards the superior battery
11 performances.

12 Besides microalgae and pollen, wood is also a naturally structured hierarchical material, which is
13 one representative cellulose biomass livestock (Fig. 6a).¹³⁰ Along the direction of the tree growth, the
14 wood blocks show a porous channel structure, which is composed of nano-scaled cellulose,
15 hemicellulose, and the natural binder of the lignin polymer. To maintain the whole 3D structure while
16 achieving the optimization of the chemical components in the wood, Hu and coworkers proposed a
17 facile and efficient method that has been widely used in the paper fabricating industry for a long
18 time,¹³¹⁻¹³⁴ which comprises the step-wise dissolution of the hemicellulose and lignin by a
19 NaOH/Na₂SO₃ solution (nucleophilic sulfite) and a hydrogen peroxide (H₂O₂) solution (Fig. 6b).⁵⁷
20 Subsequently, arched wood layers with a stacked lamellar structure can be harvested after freeze-
21 drying, during which the broken cellular walls attach to each other as a result of the ice template. As
22 can be seen in Figure 6c, the natural wood block exhibits a brown color and contains several lumina
23 (tubular channels are 20–80 μm in diameter) along the direction of tree growth, which is composed
24 of orientated cellulose aligned at the microscale (Fig. 6d). After removing the hemicellulose and
25 lignin, the wood block becomes a white light foam (inset of Fig. 6e). Top-view SEM image shows an
26 obvious porous lamellar structure with arrays of arched layers stacked together (Fig. 6e), while the
27 magnified cross-section image exhibits the remained alignments of the cellulose nanofibers (Fig. 6f).
28 The obtained 3D foam-like wood block (high-quality cellulose foam) exhibits superior flexibility,
29 light-weight, and a 3D porous structure for use in fabricating multidimensional materials towards a
30 variety of applications. Of note, such a robust cellulose product shows high potential for fabricating

highly conductive separator, stretchable polymer matrix for gel polymer electrolytes, and 3D netted electrodes. Moreover, the mature techniques for fabricating paper may be borrowed to rapidly achieve the industrial-scale production of this wood foam product.

Briefly, these findings not only emphasize the advantages of natural hierarchical structures in constructing high-performance batteries, but also indicate the importance of maintaining the structures and purifying the components of biomasses. Moreover, the hierarchical structures and superior morphologies enable the biomass specific biophysical/biochemical properties and make it a charming “biotemplate” for the fabrication of composite carbon-based active materials. The biophysical/biochemical properties (*e.g.*, the bio-adsorption, bio-concentration) of biomass can be delicately used to uniformly combine the biomass with additive materials to harvest superior 3D composite structures. Additionally, it is noted that the fixation process can be designed to introduce the target components simultaneously to obtain the final product, while different structure-retaining strategies can be combined and employed.

2.2 Carbonization

Carbonization is an important method during the biomass processing, which not only can remove the impurities in the biomass, but also can fix the morphology of biomass-derived products (biochar). Biochar has vast prospective applications in battery chemistry, including as the conductive additive, electrode scaffolds, and the active materials.^{130,135-144} There are several carbonization methods, including pyrolysis, gasification, hydrothermal carbonization (HTC), and flash carbonization.^{145,146} Figure 7a compares the differences among these five methods with respect to the typical process, residence time, solid product yield, the carbon content in the product, and the carbon yield (the mass ratio between the carbon and the used carbon feedstock).¹⁴⁶ In this review, the pyrolysis and hydrothermal carbonization are selected and systematically discussed as the best-developed and promising technologies.

During carbonization, biomass (taking cellulose plant biomass as an example) experiences several phase transitions ranging from microcrystalline cellulose to amorphous intermediate and finally to the turbostratic crystallites.¹⁴⁷ In these transitions, four kinds of distinct biomass-derived carbon can be obtained. To understand the entire carbonization process of biomass from low to high temperatures, Keiluweit *et al.* proposed the dynamic molecular structure of plant biomass-derived

biochar across a charring gradient and schematic representations of the four proposed char categories (transition char, amorphous char, composite char, and turbostratic char) with their respective phases (Fig. 7b, c).¹⁴⁷

(1) Stage 1: During the initial carbonization stage, the main changes to the biomass are ascribed to the loss of water from evaporation and dehydration reactions, while the biopolymers in the biomass, including the cellulose, hemicelluloses, and lignin in the biomass, remain nearly unchanged (Fig. 7b).

(2) Stage 2: At this stage, the biomass increasingly experiences dehydration and depolymerization reactions that release small volatiles (*e.g.*, furans, pyrans, and anhydro sugars) and low molecular products (*e.g.*, aldehyde, ketones, and carboxyl carbon) (Fig. 7b). Although experiencing certain dissociation, the lignin and cellulose in the biomass are still partially crystalline.

(3) Stage 3: The obvious characteristic of this stage is the formation and increase of aromatic carbon from condensation reactions. Instead of long-range ordered structures, the dominance in the biomass at this stage is the small aromatic units that are arranged randomly. Therefore, intermediates, including pyranones, anhydro sugars, phenols, quinines, pyrroles, furans, and small polyaromatic units, could be detected at this stage. Meanwhile, the stable aromatic lignin residues are enhanced, which is ascribed to losses of materials with lower heat-resistance and indicates a dramatic reduction in biomass-derived carbon, non-carbon atoms, and volatile matters content. All these pieces of evidence prove that the crystalline cellulose has been nearly disintegrated, causing the formation of a disordered carbon phase.

(4) Stage 4: As the temperature continues to increase, the crystal turbostratic carbon grows within the former amorphous phase. Due to the lack of abundant atomic pore space in the crystalline carbon phase and the trapped volatiles in the pores, the specific surface area (SSA) of the composite biomass carbon is much lower than that at higher temperatures. In addition, the retained aromatic, aliphatic and oxygen-containing compounds promote the formation of an amorphous matrix, which tightly covers the crystalline turbostratic carbon.

(5) Stage 5: At higher temperatures, the carbon further changes with the growth and enhancement of long-range order of the crystalline turbostratic carbon, leading to the formation of high-degree crystal structures. It is noted that the SSA of the heated biomass during this stage shows incredible improvement, which is related to the additional cross-sectional transformation from amorphous carbon to graphene-like matter. As the graphitic carbon is denser than the former amorphous carbon,

the above transformation causes the appearance of nanoscale pores (less than 2 nm). However, the generally lower crystallinity of the biomass-derived carbon is an unequivocal characteristic different from graphite. In addition, biochar has other characteristics including the high content of heteroatoms, large SSA, low electronic conductivity, and the richness of unpaired electrons.

Wood and grass are the most common plant biomasses and are investigated to further illustrate the carbonization effect of biomass.¹⁴⁷ Figure 7d, e help to understand the relationships between the carbonization temperature, product yield, and Brunauer-Emmett-Teller (BET) surface area. For wood (Fig. 7d), an increase in the temperature reduces the product yield, especially at temperatures higher than 200 °C, while the content of volatile matter steadily decreases. The BET surface continues to increase and reaches more than 400 m² g⁻¹ at 600 °C, after which the BET surface starts to decline. In addition, the biochar and ash contents in the final product increase with increased temperature. For grass, a similar phenomenon is observed (Fig. 7e). One evident difference between grass and wood is that the ash content in grass is much higher and the BET surface continues to increase until about 700 °C, but its value is generally below 150 m² g⁻¹.

With the above discussion on the carbonization of biomass like wood and grass, it is obviously seen that there is a large amount of biomass loss and the yield for biochar is quite low. This undoubtedly reduces the utilization of biomass and produces pollutive wastes. To achieve the real sustainability of both the processing and application of biomass as well as to render the large-scale production of biomass-based battery materials, these issues during carbonization should be comprehensively understood and resolved. This greatly depends on the effective collection and catalytic conversion of emissions to harvest useful byproducts. Alternatively, new advances in the carbonization technique that directly enables the emissions to be recycled or to be selectively/regionally processed into various biochar products (*e.g.*, carbon fiber, carbon tube, activated carbon) in the carbonizing system.

2.2.1 Pyrolysis carbonization

Biochar with various structures and different morphologies can be easily obtained from the pyrolysis carbonization of biomass or its pretreated precursor in inert gases, such as nitrogen (N₂) and argon (Ar). In this process, the biomass mainly experiences pyrolysis reactions, in which water and carbon-containing small molecules are derived from the organic components, leading to the formation of biochar. Besides the inert gases, some reactive gases can sometimes be used to fabricate biochar with

1 heteroatomic dopants. For instance, if NH_3 is introduced, nitrogen atoms will ingress into the carbon
2 skeleton so that N-doped biochar can be harvested. In addition, pyrolysis carbonization of a mixture
3 of biomass and certain chemical agents can also lead to the formation of various types of heteroatom-
4 doped biochar and biochar composites.

5 There have been numerous works reporting the fabrication and applications of biochar from
6 pyrolysis carbonization.^{148,149} Manthiram and coworkers directly carbonized the commercial cotton
7 pads (high-quality cellulose fabric) to harvest carbon “cotton” with hierarchical macro-/microporous
8 architecture.¹⁵⁰ When this biochar without any modification was used to host the sulfur cathode, a
9 remarkable high sulfur loading of up to 61.4 mg cm^{-2} and sulfur content of 80% with high
10 areal/volumetric/gravimetric capacities were obtained. In addition to direct carbonization, some
11 pretreatments to biomass may help develop hierarchical structures of obtained products. For example,
12 Zhong *et al.* carbonized the instantaneously puffed rice livestock to produce a 3D carbon structure
13 (PRC, Fig. 8a).¹³⁵ With this method, the starch in the rice livestock expands rapidly in a sealed
14 container at a high temperature ($\sim 200\text{--}300^\circ\text{C}$) and large pressure (0.5–1.5 MPa). Figure 8b shows
15 that the rice puffed by a factor of approximately 20 in volume, while the outer shell boundaries were
16 maintained. Then, the carbonized rice with a 3D porous structure consisting of abundant
17 macrocellular pores was used as the host for a sulfur cathode, which showed much better cycling
18 stability and higher capacity than that of 3D reduced graphene oxide (rGO) (Fig. 8c, d). This facile
19 and cost-effective method could be extended to other starch-containing biomasses; meanwhile,
20 biochar composites can be easily obtained by introducing chemicals before the instantaneous puffing
21 treatment and carbonization.

22 Since a portion of biomass does not show desirable structures or morphologies for specific
23 applications after the carbonization, templates are often used to shape the biochar. For instance, Zhou
24 *et al.* prepared N-doped double-shelled hollow carbon spheres (N-DSHCS) by using a hollow TiO_2
25 sphere template and an N-containing biomolecule of dopamine (Fig. 8e).¹⁴⁹ The N-DSHCS are
26 collected after carbonization and template removal, which have a uniform size distribution and well
27 distinguished double shells (Fig. 8f). By wrapping the N-DSHCS with graphene, an additive-free
28 (binder and conductive additive) and electronic/ionic conductive network (G-NDHCS) was collected.
29 This composite host can provide a highly conductive network, accommodate the volumetric effect of
30 sulfur, and stabilize the polysulfides by heteroatom dopant. As a result, the Li-S battery based on this

1 composite cathode is able to deliver a much better rate capability performance than the bare
2 graphene/sulfur cathode (Fig. 8g). Additionally, this strategy can be extended to fabricate biochar
3 with multi-layered shells. With a different soluble template of sodium chloride (NaCl), Li *et al.*
4 carbonized glucose to fabricate 3D porous graphitic carbon (PGC) (Fig. 8h).¹⁵¹ In this design, NaCl
5 template and Na₂S (the sulfur source) were mixed with glucose and were self-stacked in the solution,
6 which was followed by freeze-drying to obtain uniform restricted crystals coated with a glucose
7 film.¹⁴⁴ During the carbonization at high temperature in an Ar atmosphere, glucose experiences
8 graphitization and develops both micro- and meso-pores. Then, the Fe(NO₃)₃ aqueous solution was
9 introduced to remove the NaCl and oxidize the Na₂S into sulfur, forming a high-performance
10 carbon/sulfur cathode material. In addition to glucose, other soluble biomasses could be adopted using
11 this strategy to obtain various composite electrode materials. The template strategy can be employed
12 to shape the biomass materials with desirable structures. However, it also faces obvious limitations
13 caused by the solubility of biomass within the mixing solvents and the affinity between the biomass
14 and the templates, which will greatly influence the structures and morphologies of the final product.
15 And the recycling of templates should be considered since the use of sacrificial templates may
16 increase the total fabricating cost as well as the possible involvement of toxic agents for removing
17 the template.

18 Besides the use of templates, coordinated reactions between biological polymers (polysaccharides,
19 proteins, polypeptides, DNA, *etc.*) and metal ions could also be engaged for the structural design of
20 biomass before carbonization, especially for 2D structures.^{144,152} Zhang *et al.* carbonized the mixture
21 of agarose (AG) and metal nitrate to successfully prepare 2D carbon hybrids (Fig. 8i).¹⁵² They
22 confirmed that a 2D structure is formed during the coordination reaction between agarose and metal
23 nitrate rather than during the carbonization process (Fig. 8j). The Fe³⁺ ions promote the cross-linking
24 of the agarose molecules *via* dative bonds through the -OH bond, while NO₃⁻ during carbonization
25 produces a significant amount of gas to drive and support the formation of layered metal-polymer
26 nanosheets (Fig. 8k). With this strategy, 2D biochar embedded with various metal or metallic
27 compounds can be readily prepared, serving as a potential cathode and anode materials. In addition,
28 2D porous biochar sheets with a high surface area and abundant porosity can be harvested by
29 removing the metal or metallic compounds, which can be employed as electrode skeletons, protective
30 interlayers and carbon film electrodes for LSBs.

In summary, the pyrolysis carbonization can purify and transform the biomass with abundant organic/inorganic substances into biochar comprised of various structures and morphologies. This process can also stabilize/fix the original structures of biomass or incorporate additive materials and heteroatom dopants to the backbone of biochar to form composite materials with desirable components and functions. As for biomass without superior structures for battery applications, the employment of suitable templates or the assembling reactions may also enable the development of advanced biochar products with interesting structures. Additionally, the structural design and removal of templates are supposed to be further studied to resolve the concerns for fabricating cost from sacrificial templates and toxic wastes from template removers.

2.2.2 Hydrothermal carbonization

In addition to the traditional routes of carbonizing biomass in inert gases, HTC processing is also a widely used and environmentally friendly approach for developing carbon materials with various structures and components. Generally, hydrothermal treatments are conducted under specific temperatures and pressures to promote the solubility of biomasses, enhance the physical/chemical interactions between biomasses and the applied solvents, accelerate the ionic and acid-base reactions, and contribute to the final formation of various carbon materials. In general, HTC methods are categorized into two major groups according to the treatment temperature. For the high-temperature HTC (300 to 800 °C), the organic biomass is unable to maintain its chemical stability and will release reactive gases while producing carbon debris, which can be applied to prepare graphitic carbon, carbon nanotubes, and activated carbon. The low-temperature HTC (<300 °C) is similar to the well-known biomass coalification process, in which peats and coals are produced in nature *via* dehydration and polymerization reactions.¹³⁶ The HTC method is distinguished from a natural process as it is highly accelerated to reduce the reaction time from hundreds (for peat formation) or millions (for coal formation) of years buried in the earth to a few hours in laboratories. Overall, this is an environmentally friendly and universal approach for synthesizing carbon materials. Since the HTC is conducted within a solvent-filling sealed container, the byproducts/wastes are well restricted, which can not only largely reduce the emissions of pollution, but also promote the convenience for collection and recycle of the solvent and byproducts/wastes. In addition, introducing appropriate templates, additives and catalysts allow converting many types of biomass into interesting carbon structures at various scales for certain applications accompanied with control over their chemical components,

1 microstructures, and surface functional groups. Of note, this HTC technique for fabricating biochar
2 products and byproducts to recover energy from biomass wastes has already been commercialized by
3 several companies (*e.g.*, TerraNova Energy, HTCycle, Antaco, C-GREEN Technology that produce
4 HTC coal from bio-wastes). This undoubtedly can also be used to commercially produce HTC battery
5 materials from biomass, especially from the biomass wastes, in a manner of environmental
6 friendliness, low cost, and sustainability.

7 Glucose derived carbon spheres are typical biochar obtained by the HTC method and have
8 tremendous applications in LSBs, which can be directly achieved using only water and glucose (Fig.
9 9a).¹⁵³ HTC shows high feasibility for harvesting products with variable structures and morphologies.
10 With the addition of organic monomers, a new type of hybrid HTC-derived biochar functionalized
11 with the polymerized additives can be produced through copolymerization and cycloaddition
12 reactions. For instance, Titirici and coworkers successfully collected hydrophilic HTC-derived
13 biochar by doping some acrylic acid into the glucose and water mixture,¹⁵⁴ which delivered an
14 aggregated secondary structure that was distinguishable from the bare carbon spheres (Fig. 9b). In
15 addition to these organic monomers, some inorganic additives (structure-directing agent, catalyst, *etc.*)
16 can also play effective roles in designing HTC-derived biochar with special structures.¹⁵⁵ For instance,
17 Chen *et al.* proposed that CaCl_2 can lead to the formation of biochar spheres with surface pores (Fig.
18 9c), which are developed from interactions between the alginate and metal ions.¹⁵⁶ Moreover,
19 changing the dosage of CaCl_2 , HTC-derived biochar with different morphologies can be harvested.
20 This strategy could be extended through the employment of different metallic compounds to fabricate
21 various carbon/metal-based (metals, oxides, fluorides, nitrides, sulfides, *etc.*) composites with
22 specific structures in addition to the hierarchical porous biochar, which can be employed as promising
23 electrode materials. Additionally, it is noted that experimental settings (such as the reacting time,
24 temperature, pressure, and physical fields) can also be controlled to synthesize various HTC-derived
25 biochar species.¹⁵⁷ Microwave irradiation is a typical strategy to assist the production of HTC-derived
26 carbon quantum dots (CQDs),¹⁵⁸ which possesses some specific merits including high efficiency,
27 satisfactory product yield, and good purity.¹⁵⁹ Si *et al.* proposed a one-pot microwave-assisted HTC
28 strategy for preparing both the CQDs (Fig. 9d and the inset) and the lignin nanoparticles (LNPs) from
29 lignin.¹⁶⁰ As shown in Fig. 9e, the lignin and holocellulose will release monosaccharide and organic
30 acid, respectively, under the microwave-assisted acidolysis, which can further be transformed into

high-quality CQDs after the processes including dehydration, polymerization, condensation, aromatization, carbonization, and final burst nucleation. Regarding the protein, it can also be used to produce CQDs after experiencing several steps (pyrolysis, carbonization, oxidization, doping and burst nucleation, Fig. 9e).

Of note, templates (both soft and hard) mentioned before can also be applied in the HTC process to build specially designed biochar structures. Yu and coworkers reported HTC-derived carbon nanofibers consisting of monolithic hydrogels/aerogels (Fig. 9f), using glucose as the carbon source and the metallic tellurium wires (a metal anode material) as the template.¹⁶¹ The obtained product shows promising applications in building 3D electrodes with a high mass loading of the active materials. Another group confirmed that anodic aluminum oxide as an efficient exo-template can also facilitate to produce glucose-derived biochar nanofibers with the HTC method.¹⁶² In addition to the above hard templates, soft templates such as surfactants [sodium oleate, polyethylene oxide-polypropylene oxide-polyethylene oxide (P123), poloxamer (F127), trimethylammonium cation (CTAC)] with various functional groups can also be employed to prepare HTC-derived biochar. These surfactant templates can drive the self-assembly of biomass from its interactions with both the surfactants and solvents to form special structures (such as coaxial nanocables, 2D nanosheets ordered mesoporous materials, *etc.*).¹⁶³⁻¹⁶⁵ Obviously, with the adoption of templates, HTC is enabled with superior feasibility to produce biochar with desirable structures and components. However, this is achieved at the expense of the extra process of template removal and increasing production cost, meanwhile the quality of products highly depends on that of the templates.

Considering that the properties of templates are responsible for the morphologies and structures of the obtained HTC-derived biochar, Titirici and coworkers conducted a systematic investigation that revealed the effects of the surface chemistry and pore structure of templates (SiO₂) on the HTC-formed biochar (Fig. 9g-j).¹⁶⁶ It was found that hydrophobic templates with or without pores lead to the formation of carbon casts (Fig. 9g, h). In contrast, methylated mesoporous silica spheres promoted the formation of porous carbon spheres, while methylated nonporous silica spheres resulted in hollow carbon spheres without obvious pores (Fig. 9i, j). These findings show the potential to predesign carbon materials with certain morphologies, structures, and polarities (functional groups on the surface) by adopting appropriate templates. In addition, if active materials are directly used as the templates, composite electrode materials can be directly prepared without the need/cost for removing

1 the templates.

2 All in all, pyrolysis carbonization is a facile and promising strategy for harvesting biochar at a
3 large scale, which can inherit the original structures of biomass and biomass-derived precursors. This
4 to some extent may reduce the processability toward the structures and morphologies of biomass
5 products. Additionally, it suffers from the inferior utilization of biomass, unavoidable emissions of
6 polluting wastes, and variable quality of products. In contrast, HTC may be a more efficient and
7 sustainable approach, since all the materials are restricted within the container, indicating a
8 convenience for separating and recycling byproducts/wastes. Moreover, due to the highly controllable
9 reacting conditions at high temperature/pressure, HTC may be a better choice for designing and
10 producing biomass products with complex hierarchical structures and components.

11 **2.3 Activation of biomass-derived carbon**

12 Biomass-derived carbon materials *via* direct carbonization or HTC methods are usually found with a
13 relatively low SSA and limited porosity.¹⁶⁷ However, when employed as the scaffolds, an increased
14 SSA and hierarchically porous structures are usually important for improving the mass loading of the
15 active materials (*e.g.*, sulfur cathode), enhancing the electron/ion transport, and promoting the
16 electrochemical behaviors in LSBs. Therefore, various activation methods are developed to enrich
17 the porous structures and SSA of biochar, which can also to some extent regulate the surface chemistry
18 and components of biochar (*e.g.*, remove/enrich the surface groups, control the content of heteroatom
19 in the carbon backbone). Gas and chemical activations are the two most widely-used strategies to
20 fabricate high SSA biochar, while many other novel activation techniques, like plasma, have
21 progressively been developed and are gaining attention.¹⁶⁸

22 **2.3.1 Gas activation**

23 Reactive gases are effective activation agents aimed at enhancing the porosity and SSA of biochar,¹⁶⁹
24 which is achieved by the gradual gasification of carbon at high temperatures. Carbon dioxide (CO₂),
25 oxygen (O₂), and water (H₂O) streams are the most typical gas activation agents, on the basis of the
26 Boudouard reactions between carbon and CO₂/O₂/H₂O at elevated temperatures. Of note, this concept
27 of using oxygen-containing gases (steam and CO₂) to obtain activated carbon has been designed by
28 Woodruff *et al.* as early as in 1924 accompanied by the detailed flow chart and equipment, which has
29 been further investigated and developed by many researchers.^{170,171} As shown in Figure 10a, Chen *et*

al. proposed the fabrication of activated wood carbon (AWC) by employing a CO₂ agent.¹⁷² They first stabilized and carbonized a wood block at a low temperature, followed by activation in CO₂. The AWC maintained its channel structure from the original wood, and a hierarchical structure with macro-/meso-/nano-pores was largely developed (Fig. 10b, c), which was further confirmed to be an ideal 3D substrate for accommodating both anode (TiO₂, Li₄Ti₅O₁₂, and LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂) and cathode (MoS₂ and TiS₂) materials at high mass loading. However, considering the limited activation degree, emissions of greenhouse gases, and the high cost of the activation gases as well as the expensive equipment required, this strategy still requires significant development to overcome these issues and enhance its practical application value.

2.3.2 Solid chemical activation

Solid chemical activation is a widely used approach to fabricate biochar with an ultrahigh SSA and a well-defined pore distribution, which is achieved using activation agents (AAs) to react aggressively with biochar (or biomass). Potassium hydroxide (KOH) is a well-known agent to enlarge the SSA and enrich the abundant pore network in biochar.^{3,167,169,173-177} However, the activation mechanism has not yet been clearly understood due to the complexity arising from the numerous variables in both experimental parameter settings and the biochar used for activation. One commonly accepted assumption is that the activating reactions between the biochar and KOH begin with a solid-solid reaction and followed by a solid-liquid reaction (Fig. 10d), which can be described by the equations below.^{167,178}

At temperatures lower than 300 °C, a significant amount of water steam is generated due to the dehydration of the biomasses. When the temperature increases to approximately 400 °C, the KOH decomposes into K₂O and water [Eq. (1)]. The carbon in the biomasses is then consumed and sculptured from the water and gas reactions, which releases H₂ and CO [Eq. (2)]. The emission of CO will further react with H₂O to produce CO₂ and more H₂ [Eq. (3)]. Then, K₂CO₃ is formed from the

1 reactions between CO_2 and K_2O [Eq. (4)]. When the temperature further increases to over $800\text{ }^\circ\text{C}$,
2 K_2O is reduced by the abundant H_2 and C [Eq. (5, 6)] to obtain metallic K (boiling point of $762\text{ }^\circ\text{C}$).
3 It is proposed but unproven that the generated K penetrates the formed pores and the layers among
4 the graphite, which continuously catalyzes and promotes the activation reaction. Besides the reactions
5 listed in these equations, there are many other reactions among the various products that are believed
6 to occur.

7 Overall, the high SSA and abundant pore network are generated during the complex reactions
8 among the biochar, KOH , and the side products/intermediates. Moreover, the experimental
9 parameters, such as the activation temperatures and the mass ratios between the activation agents and
10 the biochar species, largely influence the final pore structures, including the pore size and quantity,
11 as well as the SSA. To perform the activation process, pristine or pre-calcinated biomass is either
12 directly mixed with KOH or impregnated into the KOH solution. If the KOH and biochar mixture is
13 collected from the impregnation method, an additional low-temperature drying process is needed.
14 The activation reaction is then conducted by heating the mixture within an inert gas-filled furnace,
15 after which the product is thoroughly washed with an acidic solution and deionized water to remove
16 any soluble impurities. Finally, the activated sample with a high SSA and abundant pore network is
17 collected after drying. Although activating biochar with AAs is highly efficient, some problems
18 should be recognized that it will largely reduce the yield of final products, produce greenhouse gases,
19 corrode the equipment, and complicate the producing process. To eliminate the environmental and
20 cost concerns for mass production of activated carbon in this approach, these issues must be
21 considered.

22 Long *et al.* activated natural fungus biomass (Fig. 10e) with KOH to obtain biochar with high
23 SSA.⁷⁵ They conducted systematic investigations on the influence of the KOH solution concentration
24 on the SSA and pore structures of the obtained biochar. It was found that with the increased KOH
25 concentration, the biochar obtained had apparent morphological changes that resulted in smaller
26 debris with a richer porosity (Fig. 10f). Notably, the SSA of the KOH activated biochar was effectively
27 increased to 1017 , 1103 , and $1788\text{ m}^2\text{ g}^{-1}$ compared with the low SSA of the sample without KOH
28 ($51\text{ m}^2\text{ g}^{-1}$). Meanwhile, the power density of activated samples showed a significant decline.
29 Following the same route, Li *et al.* also reported the fabrication of a KOH activated carbon from
30 carrageenan (a red algae extractive) with the highest known SSA ($\sim 4037\text{ m}^2\text{ g}^{-1}$) for biochar.⁷⁹ Such

1 a high SSA could be ascribed to the formed hydrogel precursor [carrageenan-iron ions (Fe^{3+}) hydrogel]
2 as well as the subsequent KOH activation effect. Additionally, some pretreatments of biomass before
3 the activation process can significantly help increase the SSA and enrich the pore structure of the
4 obtained biochar. For example, Wang *et al.* made an excellent attempt in their recent work, where
5 they prepared KOH activated biochar with a high SSA of more than $3000 \text{ m}^2 \text{ g}^{-1}$ assisted by a
6 biodegradation pretreatment.¹⁷⁹ The biomass they used was cotton seed hull (CSH), which firstly
7 experienced biodegradation from fungi growth (*Pleurotus ostreatus*) to form a loose 3D honeycomb-
8 like structure (Fig. 10g), and was then activated by the KOH. Such significant cooperation between
9 the biomass and the bio-chemical/-physical properties (biodegradation, bioadsorption, biocatalyst,
10 etc.) of living things suggests a unique approach for obtaining a broad class of novel “biomass-
11 produced” biochar with hierarchical 3D structures and high SSA.

12 In addition to KOH, zinc chloride (ZnCl_2) is also a common chemical activation agent for biomass
13 materials, which can act in important roles to prepare high SSA biochar with a desirable pore
14 structure.^{74,180} Wang *et al.* soaked a peeled tomato in a saturated ZnCl_2 solution (Fig. 10h).⁷⁴ The
15 mixture was heated to 150°C to evaporate the water and promote the crystallization of ZnCl_2 at
16 different sizes (Fig. 10i). The small ZnCl_2 crystals penetrated the cellular wall and caused the
17 formation of both micro- and meso-pores at a high activation temperature (800°C), while larger
18 crystals on the surface generated macropores (Fig. 10i). In addition, the activation effect of ZnCl_2
19 could lead to biomass charring and aromatization as well as generating a monolithic structure with
20 abundant porosity in the final product of tomato activated carbon (TAC).

21 Besides KOH and ZnCl_2 , activation agents like K_2CO_3 , NaOH, Na_2CO_3 , H_3PO_4 , and H_2SO_4 can
22 all be used to activate biomass. Hayashi *et al.* systematically compared the differences among the
23 activated carbon materials from lignin with different chemical activation agents.¹⁸¹ They extracted
24 lignin from spruce wood and mixed it with KOH, NaOH, H_3PO_4 , ZnCl_2 , K_2CO_3 , and Na_2CO_3 for
25 activation in N_2 atmosphere at various temperatures (Table 2). It was found that the activation by
26 KOH and NaOH generated carbon with the largest surface area (>that of commercial AC) at 800°C .
27 In contrast, the H_3PO_4 and ZnCl_2 activated carbons obtained at 600°C showed the largest surface
28 area with a well-developed pore structure. However, at higher temperatures, the ZnCl_2 activated
29 sample showed a decreased surface area due to the thermal shrinkage.^{169,181} K_2CO_3 functioned as a
30 dehydrogenation agent at temperatures below 500°C but consumed carbon and greatly increased its

1 surface area at temperatures above 600 °C. Na₂CO₃ is similar to K₂CO₃, but its activation capability
2 is much weaker than that of K₂CO₃. As a result, the Na₂CO₃ activated carbon material showed the
3 lowest surface area under the same conditions.¹⁸¹ The choice of activation agents and the setting of
4 activation condition is of great significance for constructing biochar with desirable structures and
5 components. Further researches may be devoted to discovering the underlying complex mechanism
6 of activation, and provide a series of universal selective criteria for the highly controllable fabrication
7 of biochar with specific SSA and porosity.

8 In short, gas activating is conducted at high temperatures around 800 °C with the gradual
9 gasification of carbon by oxidants like CO₂ and steam. Due to the high reactivity of such oxygen-
10 containing gases, the activated carbon produced from this procedure usually suffers from
11 unsatisfactory yield, high reacting temperatures, long reacting time, and high production cost. In
12 contrast, the chemical activation process can be performed at a lower temperature to obtain activated
13 biochar with higher SSA and more desirable porosity. The disadvantages of this strategy may be
14 caused by the extra process of removing the residues and the emission of the wastes. Additionally,
15 both strategies face the challenges of the low yield in producing biochar with ultrahigh SSA and
16 emission of pollution. This appeals to the collecting technique and catalytic conversion of the
17 byproducts to achieve a high and sustainable utilization of biomass.

18 **3. Biomass-derived scaffolds/coating layers for active materials**

19 Porous carbon materials can be easily fabricated from biomass, which are electronically conductive
20 and can facilitate ion migration. Therefore, biomass-derived carbons have been widely used as
21 scaffolds (also as the coating layer) in LSBs to achieve good physical/chemical confining of the active
22 materials and to form a continuous conductive network.¹⁸²⁻¹⁸⁷ Such carbon scaffolds and coating
23 layers, in general, protect the active materials from electrolyte corrosion, suppress the electrode
24 volumetric changes, and provide ideal ion-electron transport, which all can benefit both the cathode
25 and the anode of the battery. By adjusting the microstructures, functionalizing the surface chemistry,
26 and/or introducing new components, numerous carbon scaffolds can be harvested and applied in
27 various electrode materials for different purposes. Interestingly, some biomasses (such as rice husks,
28 diatoms, rice roots, *etc.*) could be directly converted into the composite electrode materials such as
29 Si/C and Fe₂O₃/C without introducing extra chemicals.¹⁸⁸⁻¹⁹⁰

1 **3.1 For metal anode materials**

2 Metal anode materials are promising electrodes for LSBs because of their high theoretical capacity,
3 satisfactory electronic conductivity, and light weight.¹⁹¹⁻¹⁹³ However, they also have inherent
4 disadvantages like severe volumetric changes during repeated Li uptake and removal processes,
5 which jeopardizes the performance of LSBs. Carbon scaffolds or coating layers have been widely
6 used as promising approaches to optimize metal anode materials. These scaffolds or coating layers
7 can not only mitigate the detrimental effect of the volumetric changes but also provide an excellent
8 conductive matrix for both electron and ion transport. In view of the low cost and sustainability of
9 biomass, promising results for the enhancement of metal anodes have been achieved through the
10 construction of biochar/metal anode materials.

11 **3.1.1 Li-metal anode materials**

12 With the high theoretical capacity (3,860 mAh g⁻¹), low electrochemical potential (−3.040 V versus
13 the standard hydrogen electrode), and light gravimetric density (0.534 g cm⁻³), metallic Li is
14 considered as a “holy grail” anode for LSBs.¹⁹⁴ The earliest Li-metal based LSBs were developed in
15 the 1970s by Exxon,¹⁹⁴ which was for use in smart electronic devices, such as calculators and digital
16 watches. Lithium-iodine batteries were one of such first-generation Li-metal based LSBs and are still
17 widely used today in cardiac pacemakers. However, these primary batteries are essentially non-
18 rechargeable, which increases the cost, resource waste, and environmental damage. In addition,
19 lithium, as an ultra-active metallic element, suffers from electrolyte corrosion and certain safety
20 hazards (dendrite growth, short-circuits, *etc.*), which largely inhibited the commercialization of Li-
21 metal anodes.¹⁹⁵

22 Advances in nanotechnology and the desire for high energy/power density devices have recently
23 redirected attention to Li-metal anodes, which is experiencing a great revival. Numerous strategies
24 have been proposed to resolve issues from the nature of Li and achieve the practical application of
25 Li-metal anodes, among which constructing a 3D host for the Li-metal anode is regarded as one of
26 the most promising ways.¹⁹⁶ The 3D host can accommodate the significant volumetric changes during
27 the Li deposition/dissolution processes. At the same time, the 3D host can enhance the surface area
28 of the Li-metal anode, thus decreasing the local current density, which is beneficial for dendrite-free
29 Li deposition. Moreover, the 3D host promotes the migration of both ions and electrons, leading to
30 lower resistance and better battery performance. If some specific materials (*e.g.*, materials that can

induce the Li deposition behavior, homogenize the spatial distribution of Li⁺ ion flux, regulate the microstructure/component of SEI) are introduced and incorporated into the host material, there could be additional positive effects on the Li-metal anodes.

To date, conductive metallic skeletons and various carbon-based materials have been widely investigated as scaffolds for the Li-metal anodes. However, 3D metallic supports, such as Cu and Ni foams, are of high cost, and their high mass density limits the energy density of batteries.^{197,198} These metallic supports enable significant advances for half-cells in the laboratory, but might not be suitable for large-scale applications of practical devices. Carbon-based scaffolds, including carbon cloth, carbon nanotubes, and graphene,^{199,200} are highly efficient in optimizing Li-metal anodes but also problematic for commercialization until the issues of high production cost and low throughputs are addressed. In contrast, biomasses with their abundance, carbon neutrality, structural diversity, light weight, and low cost are particularly suitable as the host materials,¹⁷⁷ which may be a prospective choice for developing high-energy-density Li-metal based LSBs.

It is generally known that the formation and growth of Li dendrites can be ascribed to many factors including the mechanical strength of the SEI layer, ionic/electronic conductivity, and local current density. The widely accepted equation (7) for the “Sand’s time” is empirically proposed to indicate the correlation between the time when the dendrites grow, and the transfer nature of the Li ions/electrons.^{201,202}

$$\tau = \pi D \frac{e C_o (\mu_a + \mu_{Li^+})^2}{2 J \mu_a} \quad (7)$$

where τ is the time when the Li dendrites begin to grow, D is the diffusion coefficient, e is the electronic charge constant, C_o is the initial concentration of Li salt in the system, and μ_a and μ_{Li^+} are the anionic and Li-ion mobilities, respectively. Although the accuracy may be limited and affected by the applicable conditions and the battery configurations, it can qualitatively reveal the promising design principles for the Li-metal anode. Obviously, a large diffusion coefficient and a high Li salt concentration are beneficial to obtain a large τ , which means that the battery has a longer operation time before the growth of Li dendrites. The SEI layer can buffer and affect the μ_{Li^+} to influence τ . Therefore, Sand’s time model correlates the properties of the SEI layer and the electrode structure to the Li dendrite growth. Among all the factors, the electrode current density is a critical factor to control the Li deposition morphology. The growth of dendrites can be suppressed by reducing the

1 local current density. A simple and practical approach to accomplish this is to enlarge the SSA of the
2 current collector. In this regard, a high SSA biomass-derived carbon can act as an ideal current
3 collector to accommodate Li deposition and lower the local current density to inhibit Li dendrite
4 growth. Of note, although increasing SSA and porous structures of biochar scaffolds is beneficial,
5 ultrahigh SSA and ultralarge pore volume may be detrimental to the anode performances.²⁰³ They
6 may promote the side reaction between anode material (*e.g.*, Li) and electrolyte, lead to instable SEI
7 and inferior mechanical strength of electrode. Consequently, there is urgent need for future researches
8 revealing the correlation between SSA/pore structure and battery performances.

9 The Li affinity, also called the lithiophilicity,²⁰⁴ is related to the binding degree between the Li
10 and the substrate, which is also critical for both the Li diffusion in the melted state and the Li
11 deposition behavior during the electrochemical process. Although porous carbon can be employed to
12 improve the performances of Li-metal anodes, it in fact is not a highly lithiophilic material. Due to
13 the lattice mismatch between Li and carbon, extra energy is needed to overcome the heterogeneous
14 nucleation barrier of Li on carbon scaffolds, which may lead to non-uniform and uncontrollable Li
15 deposition. As a result, undesired Li dendrite growth may be observed sooner or later in biomass-
16 derived carbon scaffolds, which makes it necessary to combine the lithiophobic carbon with other
17 highly lithiophilic materials to produce gradient materials. Such a strategy can further enhance the
18 functionality of biomass-derived carbon supports to achieve selective electrodeposition of Li-metal
19 anodes.

20 Several biomass-derived biochar materials have been studied with the aim to achieve an optimal
21 Li-metal anode. For instance, a hierarchical porous carbon (HPC) was obtained from bamboo *via*
22 hydrothermal treatments and KOH activation (Fig. 11a), which was subsequently modified with
23 lithiophilic zinc oxide (ZnO) (ZnO@HPC, Fig. 11b, c) to guide the deposition of Li.²⁰⁵ Since ZnO
24 has better lithiophilicity than carbon, Li prefers to deposit on ZnO nanoparticles, forming a highly
25 conductive Li-Zn alloy as the initial nucleation seeds to induce the following Li depositing within the
26 pores of HPC. Therefore, plating Li into this ZnO@HPC scaffold can generate a 3D dendrite-free
27 Li/C composite anode (Fig. 11d, e). Wood as another cellulose-based biomass can also be used as a
28 host for the Li-metal anode after some simple treatment.^{206,207} For example, Hu and coworkers
29 selected a commercial wood (balsa wood) as the raw material, which was later carbonized and also
30 loaded with lithiophilic ZnO (C-wood).²⁰⁷ It was found that this 3D carbonized wood remained the

1 natural channels for transporting water and nutrition, which could be used to guide the Li
2 plating/stripping processes and suppress the formation of Li dendrites, and at the same time partly
3 accommodate the volume variation. Moreover, the 3D framework can also reduce the local current
4 density leading to a longer sand's time. Besides bamboo and wood, rice husk as a typical and abundant
5 agricultural waste can also be used to produce multi-functional scaffolds for Li-metal anodes.²⁰⁸
6 Direct carbonization of rice husk under an inert atmosphere produced a scaffold composed of SiO₂
7 and carbon. This composite scaffold was subsequently fluoridated to adjust the SiO₂ content while
8 enriching the fluoride-containing groups on the carbon. As a result, this multifunctional scaffold
9 named as RC could effectively control the deposition behavior of Li, suppress Li dendrite growth,
10 and regulate the SEI components with abundant LiF by the F-containing surface. To better
11 demonstrate the advantages and large-scale applicability of the biomass-derived carbon scaffolds, we
12 summarized and compared the electrochemical performances of Li-metal anodes on optimized
13 biomass-based scaffolds and other scaffolds (Table 3).^{65,205,206,209-212} It's noted that the Li-metal anode
14 stabilized by the biomass-based scaffolds (MgO modified wood carbon, MgO@WC; ZnO@HPC)
15 shows much longer lifespan, lower Li nucleation overpotential, and larger operable current density
16 compared to the conventional scaffolds including layered reduced graphene oxide (rGO), carbon
17 nanotube (CNT) modifying carbon cloth (CC/CNT), 3D nickel, nitrogen-doped graphitic carbon
18 foams (NGCFs), and Cu current collector with vertically aligned microchannels (Cu-
19 VAMCs).^{200,206,210,211} When coupled with a commercial cathode, Li-metal anodes on these biochar
20 scaffolds also deliver higher capacity and better capacity retention, indicating the great significance
21 of biomass-derived scaffolds in optimizing the Li-metal anode.

22 In addition to developing 3D robust structures and introducing the lithiophilic seeds, the design
23 for functionalized carbon scaffolds can be further extended. With the more and more comprehensive
24 understanding supplemented by emerging characterization techniques (*e.g.*, cryo-electron
25 microscopy), the identification for ideal carbon hosts may be evaluated by new standards.
26 Considering the fact that the Li deposition in the battery is a complicated heterogeneous nucleation,
27 factors that can influence the surface energy of Li metal, the contact angle between Li and scaffold,
28 and the nucleus size/quantity may be employed to enable the carbon scaffolds to facilitate control of
29 the Li nucleation and deposition.^{206,213,214} Additionally, the reality that the enhanced SSA and enriched
30 pore structures of biochar scaffolds probably lead to serious parasitic reaction and increasing the loss

1 of electrolyte and active Li source urges more systematic studies to reveal the optimal design
2 principles for the SSA and pore structures of biochar scaffolds. Moreover, future researches may be
3 devoted to constructing a carbon scaffold that helps stabilize and even heal the SEI,²¹⁵ as well as deal
4 with the formation and accumulation of dead Li during battery operation, both of which are the
5 obstacles to the practical application of Li-metal batteries.^{38,55}

6 **3.1.2 Metal anodes beyond Li**

7 Metals such as Mg, Al, Zn, Sn, and Ge have both higher volumetric and gravimetric capacities than
8 graphite anodes at their full lithiation state, but they deliver poorer electrochemical performance when
9 applied in commercial battery systems.^{131,216-218} This is primarily due to the irreversible capacity loss
10 and insufficient Coulombic efficiency (CE), especially in the first cycle. Meanwhile, the severe
11 volumetric change is always a vital issue that leads to the unstable cycling performance of batteries
12 using metal-based materials.

13 Tin (Sn)-based anode materials are regarded as one of the most promising candidates for replacing
14 graphite anodes due to the high theoretical capacity of Sn (992 mAh g⁻¹ for Li_{4.4}Sn) and enhanced
15 safety. However, Sn-based materials have not yet been widely used because of their severe volumetric
16 variations in the alloy and de-alloy processes with Li, which easily causes a loss of electronic contact
17 of the active material with instant battery failure. One of the most effective resolutions for these issues
18 is to construct a highly conductive and robust carbon scaffold to accommodate the Sn metal.
19 Moreover, the interaction between Sn and carbon scaffold as well as the uniform distribution of Sn
20 within the carbon is of great importance for obtaining a high-performance Sn-based anode. Of note,
21 biomasses that are rich in amino groups, phosphoryl groups, hydroxyl groups, and carboxyl groups
22 can easily bind with metal ions to harvest the homogeneous mixture of the carbon and metal sources,
23 which is also called the bio-adsorption and can be used to fabricate metal/carbon composite anode
24 materials for improved electrochemical performance. Tao *et al.* reported the fabrication of an
25 advanced Sn/C anode material by employing microalgae (*Spirulina platensis*), which functioned as
26 both a bio-template for absorbing the Sn cations and carbon source.²¹⁷ And the obtained Sn/C anode
27 with uniformly dispersed Sn nanoparticles delivered superior cycling capacity and rate performance
28 compared to many Sn/C anodes produced by carbonizing the mixture of the organic matrix and Sn-
29 containing chemicals.^{219,220} In addition to microalgae, bacteria could also show biological adsorption
30 towards metal ions. Some researchers recently exploited bacteria (*Bacillus subtilis*) to adsorb Sn

1 sources from an electroplating sludge for preparing Sn/C composites (Sn@C).¹⁰² The resultant
2 bacteria with Sn ions was then freeze-dried and carbonized to obtain an Sn@C composite in an Ar
3 atmosphere (Fig. 11f), which maintained the rod-like structure of the bacteria with Sn nanoparticles
4 evenly dispersed over the entire carbon matrix (insets of Fig. 11g). The well-distributed elemental Sn
5 particles could be attributed to the following adsorption process: 1) The metal ions are passively
6 adsorbed on the cell surface due to the bonds between ions and functional groups on the cell wall. 2)
7 The metal ions are gradually transferred into the cells during the metabolism of the living cells. When
8 this Sn@C composite anode was tested, it delivered superior lithium storage performance, including
9 a high reversible capacity close to 560 mAh g⁻¹ at 1 A g⁻¹ and a prolonged cycle life of over 1500
10 cycles (Fig. 11g). In addition, *in situ* TEM observations confirmed the advanced structural stability
11 of this biochar-strengthened composite anode during lithiation and de-lithiation processes. This work
12 successfully utilized bacteria and its biological properties, indicating the special advantages of
13 biomass in the design of battery materials. In addition to biomass template, other designed templates
14 can also be employed to synthesize the metal/biochar composites. For example, Zhou *et al.* reported
15 to prepare another advanced Sn/C composite (Fig. 11h) with a MnO_x nanowire template and
16 polydopamine (PDA) carbon precursor.²²¹ The SEM and TEM images (Fig. 11i, j) show that the
17 obtained Sn/amorphous carbon nanotube composite (Sn@aCNT) displayed the morphology of
18 amorphous nanotubes with a length of 1.8–3.8 μm and an average diameter of 110 nm, which were
19 uniformly embedded with Sn nanoparticles. Considering the good dispersion of Sn nanoparticles
20 within the carbon matrix and the robust carbon network, the composite anode delivered high capacity
21 with long cycle life.

22 In a typical way to fabricate Sn/C anodes with the improved performances, the processes are often
23 complex and of high cost, which comprise the preparation of polymer matrix (carbon source), the
24 mixing of Sn and carbon precursor, and the carbonization of the mixture. Moreover, the Sn/C prepared
25 in such a strategy suffers a lot from the uneven distribution of Sn within the carbon scaffold and the
26 aggregation of Sn nanoparticles into large particles. In sharp contrast, the employment of biomass
27 and biological properties to fabricate Sn/C anodes at large scale is more practical, which shows the
28 apparent advantages including the low cost of raw materials, the facile producing processes, the
29 highly-conductive 3D network, and the uniform distribution of Sn nanoparticles enabled by the bio-
30 adsorption/bio-concentration. In addition to metallic Sn anodes, these advantages can also be

extended to other metals, indicating the high feasibility and prospects of producing biochar scaffolds for metal anodes.

3.2 For metal compound anode materials

Metal compounds such as metal oxides, sulfides, carbides, nitrides, and phosphates (M_xN_y , $N = C, N, O, S, P$), as well as their mixed transition-metal compounds, are regarded as promising candidates of anode materials due to their high theoretical capacity, low price, ease of availability, low operation potential, and environmental compatibility.^{3,204,222-234} However, these materials face common issues that hinder them from practical applications. For example, these materials often suffer from poor electronic/ionic conductivity. Also, other challenges include large volume changes during battery operation, low Coulombic efficiency, limited capacity retention, and poor cycle life.

The origins of the above issues are classified as follows: (1) hostless structure; (2) side reactions between the electrode materials and electrolyte; and (3) poor ionic/electronic transport. Therefore, carbon materials are bound to play significant roles as the chemically/physically stable protective hosts and the ideal ionic/electronic conductor.^{183,235,236} The M_xN_y can be easily introduced into the biomass-derived carbon materials with their biological nature of adsorbing metal ions. An appropriate transformation reaction by introducing elemental C, N, O, S, and P can easily generate the desired metal compounds. Wang *et al.* used pyrolyzed bacterial cellulose (PBC) to provide a cheap, sustainable, 3D conductive scaffold for loading nanostructured SnO_2 anode material (PBC- SnO_2 , Fig. 11k-m).²³⁷ Such a conductive PBC scaffold enabled the high electron and Li ion conductivities of the composite electrode. Comparisons of the electrochemical performance between bare SnO_2 particles and PBC-supported SnO_2 indicated the particularly positive effects of this scaffold on the anode performance (Fig. 11n). Obviously, such 3D, freestanding, binder-free carbon scaffolds derived from bacterial cellulose can be extended to enhance the mass loading and electrochemical performance of a broad range of electrode materials. In addition to the 3D freestanding conductive network, chemical modifications of the carbon scaffolds like doping of heteroatoms can further enhance the electrochemical performance of the composite electrodes. For instance, Shi *et al.* used chitosan and red phosphorus to prepare N and P dually-doped carbon nanosheets (NPC), which was later uniformly loaded with Ni_2P nanoparticles ($Ni_2P@NPC$).²³⁸ Beneficial from the good dispersion of Ni_2P nanoparticles during battery operation that was enabled by the strong covalent coupling (by DFT

calculations) between Ni₂P and the heteroatom doped carbon scaffold, the composite anode delivered high capability and improved cycling stability. Notably, phosphorus-containing biomass derivatives (such as phytic acid) can be directly used to replace the extra phosphorous source in the fabrication of metal phosphates.²³⁹

Based on the features of low cost, 3D hierarchical structures, and abundant elemental components of the biomass materials, it is not difficult to convert them to a variety of biochar or heteroatom doped carbon scaffolds for the metal compound anode materials, which can largely alleviate the destructive volume effect, provide a 3D electron-conducting network, and facilitate the ionic transport. However, the practical application of metal compound anodes is still inhibited by the low initial CE, large operating overpotential, and high electrochemical potential, which urge further studies to incorporate the biochar scaffolds with other anode designs or to develop more powerful biochar scaffolds (*e.g.*, SEI-inducing, infusion/transfer-accelerating, electrochemical kinetic-promoting properties) that can regulate the electrochemical behavior.

3.3 For Si-based anode materials

Silicon with the advantages of ultra-high theoretical capacity of 4200 mAh g⁻¹, low cost and stable lithiation state, has also been regarded as one of the most promising substitutes for graphite anodes.²⁴⁰⁻²⁴² However, its practical applicability is hindered by its low electronic conductivity and poor cycling stability due to serious volumetric variations during the lithiation/delithiation processes.^{58,243,244} Introducing carbon scaffolds into Si anodes has great potential, as this can greatly increase the conductivity and serve as a buffering zone for the volume expansion/shrinkage. Various strategies involving the biomass materials have been developed to prepare carbon scaffold-supported Si anodes, including chemical vapor deposition, thermal vapor deposition, and pyrolytic processes.

To accommodate the Si particles within the voids of a hollow carbon scaffold, a yolk-shell structured Si/C composite (Si@void@C) was fabricated by adopting a sacrificial SiO₂ layer and a *in situ* polymerized PDA layer (Fig. 11o, p).²⁴⁵ The designed multi-hierarchical structure protected the nano-sized Si particles in the carbon shell, while the electron conductivity was greatly enhanced. As a result, the Si@void@C anode delivered an ultra-high capacity and stable cycling performance at a high C-rate (Fig. 11q). With a similar route, Hu *et al.* also proposed a rather simple, green, and energy-saving method to fabricate Si composite materials coated with SiO_x and glucose-derived carbon layer

(Si@SiO_x/C), which delivered much higher capacity and better stability than bare Si nanoparticles.²⁴⁶ In another contribution, Xu *et al.* also reported to coat the Si particles with biomass-derived carbon layer by using spray drying and a CVD method.²⁴⁷ Glucose, carboxyl methyl cellulose (CMC) and polyvinylpyrrolidone (PVP) as the carbon sources were dissolved and mixed with Si powder, which was then spray-dried and calcined to directly obtain the Si/C composite. This simple but efficient method is also applicable for other soluble biomasses and their derivatives to prepare biomass-derived electrode materials. To further improve the electronic conductivity of composite Si-based materials, a sodium alginate (SA) (a natural biomass-based binder for Si-based anodes) derived 3D carbon scaffold embedded with copper nanoparticles was produced.¹⁰¹ SA is a type of linear copolymer composed of two parts [β -D-mannuronic acid (M) and α -L-guluronic acid (G) residues]. The introduction of multivalent ions such as Cu²⁺, Ca²⁺, Ni²⁺, Fe³⁺, and Al³⁺ can promote the formation of coordination bonds *via* G-G blocks, and the adjacent alginate chains will be connected.¹⁰¹ The authors used the biochemical properties of the biomass and introduced Cu²⁺ (gradually released from the reaction between CuO and glucolactone) as the crosslinking ion to *in situ* coat the Si powder with a SA-based gel, which was carbonized to obtain the final 3D multilayer porous Si@C@Cu composite anode. The 3D carbon matrix improves the electronic conductivity of the composite anode, protects Si from electrolyte corrosion, and buffers volumetric variations during the lithiation and delithiation processes. As a result, this Si-based composite material delivered a high capacity of 1500 mAh g⁻¹ at a current density of 1 A g⁻¹ and is stable for over 900 cycles, as well as superior high-rate capability (1035 mAh g⁻¹ at 4 A g⁻¹).

As discussed above, the Si/C anodes prepared from biomass show comparable and even better capability and cycling stability than the conventional Si/C anodes, which are promising for large-scale production and application. The reasons for such advantages can be understood as (1) biomass-derived biochar scaffolds are cost-effective and sustainable with satisfactory mechanical and electrochemical properties; (2) Due to the specific biological/biochemical/biophysical properties of biomass, it facilitates the interaction between biomass and active materials (*e.g.*, the binding between Si and SA with carboxylic groups),¹⁰⁵ promoting the fabrication of composites with hierarchical structures and various morphologies, as well as resulting in effective and uniform accommodation of active materials within a 3D robust conductive network. To fabricate Si/C with both the superior architectures and high performances, future efforts can be devoted to employing and extending more

1 chemical/physical interactions between biomass and Si.

2 **3.4 For cathode materials**

3 Most commercial LSBs are coupled with cathode materials such as LiCoO_2 (LCO), LiFePO_4 (LFP),
4 and LiMn_2O_4 (LMO), which are classified as the lithium metal oxides. These cathodes could offer a
5 relatively stable capacity but are limited by low theoretical capacities.^{100,240,248-250} Therefore, many
6 high-performance cathode materials have been developed as candidate substitutes for lithium metal
7 oxides, including sulfur, selenium, iodine, V_2O_5 , and transition metal fluorides.^{99,251-253} However, both
8 lithium metal oxides and lithium-free cathode often suffer from insufficient electronic conductivity
9 and show certain detrimental volumetric effects, indicating the necessity of introducing a conducting
10 carbon additive or a carbon scaffold. In addition, the inferior electrochemical stability of some
11 cathode materials (e.g., sulfur) during battery operation will also inhibit their practical application.
12 Therefore, biochar scaffold for cathode materials should own adequately high SSA and hierarchical
13 pore structures as well as affinity for confining the cathode materials, which can not only achieve a
14 large mass loading of cathode electrode for high energy density, but also effectively stabilize the
15 cathode materials, delivering superior electrochemical performances.^{254,255} For instance, the spinel
16 LMO suffers greatly from capacity fading due to the Jahn-Teller distortion caused by Mn^{3+} ,
17 dissolution of manganese in the electrolyte, crystallinity loss during repeated cycling, and electrolyte
18 decomposition at a high operating potential.²⁵⁶ However, it is still an attractive cathode candidate as
19 a fast-charging material for advanced LSBs that has the advantages of high-operational-voltage
20 tolerance, natural abundance, low processing cost, and low toxicity over commonly used cathodes
21 like layered LiCoO_2 .²⁵⁷ To solve the mentioned drawbacks of LMO, Lee *et al.* used a sucrose-derived
22 biochar coating layer on LMO nanoparticles (CSC-NPs) to electrically connect each LMO primary
23 particle and form a highly electronic/ionic conductive network within the secondary particle (Fig.
24 12a).²⁵⁷ This biochar coating layer promotes the satisfactory electronic/ionic conductivity within the
25 assembled secondary particles, resolves the low electrode density problem during the packing of
26 nanosized LMO, and restricts the Mn dissolution at elevated temperatures. Therefore, the CSC-NPs
27 show much higher capacities and better C-rate performances, even charging at 100 C and discharging
28 at 300 C (Fig. 12a). Of note, the CSC-NPs were calculated to deliver a gravimetric energy density as
29 high as 300 Wh kg^{-1} on the basis of the active material, which again indicates the applicability of

CSC-NPs in practical cells for mass production. As the conducting agents are electrochemically inactive, a high content of addition will largely reduce the battery energy density, while the low adding content may lead to incomplete conducting network within the electrodes. In contrast, a dense and thin biochar as a multifunctional coating layer may not only provide an electrically conductive network with a tolerant amount of carbon additive, but also serve as a robust scaffold/protective layer for cathode materials (*e.g.*, volumetric effect, electrode dissolution). Regarding the future electrode design, a binder-/conducting agent-/current collector-all-free electrode that comprises 3D hierarchical biochar scaffolds/coating layers and hosted active materials (*e.g.*, active materials anchoring on/within the free-standing biochar scaffolds) can be expectedly produced.

Metal fluorides are promising conversion compounds for cathodes due to their high capacity, low cost, and low toxicity.^{258,259} The issues that hinder the application of metal fluorides mainly include poor electronic conductivity, sluggish reaction kinetics, and significant structural changes during operation. Fabrication of carbon/metal fluoride composites has been suggested as an efficient way to enhance their electrochemical performance. Of note, some biomasses with functional groups can interact with metal ions through coordination reactions, indicating a potential route for harvesting composite metal fluoride cathode. For example, sodium alginate derived from algae could experience gelation with multivalent metal ions,¹⁰¹ such as Cu^{2+} , Ca^{2+} , Ni^{2+} , Fe^{3+} , and Al^{3+} , which could then be carbonized and fluorinated to obtain a metal fluoride-embedded 3D biochar cathode (Fig. 12b). At present, there is a limited number of works on preparing metal fluoride/carbon nanocomposites from biomasses, in spite of its unique advantages in constructing 3D conductive structures and guiding the uniform dispersion of metal fluoride nanoparticles.

Among the cathode candidates, sulfur has been widely studied over recent years due to its ultra-high capacity, low cost, and natural abundance.^{40,260-262} The critical issues that inhibit sulfur from practical applications include its poor electronic conductivity, soluble intermediate loss, and side reactions with the Li-metal anode. To resolve these issues, Nazar and coworkers proposed an efficient approach to optimize sulfur cathodes by encapsulating sulfur into ordered nanostructured CMK-3 carbon.^{263,264} Since then, various carbon scaffolds have been developed to produce high-performance composite sulfur cathodes (S/C), including biomass-derived carbon scaffolds and their composites.^{99,252,265-267} For example, Zhang *et al.* reported the successful fabrication of double-shelled hollow carbon spheres (DHCS) using glucose carbon source and a SnO_2 hollow sphere template (Fig.

12c-g).²⁶⁸ The DHCS showed a porous structure with a high SSA, which is beneficial for accommodating volume changes of sulfur, trapping both sulfur and sulfide intermediates from dissolution loss, and guaranteeing the transport of ions and electrons.

In addition to pristine biochar, heteroatom dopants (such as B, N, O, S, and P) are often introduced to enrich defects and improve the conductivity of biochar scaffolds, which can also enhance the chemisorption towards sulfur and its discharge products.²⁶⁹⁻²⁷³ Since many biomasses are rich in nitrogen content, N-doped biochar can be easily harvested with simple carbonization of these biomasses. Additional chemicals are typically employed for other types of dopants. Pang *et al.* used cellulose nanocrystals along with polyrhodanine to prepare a N and S dually-doped carbon (NSC),²⁷⁴ which was mixed with sulfur to obtain a composite cathode (NSC-S, Fig. 12h). The sulfide adsorption results in Fig. 12i indicate that the NSC has the highest sulfide adsorption ability compared to other carbon samples (Super P, Vulcan carbon, cellulose nanocrystal derived carbon, meso-TiO₂). Therefore, the NSC can effectively suppress the shuttle effect and contribute to a higher capacity and better cycling stability (Fig. 12j) than other scaffolds hosted sulfur cathodes.

Besides heteroatoms, metal oxides, sulfides, nitrides, *etc.*, have also shown strong chemisorption towards polysulfides, which may catalyze to reduce the activation energy and facilitate the transformation for/of the discharge product of Li₂S.²⁷⁵ Tao *et al.* have employed kapok tree fibers (serving as both the template and the carbon source) and metal nitrate salts to fabricate five types of non-conductive metal oxide-modified carbon nanosheets as bipolar scaffolds for sulfur (Fig. 12k).⁴¹ The MgO-modified carbon/sulfur composite delivered the best capacity and cycling stability performances (Fig. 12l) among all the bipolar scaffolds hosted sulfur cathodes. The reason for improved electrochemical performances from MgO modified carbon scaffold were confirmed by the adsorption tests and DFT calculations, which implied that both the sulfide adsorption and the surface diffusion played important roles in constructing advanced Li sulfur batteries.⁴¹ Additionally, this work shows the advantages of biotemplating method in designing carbon-based materials and provides a universal selection criterion to construct multifunctional carbon scaffolds for high-performance Li-S batteries. Following the same design criteria, Wu *et al.* fabricated anatase TiO₂-coated carbon microcapsules (SDS@TiO₂) from the bacteria *staphylococcus aureus*.²⁷⁶ This bipolar carbon scaffold can adsorb sulfur within the carbon core, which suppresses the polysulfide dissolution from the polar TiO₂ shell and facilitates Li⁺ ion transport through the shell. Besides metal oxides, nitrides could also

1 play significant roles in optimizing the sulfur cathode. For instance, Shen *et al.* reported the
2 fabrication of a *trichoderma spore*-derived carbon (TSC, Fig. 12m), which was modified with both
3 self-doped heteroatoms (N and P) and embedded NbC (TSC/NbC, Fig. 12n).²⁷⁷ Of note, the
4 implantation process of NbC has an obvious impact on conductivity improvement and pore-formation
5 that develops numerous mesopores (30–50 nm). The synergistical effects of doped heteroatoms and
6 conductive polar NbC nanoparticles are beneficial as they effectively increase the intrinsic reactivity
7 and enhance the chemisorption towards polysulfides, enabling the sulfur cathodes to deliver high
8 capacity and stable cycling performance (Fig. 12o). Obviously, biomass with naturally confined
9 elements like N, O, S, and P is of great advantages for fabricating heteroatom doped biochar,^{96,278,279}
10 which can further combine with polar materials to harvest bipolar scaffolds for advanced sulfur
11 cathodes.

12 In summary, biomass-derived biochar scaffolds and protective layers can be applied to optimize
13 various kinds of cathodes by providing a highly-conductive network to facilitate the transfer of both
14 the electrons and ions, serving as a robust skeleton to release the volumetric changes, and buffering
15 the dissolution and loss of active materials by strong chemical/physical interactions. Moreover,
16 considering the inherent advantages of biomass including low cost, environmental friendliness,
17 processability, hierarchical spatial structures, and abundant components, it is highly applicable to
18 produce advanced composite cathodes from biomass. In addition, the success of biochar scaffolds in
19 laboratory-scale cells can shed significant light on promising material design and electrode
20 construction for practical cells. Although there may be concerns on the variable quality control and
21 producibility of biomass for mass production, they can be resolved with advanced processing
22 techniques and material science (e.g., purification, regeneration, extraction, catalytic conversion).

23 **3.5 For catalytic transition-metal cathodes in Li-oxygen/carbon dioxide batteries**

24 Lithium-oxygen (Li-O₂) and lithium-carbon oxide (Li-CO₂) batteries are novel LSBs that have been
25 widely investigated in view of their ultra-high energy density compared with conventional LSBs.²⁸⁰⁻
26 ²⁸⁴ The Li-O₂/CO₂ batteries are composed of four essential parts, a Li-metal anode, separator,
27 electrolyte, and a catalytic cathode. The cathode is usually composed of catalysts and conductive
28 carbon scaffolds that play vital roles in the performance of batteries since these are directly related to
29 the ion transfer kinetics, electron migration, oxygen diffusion, and discharge product deposition.

Carbon materials like carbon cloth and graphene have been confirmed to be effective catalyst supports with abundant porous structures, satisfactory electronic/ionic conductivities, and excellent mechanical properties.²⁸⁵⁻²⁸⁸ Besides these expensive carbon products, it is anticipated that cheap and abundant biomasses derived carbon materials like carbonized-wood are potential scaffolds for loading catalytic cathode materials.²⁸⁹ For example, Xu *et al.* adopted carbonized natural wood for loading carbon nanotubes and Ru catalysts to fabricate a flexible wood-based cathode for Li-CO₂ batteries,²⁹⁰ which employs the natural channel structures of the wood for efficient transport of ions and gas molecules while confining the discharge products (Fig. 13a, b). Enhancements in mass transport and catalyst confinement enabled fast kinetics that resulted in significantly improved electrochemical performances with reduced overpotential and enhanced cycling stability (Fig. 13c), which were even better than many reports with other carbon supports (*e.g.*, graphene).^{282,291,292} They also used carbonized-wood as a catalyst support to construct an advanced cathode (CA-wood/Ru) for Li-O₂ batteries (Fig. 13d, e).²⁹³ Compared with widely-used carbon supports such as graphene, the biomass-derived scaffolds have apparent advantages of low cost, simple fabrication processes, natural multidimensional structures, flexibility, and accessibility with functional treatments. However, such results on biochar scaffolds for catalyst cathodes are incomprehensive and quite limited at present, which are impeded by the challenges in biomass transformation and control over the structures and properties of biochar. It is of great significance to develop new technologies for biomass processing and strategies for designing superior electrode structures, which may shed new light on promoting the practical application of Li-air batteries.

4. Biomass-derived active materials

Besides their employment as the host for cathode and anode materials, biomass-derived materials have the potential to be directly used as the active materials. One of the most commonly used biomass-derived active materials is the carbon anode in commercial LSBs.²⁹⁴⁻²⁹⁶ Of note, the difference of natural structure and components has led to various forms of functional carbon anode materials, including heteroatom-doped carbon, composite carbon (loaded with a limited amount of transition metal compounds in contrast to the carbon used for scaffolds), and graphene.²⁹⁶⁻²⁹⁸ These materials can deliver much better cycling stabilities and higher capacities than graphite anodes. Meanwhile, since some biomasses are particularly rich in non-carbon elements like Si in rice husks and diatoms,

1 these materials are often used to prepare Si-based anode materials.²⁹⁹ Additionally, it has been found
2 that some biomolecules and biopolymers could directly be employed as active materials, which are
3 called organic electrode materials. Due to the complex multi-electron redox reactions, these organic
4 electrode materials can deliver ultrahigh capacity and are particularly promising for constructing
5 flexible energy storage devices.

6 **4.1 Carbon- and silicon-based anodes**

7 As discussed above, biomass after carbonization and activation can be converted to various carbon
8 materials with different pore structures and morphologies. With a high SSA, abundant porosity,
9 hierarchical 3D structures, and a trace amount of heteroatom dopants, biomass-derived carbon
10 materials can have a better performance in LSBs (*e.g.*, higher capacity) compared with commercial
11 graphite due to additional fundamentally different mechanisms (*e.g.*, reversible ion absorption at
12 heteroatom or defects).^{294,300,301} For instance, Mitlin and colleagues used egg white and a template
13 (mesoporous cellular foam, Fig. 14a) to fabricate a protein derived mesoporous carbon (PMC) with
14 rich nitrogen (6%) and a high SSA of $\sim 800 \text{ m}^2 \text{ g}^{-1}$ (Fig. 14b).³⁰² Due to the successful balance among
15 high SSA, appropriate pore distribution, and abundant heteroatom dopants, the PMC delivered
16 superior rate capabilities than graphite anode (Fig. 14c), which indicates the possibility of
17 constructing next-generation high-energy-density LSBs with novel carbon-based anodes. Silk is
18 another common protein-containing biomass that is composed of fibroin and sericin. Hou *et al.* used
19 silk to fabricate a kind of hierarchical, porous, N-doped carbon nanosheets (HPNC-NS).⁹⁶ The 2D
20 nanosheets had thicknesses ranging from 15 to 30 nm and an ultrahigh SSA of $2494 \text{ m}^2 \text{ g}^{-1}$ with
21 various active sites dispersed over the hierarchical pores). The improved electronic conductivity,
22 enriched active defects, and increased active sites enabled the 2D carbon nanosheets to deliver
23 superior lithium storage with a high reversible capacity of 1865 mAh g^{-1} and satisfactory rate
24 capability.

25 Biochar with the increasing SSA, enriching pore structure, and introducing heteroatom dopant
26 can deliver higher capacity and better capability than conventional graphite anode, benefiting from
27 the extra fundamentally different mechanisms of storing Li-ion. However, the high SSA will cause
28 more exhaustion of Li source and electrolyte to form SEI, consequently the low initial CE. As shown
29 in Fig. 14d, we summarized the SSA, capacity and initial CE of several kinds of biomass-derived

1 carbon anodes named as carbonized cap skin tissue (CST), surface-carboxylated carbon nanoparticles
2 (c-CNPs), banana peel pseudographite (BPPG-800-A), N-doped porous graphitic carbon nanofibers
3 (N-PCNFs-600), N-doped fused carbon fibers (N-doped fused CF), corncob carbon (CC), PMC,
4 hierarchically porous nitrogen-rich carbon (HPNC), MgO templated cotton-derived carbon (Mg15),
5 ox horn derived carbon (OHC), and HPNC-NS. The CST as a pure intercalation-type carbon has the
6 lowest capacity and SSA, but the highest initial CE. As for other kinds of carbon with higher SSA or
7 heteroatom dopants, the capacity principally increases compared to the CST, while the initial CE of
8 these carbons declines ranging from 50 to 80%. Of note, BPPG-800-A having a lower SSA than N-
9 PCNFs-600, N-doped fused CF, and CC delivers higher capacity but the lowest initial CE. This
10 indicates the fundamentally different energy storage mechanism of BPPG800-A consisting of the
11 defective graphene in the pseudographitic arrays that not only reversibly binds the Li, but also
12 provides ample near-surface nanopores for accommodating Li metal at low voltage.³⁰¹ Another
13 interesting phenomenon is that the N-doped fused CF with an SSA of $\sim 400 \text{ m}^2 \text{ g}^{-1}$ and a low capacity
14 $\sim 400 \text{ mAh g}^{-1}$ owns the second-highest initial CE over 80%. This is thought to be beneficial from
15 the rich heteroatom of N (12.6 wt%) which may regulate the formation of SEI and reduce the
16 irreversible loss of capacity in the first cycle. On basis of the above findings, novel high-performance
17 carbon anodes can be constructed by (1) enlarging the SSA for more active Li-binding sites; (2)
18 designing advanced hierarchical porous structures to facilitate the fast diffusion of ions and improve
19 high-C rate capacity; (3) performing modification towards carbon skeleton with functional
20 heteroatom/defect/surface groups which can further increase the electrochemically active sites as well
21 as resolve the problem of low initial CE from the irreversible Li loss and electrolyte decomposition.³⁰³
22 Future studies should pay more attention to revealing the balance between SSA/pore structure and
23 battery performances (capacity and CE). Alternatively, extending strategies (*e.g.*, pre-lithiation,
24 excess Li supply, functional modification) which can deal with the extra loss of Li and electrolyte
25 during SEI formation in the initial cycles would also promote the practical application of such carbon
26 anodes with high SSA and capacity.

27 In addition to carbon anodes, Si-based anode materials could also be derived from biomass
28 materials that contain abundant Si material, such as rice husk and diatoms.^{97,304} One of the most
29 widely used approaches to derive elemental Si is the magnesiothermic reaction method, during which
30 evaporated Mg (600–900 °C) will reduce the SiO_2 to Si. However, this strategy suffers from both the

1 energy- and time-consuming drawbacks with a varied yield depending on pressure and interparticle
2 interaction during the reaction. To solve these issues, Cho *et al.* proposed a magnesio-milling process
3 to chemically reduce rice husk-derived SiO₂ to a high-purity porous Si (Fig. 14e).³⁰⁵ They found that
4 the accumulated energy during particle collisions can trigger the reaction at an ignition point, which
5 enables the reaction progress to be monitored by temperatures or pressure. Of note, this promising
6 strategy can be successfully extended from the lab-scale to a 5L-scale, which can be improved and
7 extended for practical application. With the purpose of successfully inheriting the natural structures
8 during the SiO₂ reduction process, Gao *et al.* utilized an ultrathin dopamine coating layer as the
9 diffusion mediator, which stabilizes the hollow porous structure of transformed Si.³⁰⁶ Additionally,
10 they originally used Al metal in the molten salt system (AlCl₃-NaCl) to reduce SiO₂ in diatom
11 frustules. As shown in Fig. 14f, the pristine Aulacoseira frustules showed a micro-scale 3D structure,
12 while the derived product consisting of uniformly distributed Si and C elements developed a rougher
13 and more porous morphology (Fig. 14g, h). Such hollow Si structure with coated carbon layer at pre-
14 lithiated state delivered superior rate capabilities and stable cyclic performance, which was as high
15 as ~750 mAh g⁻¹ at 8 A g⁻¹ after 1000 cycles (Fig. 14i). In contrast to introducing extra carbon sources
16 (e.g., dopamine), Fan *et al.* made full use of rice husk (both Si and carbon sources) to directly obtain
17 a 3D porous Si/carbon composite material, which facilitates the rapid transfer of lithium ions and
18 effectively accommodates the volumetric changes during battery operation, resulting in improved
19 electrochemical performances.³⁰⁷ Considering the worldwide availability on a massive scale (~740
20 million tons were produced globally in 2013) and the natural hierarchical porous structures of Si
21 sources that facilitate the electrochemical processes in biomasses,³⁰⁵ it is of great significance to
22 develop practical procedures to derive high-performance Si-based (Si, Si/C, *etc.*) electrode materials
23 from biomass for large-scale applications. Moreover, with the removal of impurities in the raw
24 materials, such high-performance Si/C anodes can be easily produced at large-scale due to the high
25 processability of Si-rich materials and mature processing techniques for reducing silica.

26 **4.2 Organic electrode materials**

27 To develop and revolutionize energy storage systems beyond conventional LSBs, numerous strategies
28 have been proposed and considered, including the battery chemistry, material science, process
29 engineering, and theoretical simulations. One intriguing direction is the application of organic

1 electrode materials, which can undergo rapid redox processes to reversibly store energy in
2 rechargeable batteries and are especially suitable for constructing high-performance flexible LSBs.³⁰⁸⁻
3 ³¹⁴ Generally, molecules and polymers that can reversibly interact with Li are promising organic
4 electrode materials, which contain conducting polymers, layered organic compounds, organosulfur
5 compounds, organic free radical compounds, non-conjugated redox polymers, and organic carbonyl
6 compounds.³¹⁵ On basis of the electrochemical behaviors during battery operation, the organic
7 electrode materials can also be classified into three typical categories: p-type organics represent the
8 organics that are oxidized during charging, yielding cations, while the n-type is reduced to release
9 anions, and b-type organics can be both oxidized and reduced.³¹⁶ The advantages of these organic
10 electrode materials include: (1) lower hazard and toxicity compared with normal inorganic electrode
11 materials; (2) multiple-electron chemistries with high theoretical capacity beyond normal inorganic
12 electrode materials; and (3) low cost, reduced environmental impacts, and little harmful wastes
13 generated during material fabrication.

14 However, several vital issues restrict the applicability of organic materials. One drawback is the
15 large solubility of organic electrode materials in common organic electrolytes, which causes the
16 battery to suffer from significant performance degradation and rapid battery failure. In addition, the
17 complex and controversial working mechanisms remain unclear for most organic compounds. Many
18 strategies including designing stable structured organic molecules,^{317,318} using quasi-/solid-state
19 electrolytes,³¹⁹ polymerizing small organic molecules,^{320,321} bonding organic electrode materials with
20 matrixes (binders, carbon scaffolds, insoluble non-carbon matrixes, *etc.*),^{315,322-325} building large
21 conjugated structures, and preparing organic salts³²⁶⁻³²⁹ can efficiently lower the solubility of organic
22 materials in battery electrolytes, thus enhancing the battery performances in terms of capacity and
23 cyclic life. Of note, organic electrode materials are usually composed of naturally rich elementals like
24 C, N, O, and S, which suggests that they could be simply extracted from renewable biomass
25 resources.^{309,330} Since biomass is abundant, low cost, and sustainable, organic batteries based on
26 biomass-derived organic materials are potentially promising in the long run.

27 Figure 15a shows the fabrication of a PDA based organic electrode material, which was inspired
28 by mussels and could be extracted from natural biomass.³³¹ The DFT calculations of the stabilization
29 energy for Li bonded PDA (Fig. 15b) indicated that Li⁺ ions will favorably bond with the carbonyl
30 oxygen atom, which could be verified using *ex-situ* Raman and XPS measurements. In addition, PDA

1 delivered an ultra-high anodic capacity in the half cell as high as 1,500 mAh g⁻¹ for over 500 cycles
2 without an obvious decline in capacity (Fig. 15c). Such electrochemical performances are remarkably
3 better than many conventional electrode materials, indicating the potential for their practical
4 application. With a similar polymerization method, Schon *et al.* also prepared a pendant flavin
5 polymer denoted P3 (Fig. 15d),³³² which can be derived from riboflavin (vitamin B₂). Of note, these
6 biomass-derived redox-active pendant polymers show high capacity (125 mAh g⁻¹) at an operation
7 voltage of 2.5 V, which provides a positive influence towards the development of sustainable energy
8 storage applications. These works are typical examples that demonstrate the significance of producing
9 organic electrode materials with the assistance of biomass derivatives and polymerization processes.³³³
10 In addition to polymerization for resolving the solubility issue, Poizot and coworkers conceptualized
11 the fabrication of organic electrode materials at their lithiation state to efficiently solve this issue.⁹⁸
12 Starting from D-glucose, they applied an environmentally friendly route to fabricate the dilithium
13 (2,5-dilithium-oxy)-terephthalate (Li₄-p-DHT), which could serve as a satisfactory organic electrode
14 material (Fig. 15e) with elevated operating potential and improved capacity.⁹⁸

15 After resolving the issue of solubility, high-performance organic materials for both cathodes and
16 anodes might be used to construct all organic batteries with high electrochemical performance,
17 flexibility, and sustainability. Following this conception, Hu *et al.* designed a biomolecule-based full
18 LSB that engaged two types of redox-active biomolecules (Fig. 15f).⁷¹ Emodin (6-methyl-1,3,8-
19 trihydroxyanthraquinone) with redox quinone groups was hybridized with single-wall carbon
20 nanotubes (SCNT) and used as the cathode material. This biomass can be harvested from common
21 plants like polygonum cuspidatum and herbal rhubarb. On the other hand, humic acid, which is one
22 of the most widely-distributed biomaterials as a principal component of humic substances produced
23 through the biodegradation of dead plants under microbial metabolism, serves as the anode material
24 after a simple lithiation process with lithium hydroxide (LiOH). Both the emodin/SCNT cathode and
25 lithium humate anode delivered excellent electrochemical performances in half-cell tests. More
26 importantly, the prepared full LSB combining the two electrodes delivered a capacity of
27 approximately 60 mAh g⁻¹ over 100 cycles with a satisfactory Coulombic efficiency of 99%. This
28 work has provided an inspiring prototype of all-green battery based on eco-friendly and sustainable
29 biomass-derived electrode materials. Since Armand and Tarascon proposed a prospect for developing
30 all-biomass batteries about 11 years ago,³³⁴ there has been a gradual increase in the number of works

devoted to this field.^{71,335} This has further inspired the application of organic electrode materials for both the cathode and anode materials to construct sustainable, low-cost, and high-performance “green LSBs.” Considering the fact that mass production of biomass-derived organic electrode materials can be achieved by mature bio-extraction and conversion techniques, the practical application of the biomass-based organic electrodes needs more attention on resolving the material challenges including unsatisfactory operating potential and low capacity in full-cell configuration as well as comprehensive mechanism understanding.

4.3 Catalytic carbon cathodes for Li-oxygen/carbon dioxide batteries

Considering the poor electronic conductivity of discharged products in Li-O₂ and Li-CO₂ batteries in addition to the sluggish kinetics, an electrochemically stable, highly conductive, and porous cathode is of great importance to enable the electrochemical performance of Li-air batteries. In this situation, the carbon materials can be directly employed as the catalytic cathodes instead of being used as sole scaffolds for rare metal and transition metal-based catalysts.³³⁶⁻³⁴² Particularly, biomass-derived carbons have obvious advantages including low-cost, abundance, naturally hierarchical 3D structures and well-developed porosity, which make them show huge potential as high-performance air cathodes in Li-air battery systems.

Luo *et al.* confirmed that wood-derived N-doped carbon (wd-NC) can be considered as a freestanding, hierarchically porous, conductive electrode for Li-air batteries.³⁴³ It should be mentioned that the N dopant gave rise to both improved electronic conductivity and catalytic activity in terms of a reduced charge-discharge overpotential and enlarged capacity. Additionally, reversible formation and decomposition processes of Li₂O₂ within the pores and on the surface of the carbon walls can be observed during the battery operation (Fig. 15g-i), which considerably identify the improved performance of Li-air batteries with wd-NC cathode. In contrast to obtain doped carbon with extra process and added dopant, Jing *et al.* deployed silkworm cocoon as both the carbon and nitrogen sources to directly produce the N-doped carbon electrode,³⁴⁴ which successfully maintained the fibrous structure of the natural cocoon film and highly reversibly accommodated the discharge product of Li₂O₂ with perfect toroidal structure during battery operation (Fig. 15j, k). These natural biomass-derived carbon materials through simple carbonization, functionalization, and hybridization with other carbons (carbon nanotubes, graphene, *etc.*) can well function as advanced carbon cathodes

1 for Li-O₂/CO₂ batteries. However, it's found that carbon with activated double bonds or aromatics
2 superoxide radicals can react with superoxide radicals that were generated at the cathode side during
3 discharge to form epoxy groups and carbonates,³⁴¹ which largely reduces the reversibility of
4 electrochemical processes and inhibits the practical application of carbon cathodes in Li-air batteries.
5 Consequently, more attention should be paid to enhance the stability of carbon cathodes as well as
6 improve their catalytic properties.

7 **5. Biomass-derived additives**

8 Binders, electrode additives, and conductive additives are important components in batteries that
9 significantly affect the electrochemical performance of the batteries including the cycling stability,
10 capacity, and Coulombic efficiency.^{48,345-354} However, the performance enhancement from these inert
11 components (binders and conductive additives) is often accompanied by a reduction in the energy
12 density of batteries. It is anticipated that a highly conductive 3D architecture design may function as
13 a binder- and current collector-free electrode with minimum conductive additives and high mass
14 loadings of active materials.

15 **5.1 Natural binders for cathode and anode materials**

16 Among all types of binders, biomass-derived natural binders and their derivatives are of great
17 importance due to their environmental friendliness, low cost, sustainable properties, and special
18 functional groups.^{43,105,355-358} Many natural binders have been widely employed in battery fabrication
19 for both cathodes and anodes,^{359,360} among which gums, alginate, and CMC are three typical and
20 popular natural binders.^{105,355,361,362}

21 As described earlier, Si-based anodes are promising for LSBs; however, they suffer from severe
22 volumetric changes and thus poor cycling stability. It has been shown that synthetic or biomass-
23 derived binders containing carboxy groups, like polyacrylic and carboxymethyl cellulose, can
24 significantly improve the electrochemical performance of Si-based anodes.^{105,349,351} One typical
25 hypothesis regarding the positive effects of these binders is that the polar hydrogen bonds between
26 the carboxyl groups in biomass binders and the SiO₂ layer on the Si surface could induce a self-
27 healing capability against local electrode breakage.¹⁰⁵ Additionally, it is also suggested that these
28 binders with some rigidity but poor extensibility may plastically deform the Si powder during the
29 lithiation process and controllably expand them towards the voids among the particles.

1 Yushin and coworkers reported a natural biomass-derived binder for Si-based anodes and
2 systematically investigated its effects on the electrode performance.¹⁰⁵ The authors extracted the
3 alginate (Alg) (a high-modulus polysaccharide) by heating the natural brown algae in a hot soda
4 solution and applied it directly as the binder to obtain a stabilized Si anode (inset of Fig. 16a). Brown
5 algae as a typical aquatic microorganism contains rich polysaccharide with abundant carboxylic
6 groups in the polymer chains. The prepared alginate binder from algae was shown to be a superior
7 binder for Si-based anodes compared with the commercial anode binders like CMC and
8 poly(vinylidene fluoride) (PVDF). The advantages of this binder extracted from brown algae are
9 attributed to the higher concentration and more uniform distribution of the carboxylic groups in the
10 polymer chains of the binder. This leads to a better migration of Li^+ ions around the Si particles, a
11 more uniform coverage on the active particles, and more significant effects towards building a stable
12 SEI layer on the Si particles. In addition, the alginate binder is much more polar and has a higher
13 modulus than that of commercial binders such as PVDF (Fig. 16a). This property ensures stronger
14 interactions between the binder and Si particles while enhancing the adhesion between the electrode
15 materials and the current collector (Fig. 16b). As a result, batteries with this natural binder delivered
16 improved stability, high capacity, and prolonged cycling performance (Fig. 16c). In addition to single
17 polymer binders, biopolymers or biomolecules assembled binders can also show satisfactory
18 performances in batteries. For example, Kim *et al.* fabricated an amphiphilic renatured DNA/alginate
19 hybrid binder (reDNA/ALG hybrid binder) for Si.³⁶¹ The amphiphilicity of both components (DNA
20 and alginate) and the 3D network architecture of the biopolymer binder guaranteed the uniform
21 distribution of electrode components and high adhesion with current collectors. Such a superior Si
22 electrode enabled by the biopolymer binder could deliver a high capacity of $\sim 1000 \text{ mAh g}^{-1}$ after 300
23 cycles even at a high C-rate of 10.5 A g^{-1} , having a capacity retention of 84.6%. With the inspiration
24 from strong wet-resistant adhesion of mussels, Ryou *et al.* introduced catechol groups into Alg binders
25 and poly(acrylic acid) (PAA) to obtain the catecholic binders (PAA-C and Alg-C) for constructing Si
26 anodes (Fig. 16d).³⁶³ Due to the strong interactions between the biopolymer binder and Si *via*
27 catecholic adhesion and hydrogen bonding, the obtained Si electrode could maintain high integrity
28 during repeated battery operation, and deliver higher capacity and better cycling stability than those
29 electrodes with binders like PVDF and alginate (Fig. 16e).

30 Besides alginate-based binders, other biopolymers could also be processed into excellent binder

1 materials. For example, Liu *et al.* used guar gum (GG) as the binder for Si anodes.³⁵⁵ Due to the
2 abundant polar hydroxyl groups in such a biopolymer, there would be a strong interaction between Si
3 and this binder, leading to a stable electrode during battery cycling. Kwon *et al.* introduced a
4 distinguished binder concept of “dynamic crosslinking” by promoting host-guest interactions
5 between the β -cyclodextrin polymer (β -CDp, one type of starch derivate) and a dendritic gallic acid
6 (an organic acid found in several plants) supramolecular cross-linker that incorporates six adamantane
7 (AD) units (Fig. 16f).³⁶⁴ This special dynamic cross-linking within the binder named as β -CDp/6AD
8 ensured a uniform cross-link among the polymer chains and achieved a self-healing effect to
9 guarantee the structural integrity of the Si anode during cycling (Fig. 16g). Consequently, this
10 biopolymer binder with the optimal component showed satisfactory capacity and cycling stability,
11 which was comparable to that of other binders including PAA, alginate, and CMC (Fig. 16h). As
12 shown in Fig. 16i, the Si electrodes after cycling for 150 cycles still maintain a clear morphology
13 without any signs of damage. This demonstrates a stable SEI layer throughout the entire
14 electrochemical process as enabled by the designed “self-healing” binder.

15 In addition to anodes, biomass-derived binders also play a significant role in cathode materials
16 such as sulfur. As an example, Li *et al.* used natural gum arabic (GA) as an advanced binder for a
17 sulfur cathode, which could effectively increase the cathode capacity and cycling stability compared
18 with batteries using gelatin or PVDF binders (Fig. 17a, b).³⁵⁵ With the similar design criteria, the
19 authors in another work reported the fabrication of a 3D network binder (N-XG-GG) composed of
20 xanthan gum (XG) and guar GG *via* the intermolecular binding effect.³⁶² The sulfur cathode prepared
21 showed significant advances in terms of the areal sulfur loading (19.8 mg cm^{-2}) and areal capacity
22 (26.4 mAh cm^{-2}) compared with previously reported results. The enhancements were related to the
23 natural properties of such biopolymer network binders, including its abundant oxygen-containing
24 groups facilitating the cycling performance and mechanical robustness promoting the high mass
25 loading. Besides direct employment of natural biopolymers, using biomass-based polymers as the
26 starting materials to design binders with desirable properties is also an effective solution. For instance,
27 Jin *et al.* successfully fabricated a 3D network binder (DSM), which was composed of N-(3, 4-
28 dihydroxyphenethyl) acrylamide (DAA, a dopamine derivate), sulfobetaine zwitterion (SBMA), and
29 poly(ethylene glycol) methyl ether methacrylate (PEGMA).³⁶⁰ This DSM binder can not only well
30 accommodate the volumetric changes of the active sulfur electrode during battery cycling, but also

efficiently trap the lithium polysulfides with the strong anchoring ability from the O (Li-O) and N⁺ (N⁺-S_x²⁻) active sites (Fig. 17c, d). Additionally, the negatively charged sulfonate coordination and excellent electrolyte uptake ability in/of the DSM binder were beneficial for faster lithium ion diffusion and higher lithium ion conductivity. The biomass-derived binders with their naturally-designed functional groups and corresponding physicochemical properties might be of great importance in both the battery chemistry deployment and chemical fabrication industry.

All in all, since many biopolymers/derivates and synthesized polymers from biomass comprise abundant functional groups and show superior mechanical robustness that can facilitate the Li-ion migration, shield the active materials, and trap the intermediates of the electrochemical process, they can be produced at large scale and used as promising candidate binders for LSBs. There must be a large share of biomass-derived binders in the market of the battery community beneficial from the steadily upgrading biomass extraction/conversion techniques. Moreover, these biopolymer binders compared to synthesized polymers are eco-friendly, cost-effective, and abundant. Additionally, many biopolymers can be soluble in the water, which largely simplify the recycle procedures of expensive active materials in the spent LSBs.

5.2 Conductive additives

With the exception of metal-based anodes, most cathode and anode materials face issues related to insufficient electronic conductivity, which may lead to poor rate performance, large polarization, and limited capacity. Therefore, conductive additives with different structures and morphologies have been developed, such as carbon black, conductive graphite, graphene, CNTs, and carbon fibers.^{31,45,46,324,365,366} Each of these conductive carbon materials could be obtained from biomass by designing appropriate synthesis routes and using specific biomasses.^{367,368} However, the demand for increasingly advanced batteries with higher energy density requires new types of conductive additives considering that these battery additives barely contribute to the capacity but occupy a significant fraction of mass and volume.^{44,369} The construction of additive-free (including binder and conductive carbon additives), and electronic/ionic conductive network electrodes has been considered. These designs could lead to a high mass loading, excellent electrolyte contact/uptake, and satisfactory ion/electron transport. Research in this direction blurs the boundaries among conductive additives, binders, and electrode scaffolds. As mentioned in the former section, biomass-derived carbons may

1 serve as the scaffolds for active electrode materials, which to some extent also contribute to the
2 electronic conductivity of electrodes but accompanied by extra commercial conductive carbon. Only
3 if the electronic conductivity of the carbon scaffolds that tightly and dimensionally contact with active
4 materials can be enhanced to provide the superior electronic conduction of electrodes, no extra
5 conductive carbons are needed. For instance, networks of 3D porous freestanding carbon can be
6 readily obtained from biomass materials to serve as integrated electrode supports without the need
7 for current collectors, binders and conductive additives, such as the wood-derived 3D carbon
8 described earlier and a bacterial cellulose-derived carbon network.^{99,237} Nonetheless, further efforts
9 are required to achieve the intact interaction between 3D ion/electron conducting network and active
10 materials with the absence of electrode additives for high-performance integrated electrodes.

11 In addition to carbon-based conductive networks, conductive polymers could also be used as a
12 conductive additive that is directly coated on the active materials or further employed to build an
13 additive-free polymer network. For example, Shi *et al.* constructed a high-performance LFP cathode
14 netted by a cross-linked polypyrrole (C-PPy), where no extra binders or conductive additives were
15 added (Fig. 18a).³⁷⁰ Importantly, the polymer not only served the function of a binder but also enabled
16 a high electronic conductivity (7.8 S cm^{-1}). As seen in Fig. 18b, the hybrid framework electrode
17 delivered higher capacities and more stable cycling performance than the conventional electrode
18 prepared with a normal binder and conductive additive. In the cycling test, this robust cross-linked
19 polymer adhered tightly to the LFP particles thus leading to higher cycling stability.

20 **5.3 Electrolyte additives**

21 Biomass-derived materials with favorable structures and components, including biochar and bio-
22 organic chemicals, have the potential to be used as additives for both liquid and solid electrolytes.
23 These biomass-derived additives may increase the ionic conductivity, stabilize the electrode materials,
24 promote the formation of stable SEI/cathode electrolyte interphase (CEI), and enhance the
25 chemical/physical properties of the electrolytes in both liquid and solid states. For instance, Ma *et al.*
26 added CQDs into a solid polymer electrolyte as a functional additive.³⁷¹ The authors used acetone as
27 the carbon source to synthesize the CQDs. The CQDs with abundant oxygen-containing functional
28 groups were uniformly dispersed in the polyethylene oxide (PEO) based electrolyte, which promoted
29 the dissociation of Li/Na salts, adsorption of anions, and reduced the PEO crystallinity degree. These

1 led to the effective enhancements of the ionic conductivity and Li transference number (Fig. 18c). It
2 is noted that there have been numerous reports of fabricating CQDs using biomasses with simple
3 hydrothermal carbonization in alkali solutions (Fig. 18d).³⁷² This provides the possibility of preparing
4 biomass-derived CQDs as additives for solid-state electrolytes. Furthermore, a variety of
5 functionalized CQDs with various surface groups or heteroatomic doping may be developed to
6 achieve tailored electrolyte design. Besides biomass-derived carbon materials, biomolecules and
7 biopolymers could be extracted and used as promising functional electrolyte additives, although
8 research in this direction is still limited. For instance, Kim *et al.* used polydopamine (a type of
9 synthesized melanin) as the a radical scavenger in the electrolyte of Li-O₂ batteries, which played
10 positive roles in alleviating side reactions caused by superoxide radicals.³⁷³

11 In brief, the researches on biomass-derived electrolyte additives are limited. This is
12 understandable since the synthesis and application of commercial additives are mature and widely
13 used. However, with the emerging of the green LSBs, it sheds light on the development of novel types
14 of electrolyte additives from biomass that is sustainable and environmentally friendly. Alternatively,
15 biomass can at least serve as the raw materials for synthesizing electrolyte additives.

16 **6. Biomass-derived insulation layers and polymer electrolytes**

17 With the development of sustainable green chemistry and the increasingly significant environmental
18 issues, more renewable biomass resources have been used in polymer production industry. These
19 biomass-derived polymers could be further adopted in the fabrication of separators and solid-state
20 electrolytes, as well as their supporting matrixes. Williams and coworkers described representative
21 samples of sustainable polymers from renewable biomass, in which they listed the biomass-derived
22 monomer precursors as well as their derivate polymers, and introduced their typical applications in
23 daily life and different industries.⁸⁴ Considering the desirable trends towards sustainable technologies
24 and the mature processes for producing biopolymers and their derivatives, biomass has a significant
25 potential and has already been used in the fabrication of obstacle/insulation layers such as separators
26 for LSBs. These could further be extended for the preparation of solid-state electrolytes using high-
27 molecular weight biopolymers and electrolyte supporting matrixes of robust 3D structures grafted
28 with functional surface groups.

6.1 Separators and protective layers

A separator serves as the electron isolating layer between the cathode and the anode to prevent internal short circuits in the battery. This is an important battery component, which usually requires considerable mechanical properties, satisfactory electrolyte uptake capability, acceptable thermal stability, and excellent Li^+ ion conductivity.^{60,61,63,64,68,374-376} However, current commercial separators are mainly fabricated from polyolefins like PE and PP in the petrochemical industry. Such separators have advantages in their electrochemical stability tolerance and high Li^+ ion conductivity but often have insufficient thermal stability and mechanical strength. These insufficiencies lead to short circuits which in turn caused battery failure and can even trigger hazards under extreme operational conditions, such as high temperatures. Meanwhile, the weak wettability and small electrolyte uptake capability of polyolefin separators negatively affect the electrochemical performance of batteries. Therefore, the development of green and sustainable separators with high thermal stability, high electrolyte uptake/penetration ability, and strong mechanical properties is of great importance towards sustainable high-performance LSBs. Nonwoven fabric is a newly emerging separator for LSBs that are mainly made from polymers like poly (ethylene terephthalate) (PET) and polyimide (PI). These fabrics have obvious advantages over the conventional PP/PE separators with inferior thermal stability, which makes them suffer greatly from reduced mechanical strength and porosity at elevated operating temperatures, subsequently leading to battery failure. However, the high cost of raw fibers, the large thickness of the fabric, and the techniques for mass production are the main limitations inhibit their broad applications at present. For instance, the low-cost cellulose that can be regenerated into ultra-fine fibers is thought to be a highly promising candidate for ultrathin nonwoven separators. The common issues of cellulose fabrics including the dimensional stability/strength and porosity regulation may lead to queries and concerns for the applications of cellulose separators, which can actually be easily resolved by controlling the microstructures of cellulose with mechanical engineering (*e.g.*, highly aligned cellulose nanofibers with enhanced strength and toughness) and/or strengthening cellulose with the addition of functional materials [*e.g.*, Al_2O_3 , SiO_2 , CNT, polysulfonamide (PSA), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HPF)]. Consequently, these cellulose-based separators [cellulose nonwoven separator, cellulose/PVDF-HPF, cellulose/PSA, and flame-retardant cellulose-based composite nonwoven (FCCN) separator] not only can be produced at industrial scales with techniques like paper making, but also show superior

features including electrolyte uptake ability, strength, thermal stability, and ionic conductivity compared to commercial PP (Table 4).³⁷⁷⁻³⁷⁹

The possibility and requirements of using cellulose-based separators for LSBs at the laboratory were firstly investigated by Kuribayashi in 1996 (a fibrilliform cellulose fibers filling microporous cellulose film).³⁸⁰ Subsequently, more and more researches have been devoted to developing cellulose-based separators by controlling the structural parameters (e.g., porosity, thickness, fiber diameters), changing mechanical processing methods (e.g., electrospinning, hot pressing, filtration), chemically engineering the segments of cellulose (e.g., grafting, copolymerization), and finding effectively additives for composite films. Goodenough and coworkers directly employed a cellulose-based mask pack as the separator for Li-S batteries,⁸⁵ which was composed of robust nanopores and nanofibers (Fig. 19a). Due to a superior electrolyte uptake capability and excellent stability against Li-metal, the Li-S battery with the cellulose separator delivered stable cycling performance for 1000 cycles, while the battery with PP separator quickly failed after 100 cycles (Fig. 19b). To achieve better control of separator properties, Choi et al. used a high-pressure homogenized wood cellulose nanofibril (CNF) to prepare an ultra-thin separator (20 μm) with a well-tuned nanoporous structure.³⁸¹ The nanoporous structure of CNF enabled a tightly interlocked electrode/separator interface capable of facilitating fast electrochemical kinetics was obtained, which promoted the assembled $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell to deliver much better charge/discharge rate capabilities than the conventional cells with commercial PE separator. To further enhance the mechanical strength, flexibility and thermal stability of cellulose-based separators, Li et al. proposed a hybridization strategy (Fig. 19c) by incorporating the cellulose fiber (CF) with the hydroxyapatite nanowires (HAP, a biomineral that exists in bones, teeth, and milk) to obtain a HAP/CF composite separator.³⁸² Of note, the HAP nanowire networks could be tightly wrapped with cellulose fibers *via* hydrogen bonds as well as *van der Waals* force, and self-assemble into a hierarchical, crosslinked, hybrid fiber network (Fig. 19d), which can be easily produced into separators by simple and facile suction filtration. This composite HAP/CF separator enabled the stable cycling of the battery even at harsh operating conditions (e.g., at an elevated temperature up to 150 $^{\circ}\text{C}$, Fig. 19e), whose temperature limit could be further extended by coupling with high-temperature-resistant electrolytes.

In addition to cellulose, natural polymers like protein and chitin are also of high abundance and have been widely engaged to develop novel separators. Of note, many natural membranes/interfaces

1 (e.g., eggshell membrane, exoskeleton) with purposely designed functions (e.g., protection,
2 adsorption, selective diffusion and transfer of substances) are often composed of protein and chitin.
3 Additionally, these biopolymers with abundant highly polar groups (e.g., carboxyl, amino, carbonyl)
4 have strong interactions with Li ions, which make them a promising choice for designing separators
5 with specific features. Kim *et al.* prepared a nonwoven-mat separator with aligned nanofibrillar
6 architecture from chitin powders,³⁸³ which was fabricated through a cotton candy-inspired centrifugal
7 jet-spinning (CJS) technique (Fig. 19f). On basis of the molecular dynamic simulations, it's found
8 that both the α - and β -chitin have high affinity towards Li ions due to their surficial functional groups
9 (e.g., hydroxyl, acetylamino) as well as superior adhesion energy to electrolyte compared to nanofiber
10 in PP separators (Fig. 19g). As a result, the chitin separator manifested lower charge transfer
11 resistance and better electrolyte-uptake capability than PP and glass fiber separators. When such
12 separator was employed, the Li-O₂ batteries delivered a much more stable overpotential and a longer
13 lifespan than those using a glass fiber and PP separators. A more comprehensive example was shown
14 by Yu and coworkers.³⁸⁴ They started from purifying and fibrillating the prawn shell to harvest a
15 homogeneous chitin nanofiber suspension, which was vacuum dried to fabricate a high-performance
16 separator with tunable nanopores produced by a sodium dihydrogen citrate (SDCA) hard template
17 (Fig. 19h). This biomass separator exhibited improved mechanical strength (tensile stress of 80–120
18 MPa), thermal stability (over 150 °C), and electrolyte wettability (a low contact angle of 9.2°).
19 Consequently, the half-cell with the chitin separator at a operating temperature of 120 °C delivered
20 much better electrochemical performance than the control groups with PP, SiO₂-coated PP, and
21 cellulose nonwoven separators (Fig. 19i).

22 In addition to direct use of biomass for fabricating separators, biomass and its derivate materials
23 could also be employed to hybridize with commercial polymer separators, which has been considered
24 as an efficient route to make high-performance separators. For example, Manthiram and colleagues
25 reported that using carbon and its composite materials as the interlayer between sulfur cathodes and
26 the separator can effectively improve the cycle performance of Li-sulfur batteries.³⁸⁵⁻³⁸⁷ Such
27 interlayers could play a significant role in suppressing the polysulfide shuttling, preventing the
28 accumulation of inactive sulfur species, and promoting the reversible transformation of discharge-
29 charge intermediates. Inspired by the natural functional structures (epidermis, palisade mesophyll,
30 spongy mesophyll) within the leaf that serve as the reservoir of water, Manthiram and coworkers

1 directly carbonized the leaf (CL) and used it as the inhibiting interlayer for preventing Li polysulfides
2 shuttle in the electrolyte.³⁸⁸ In another contribution, they recycled the domestic waste to prepare a
3 carbonized sucrose-coated eggshell membrane (CSEMs),³⁸⁹ which can be used as a natural
4 polysulfide reservoir due to its hierarchical macro/microporous structure and high electronic
5 conductivity. With such biomass-derived interlayers of naturally shaped 3D porous functional
6 structures, the Li-sulfur batteries delivered high capacity and excellent long-term cycling stability.
7 However, these works showing the potential of biomass-derived interlayers in the laboratory scale is
8 still far from the mass production for practical cells. The commercialization of biomass-derived
9 interlayers relies on the further development of techniques for regeneration and artificially
10 reassembling, which can remain or even upgrade the structures and functions of interlayers. Besides
11 biochar interlayer, some biomolecules and biopolymers with superior flexibility and rigidity can be
12 directly coated onto the separator or serve as the interlayer to enhance the separator performance
13 without the necessity of carbonizing the biomass. For example, Choi and coworkers reported that a
14 PDA-coated PE separator could effectively resist Li dendrite growth, enlarge the electrolyte uptake
15 capability, promote a uniform Li^+ ion flux, and provide strong adhesion towards the Li surface, thus
16 resulting in significantly improved electrochemical performance.³⁹⁰ Following the same route, Sun
17 and coworkers used a natural biopolymer of agarose film as an interlayer between the Li-metal anode
18 and the separator.³⁹¹ The agarose film with high ionic conductivity, elasticity, and chemical stability
19 could provide a favorable Li^+ ion transfer and suppress the formation of Li dendrites (Fig. 19j, k),
20 promoting the full cell comprising LiFePO_4 cathode and Li metal anode to deliver superior rate
21 capability than control groups (Fig. 19l). This work offered a good example of building functional
22 biomass-derived interlayers towards a stable Li-metal anode, which could be further extended to
23 fabricate biomass interlayers with functional surface groups or embedded with inorganic fillers.

24 Overall, biomass-derived functionalized carbon and biomolecules/biopolymers such as cellulose,
25 chitin, and silk protein, have a great potential for the large-scale production and application of
26 sustainable green separators, interlayers, and coating layers for LSBs. By simply regulating the
27 porosity, microstructures, surface chemistries, and components during the processing, the biomass-
28 derived separators can deliver much better electrolyte uptake/wettability, thermal stability,
29 mechanical strength, Li-ion affinity and ionic conductivity than commercial PP and PE separators,
30 which are a promising candidate for building the recyclable high energy/power density battery

1 systems with a sustainable and cost-effective approach. Moreover, the biomass-derived
2 separator/interlayer family could be easily extended since the biomass materials could be hybridized
3 with other materials to broaden and enhance their functions and properties, which can promote the
4 battery to be safely used even under harsh operating conditions.

5 **6.2 Supporting matrixes for gel polymer electrolytes**

6 To improve the energy/power densities of LSBs and satisfy the desire for advanced energy systems,
7 there is a great need to develop high capacity electrode materials, such as high-voltage cathodes and
8 lithium metal anodes. However, current battery chemistries and material properties make it difficult
9 to achieve the cooperation of the high-voltage cathode with the lithium metal anode. This promising
10 battery configuration faces typical challenges including lithium dendrite growth,^{13,392} cathode
11 structure collapse,^{393,394} interfacial mismatch^{360,395} and safety hazard,^{396,397} which must be resolved.
12 Many studies have focused on solid-state electrolytes as substitutes for liquid electrolytes, which can
13 largely suppress Li dendrite growth and improve battery safety. However, before liquid electrolytes
14 can be replaced with satisfactory solid-state electrolytes, gel polymer electrolytes as a transition have
15 attracted particular attention.^{398,399}

16 Gel polymer electrolytes are usually composed of liquid electrolytes with a polymer supporting
17 matrix (skeleton). Most polymer skeletons, like PEO, usually suffer from poor mechanical strength,
18 especially when loaded with liquid electrolytes. In contrast to synthesized polymers, biomass-derived
19 polymers have some advantages due to their naturally designed chemical structure to promote the
20 dissociation of Li salts, enhance the transport of Li⁺ ions, and enlarge the electrolyte uptake capability.
21 Bacterial cellulose (BC) is a product of bacteria metabolism and is one such ideal polymer skeleton
22 for gel polymer electrolytes. Dong *et al.* successfully prepared a bacterial cellulose supported
23 composite polymer electrolyte (PMM-CPE) for high-voltage lithium metal batteries (Fig. 20a), which
24 manifested a low overpotential and excellent cycling stability at various current densities in a Li-Li
25 symmetric cell (Fig. 20b).⁴⁰⁰ This advanced gel polymer electrolyte with high ionic conductivity and
26 a wide electrochemical window could be further coupled with a 4.45V-class LiCoO₂/Li cell, which
27 showed a high capacity, excellent capacity retention (Fig. 20c). These advantages can be attributed to
28 the compact cathode/electrolyte interphase formed on the LiCoO₂ cathode and the stable SEI layer
29 on the Li-metal anode enabled by the composite gel polymer electrolyte. Moreover, this high-

1 performance bacterial cellulose-based gel polymer electrolyte shed new light on the successful
2 construction of flexible Li-metal batteries (Fig. 20d). Assisted by the BC skeleton, Xu *et al.* also
3 reported a high-performance gel polymer electrolyte.⁴⁰¹ The internal crosslinked BC network can
4 interact with the solvent through strong hydrogen bonding (Fig. 20e), indicating a potential high
5 electrolyte uptake capability. This could be confirmed by the obvious morphology changes before
6 and after adsorbing electrolyte ranging from a network structure with robust voids (Fig. 20f) to a
7 swelled and dense surface (Fig. 20g). During the half-cell symmetric test, the BC-based polymer
8 electrolyte (BC-GPE) showed much better cycling stability and lower overpotential compared with
9 batteries that possessed a liquid electrolyte-immersed separator (LE-S). As employed in LFP-based
10 full-cell, batteries with BC-GPE also showed much better rate performances. Moreover, the BC-GPE
11 showed superior thermal stability from ambient to 150 °C, while the conventional liquid electrolyte
12 and separator failed instantly (Fig. 20h).

13 The polymer matrixes with high mechanical strength and high electrolyte uptake capability are of
14 great significance toward a high-performance gel polymer electrolyte, which decisively implies the
15 potential employment of biopolymers/biomolecules that can be assembled into 3D hierarchical
16 structures and/or modified by functional surface groups showing high adhesive energy to electrolytes.
17 Moreover, the features of biomass including the sustainability, natural abundance, hierarchical
18 structures, functional surface chemistry, and low cost make the large-scale production and
19 applications of biomass-based gel polymer electrolytes significantly promising. Additionally,
20 considering the abundant species of biopolymers, more studies could be conducted to broaden the
21 family of green sustainable polymer matrixes and develop functionalization techniques for biomass-
22 based gel polymer electrolytes.

23 **6.3 Polymer electrolytes**

24 Since gel polymer electrolytes contain solvents at the liquid state, they still face problems of
25 electrolyte leakage and combustion hazards. Solid polymer electrolytes (SPE) with high flexibility,
26 low toxicity, low cost, high safety levels, and cycling stability have been widely investigated. For
27 example, PEO is one of the most studied polymers for SPEs,^{402,403} which is thought to provide
28 transport paths for Li⁺ ions *via* chain segment motion of ether oxygen (-C-O-C-) groups. Many
29 biomasses and biomass-derived materials with similar functional groups could also be used as the

polymer host for solid-state batteries. Starch, a type of polysaccharide, is a major energy storage material from plants such as rice, wheat, corn, and potatoes. Typical starch is composed of numerous glucose monomers joined by glycosidic linkages that form a steady helix structure and show the potential to transport Li^+ ions.

Marcin *et al.* made an interesting attempt by crosslinking the hydroxypropylcellulose (HPC, a cellulose derivate) with oligo(ethylene oxide) to harvest a poly(ethylene oxide)-2-hydroxypropylcellulose (PEO-HPC) for the promising polymer electrolyte.⁴⁰⁴ This polymer as a candidate polymer electrolyte exhibited improved mechanical stability and had a high ionic conductivity of $2.5 \times 10^{-4} \text{ S cm}^{-1}$. Lin *et al.* provided another reference to construct biomass-based solid-state electrolytes by employing starch as the polymer host for an all solid-state lithium sulfur battery.¹⁰³ They crosslinked the corn starch by introducing a silane coupling agent γ -(2,3-epoxypropoxy)propyltrimethoxysilane (KH560), which enabled the obtained polymer to present satisfactory stretchable properties (Fig. 20i). It is noted that this starch-hosted electrolyte has a high ionic conductivity of $3.39 \times 10^{-4} \text{ S cm}^{-1}$ and a large Li^+ ion transference of 0.8 at room temperature. When coupled with a sulfur cathode, a solid-state battery could deliver high capacities even at 25 °C (Fig. 20j). The electrochemical performances of this biomass-hosted polymer electrolyte are comparable and even better than that of many PEO-based electrolytes. Besides starch, there are various biopolymers that may be promising candidates as sustainable polymer hosts for solid-state electrolytes after appropriate chemical treatments.

By comprehensive understanding the ionic conduction behaviors in the conventional polymer electrolytes, it's found that many natural biomolecules/biopolymers consisting of functional groups (*e.g.*, -C-O-C-) can also facilitate the reversible ionic migration and be used as candidates for polymer electrolytes. The low cost, environmental friendliness, high processability and high abundance of biomass are evident advantages over synthesized chemicals. By combining the battery chemistries with the mature techniques of biomass extraction, conversion, and processing,^{2,4,405-407} it's believed that various functionalized biomass-derived polymer electrolytes can be large-scale produced at acceptable producing cost and high yields with negligible emissions of wastes.

7. Conclusion and Outlook

After almost 30 years of commercialization, LSBs are undoubtedly the landmark technology that has

greatly advanced human civilization. However, issues of environmental pollution, natural resource exhaustion, and demands for higher energy/power densities have necessitated new types of LSBs to continuously satisfy the desires of modern society. Biomass is the most abundant energy storage product for sunlight and provides great opportunities for building “green battery” systems. However, researches and developments over biomass-derived LSB materials at present are far from the successful application of “green batteries” in different aspects as outlined below.

I. Functions of biomass products in LSBs.

To date, most of the research efforts on biomass-derived LSBs materials are devoted to directly carbonizing cheap biomass byproducts (wood, nutshell, bone, *etc.*) to either obtain conductive additives or fabricate the carbon anodes. We should refresh our understanding towards the roles of biomass in LSBs, since the function of biomass could be beyond such conventional uses. In fact, biomass can be transformed into many battery products with purposeful designs for chemical components, natural structures, and biophysical/biochemical properties.

(1) Biomass products as electrode scaffolds. Multifunctional scaffolds can be harvested from biomass and used to stabilize both the cathode and anode materials in terms of naturally shaped hierarchical porous structures, robust mechanical properties, and high electric conductivity. With the modification and functionalization (*e.g.*, heteroatom doping, fluoridation, incorporating with functional additives) biomass-derived scaffolds may be enabled to further improve the battery performance with the brand-new multi-functions (*e.g.*, regulating the interface between electrode and electrolyte, promoting the redox kinetics, controlling the electrochemical behaviors, functioning as an ion/electron conducting and additive-free electrode network).^{41,205,208}

(2) Biomass products as active materials. Biomolecules and biopolymers without the need of carbonization can be extracted from biomass and transformed into novel organic electrode materials for LSBs. The abundant storage, environmental friendliness, and low cost of natural organic electrode materials as well as the mature biomass extracting industries enable the biomass-derived biopolymers/biomolecules to be competitive to the chemically synthesized organics. With the further advances of the biomolecules/biopolymers extracting/transforming techniques and comprehensive mechanistic understanding towards the redox chemistries of organic electrode materials, the biomass-derived organic electrode materials are of great significance and convenience for constructing all-green LSBs.

1 (3) Biomass products as additives. Additives (binder and conductive additive) for LSBs can be
2 fabricated from biomass, and there already have been some success in the battery chemistry. Since
3 many biopolymers/derivatives from biomass contain abundant functional groups and show superior
4 mechanical robustness that can facilitate the Li^+ ion migration, shield the active materials, and trap
5 the intermediates of the electrochemical process, a variety of green and cost-effective biomass-based
6 binders have been prepared and widely used in the battery community (*e.g.*, CMC and SA).
7 Meanwhile, the conductive additives can be easily fabricated from carbonaceous biomass materials.
8 However, the electrochemically inactive characters of these materials limit the energy density of
9 LSBs. Future attention may be devoted to the design of additive-free and electronic/ionic conducting
10 electrode structures, which can reduce or even eliminate the inactive components and guarantee the
11 battery performances.^{408,409} Such researches may blur the boundaries among conductive additives,
12 binders, and electrode scaffolds, and new understandings towards electrode configuration may be
13 established.

14 (4) Biomass products as electrolytes. Considering the swelling property of biopolymers as well
15 as effects of ether oxygen and similar functional groups on the diffusion of Li^+ ions, several biomass-
16 derived gel polymer and polymer electrolytes have been adopted in battery systems, such as the
17 bacterial cellulose and cross-linked starch.^{103,394,410} Biopolymer-based gel polymer electrolytes
18 containing liquid electrolyte still suffer from risks of combustion and reduction of the energy density
19 of batteries, while the polymer electrolytes are plagued with low conductivity and extra processing
20 treatments. As is known, many natural biomolecules and biopolymers are composed of specific
21 functional groups that may facilitate the diffusion of ions, enhance the interaction among active
22 materials, and promote the formation of a stable protective interface layer on electrodes.
23 Unfortunately, limited advances have been developed in this area, which is mainly attributed to the
24 difficulty in extracting and processing biopolymers compared to mature techniques for the synthesis
25 of organic electrolyte additives.

26 (5) Biomass products as separators. Since many biomasses consist of fibrous structures (cellulose
27 and silk), they can be transformed into fibers and then assemble into separators. Many strategies have
28 been proposed to dissolve the naturally bonded fibrous materials, while they are achieved at the
29 expense of either the usage of toxic solvents or high cost from complex treating processes. Some
30 porous biomass materials like thin wood, egg membrane, and bacterial cellulose may directly be used

1 as separators,^{172,411} but the separator properties including the pore size, porosity, thickness, surface
2 functional groups, and mechanical strength cannot be easily controlled without extra time-/cost-
3 consuming processes. More researches should be conducted to further develop the green regeneration
4 and processing of natural fibers into superior separators for LSBs. For example, the eggshell
5 membrane (ESM) as a natural porous and freestanding membrane after fluoridation might be an ideal
6 protective layer/artificial SEI for Li-metal anodes.⁴¹² This is because the ESM as a physical block
7 may help suppress the formation of dendrites (application of its structure and morphology), while the
8 abundant N/S-containing functional groups in ESM can induce uniform deposition of Li and even
9 regulate the structures/components of SEI (application of its components and biochemical properties,
10 *e.g.*, biomineralization). Moreover, the ESM can be easily hybridized with other functional materials
11 (HAP, CNT, Al₂O₃, PbZr_{0.52}Ti_{0.48}O₃, *etc.*) and functionalized by many mature strategies in the field
12 of biology (*e.g.*, fluoridation),^{382,408,413} after which a variety of membranes can be developed with
13 desirable properties including high mechanical stability, superior ionic conductivity, excellent
14 lithiophilicity, and SEI regulation ability. And the regenerating techniques of the ESM (protein) can
15 promote its mass production and practical application.

16 (6) New functions and applications of biomass in LSBs can be further extended. One interesting
17 application of biomass is to use it as an ideal template to fabricate naturally-shaped battery materials,
18 such as bulk wood-like cathodes, bacterial cellulose templated LLZO electrolytes, and inorganic
19 nanotube active materials,^{410,414,415} in which the natural templates could be either sacrificed or
20 remained. For example, inspired by the structure of wood composed of naturally vertical channels,
21 Lu *et al.* employed it as a template to load bulk LiCoO₂ (LCO) cathode with both high areal capacity
22 and superior rate performance.⁴¹⁵ Attributed to the uniform channels inherited from wood that
23 promise lower tortuosity and higher Li-ion conductivity than conventionally prepared planar LCO
24 cathode film, the optimized LCO cathode delivered significant improvements in electrochemical
25 performances. Moreover, the biochemical and biophysical properties of biomasses could also be
26 hierarchically utilized to design materials with interesting structures and specific functions. For
27 example, Gao *et al.* proposed a modification strategy to obtain functional bacterial cellulose by
28 combining the *in-situ* microbial fermentation process of *Komagataeibacter sucrofermentans* and
29 selected additives with targeted properties.⁴¹⁶ Obviously, desirable components can be easily and
30 uniformly introduced to BC due to the biochemical properties of bacteria. Such 3D porous and

multifunctional BC products can be employed as a stretchable separator, protective layer, gel polymer, and carbon anodes.^{237,394}

II. Green processing and recycling of biomass products in LSBs.

At present, the processing technique of biomass for battery products suffers from low yield and unavoidable air pollution (*e.g.*, greenhouse gases). Hence it is still far from the ideal sustainable use of biomass, which urgently appeals for more efficient, delicate and sustainable processing techniques. For instance, products derived from biomass usually have low yields (*e.g.*, biochar yield of < 30 wt%), which cause both great waste of biomass and emission of pollution to the environment. An efficient solution to this issue is proposed to trap and utilize the released gases rather than simple emissions. Zhu *et al.* used various biomasses and KOH to prepare high SSA (3560 m² g⁻¹) biochar, meanwhile utilizing the redundant K₂O and C_xH_y flow to obtain several carbons with a wide range of morphological diversity (carbon horn, carbon tube, and carbon black nanoparticles) by placing a Cu foam collector at the end of the tube furnace.¹⁷⁷ Alonso *et al.* from another aspect also proposed a strategy to increase the revenue from lignocellulosic biomass and maximize feedstock utilization.⁴¹⁷ They integrated the biomass fractionation process with simultaneous conversion of cellulose, hemicellulose, and lignin into different products at high yields, including dissolving pulp textile (40.2 wt%), furfural (13.8 wt%), and carbon foam (15.6 wt%). In brief, the highly effective collection, high-yield conversion and application of the byproducts/intermediates are promising towards the green processing and application of biomass. Of note, the advanced extracting, processing, conversion techniques and hierarchical application strategies may enable the full use of one kind of biomass into various battery products (*e.g.*, in a tree, the trunk for electrodes and scaffolds, leaf/root for conductive additives, extracted cellulose for separators, lignin for organic electrode material/binder).

Meanwhile, given the higher and higher market share of LSBs in energy storage devices, green recycling of spent LSBs to collect the nonrenewable substances is also mandatory and highly significant. At present, researches mainly focus on strategies like mechanical pulverization-sieving, thermal calcination, acid/alkali leaching, solvent-extracting and microorganisms degradation to recycle precious metals in cathodes (Ni, Co, Li, *etc.*).⁴¹⁸ These methods themselves may cause extra environmental and processing costs and are unable to recycle other battery components like anodes and electrolytes.⁴¹⁹ This situation is mainly attributed to both the nonrenewable features of present battery chemistry and unmaturing recycling technology. Fortunately, one of the typical advantages of

1 “green battery” materials from biomass is the sustainability, which eliminates the concerns raised
2 from conventional LSB materials that exhaust unrecyclable resources and produce massive end-of-
3 life wastes. Compared to presently commercial battery materials (lithium metal oxides, polymer
4 separator and binders), biomass-derived substances are much easier to be recycled from spent
5 batteries partly because of their features like nontoxicity and water-solubility. In addition to the
6 aforementioned recycling techniques towards spent LSBs, incorporation of sustainability into battery
7 design for fresh cells will greatly enhance the success of recycling battery materials. For instance,
8 Liu *et al.* designed a fully recyclable sodium-ion battery with bipolar electrode structures consisted
9 of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (electrode material) and Al foil (a shared current collector).⁴²⁰ Of note, due to this
10 special battery design, over 98% of the solid substances in a battery can be recycled without any
11 emission of toxic wastes. Such battery designs with built-in recycling features might be adopted for
12 future LSBs.

13 Additionally, the advanced and novel characterization techniques are of great importance for
14 better understanding the underlying functioning mechanism of biomass used in LSBs, which enable
15 the rational design and application of biomass-derived battery products. With the purpose of resolving
16 the detailed reactions and the corresponding (surface/interface) structural/morphological/chemical
17 evolution for biomass products in LSBs under the real-condition electrochemical operation, *in-situ*
18 characterizations are no doubt the best choice that enables the whole electrochemical process to be
19 directly evidenced.⁴²¹ More specifically, synchrotron-based X-ray diffraction (XRD), X-ray
20 absorption spectroscopy (XAS), hard X-ray microscopy, nuclear magnetic resonance (NMR), and the
21 visualization and quantification of electrochemical and mechanical degradation are the-state-of-the-
22 art *in-situ* characterization techniques,¹⁹⁹ which are powerful tools for deeply uncovering the real
23 electrochemical processes occurring within battery systems and the relevant battery failure
24 mechanism. *In-situ* electron microscopy can be applied to clearly observe the microstructural
25 evolution of even one single particle of Ni-based $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) during battery cycling,
26 which provides new understanding to the degradation mechanism of active electrode materials at
27 micro-scale and shed light on surface/interface modification to upgrade the cyclability of devices.⁴²²
28 Assisted by *in-situ* Raman spectroscopy⁴¹⁹ and Fourier transform infrared spectroscopy (FT-IR),²⁰¹
29 the detailed function mechanism of organic electrode materials can be resolved and then purposely
30 designed for high-capacity and green LSBs.⁴²³ Moreover, the cryo-electron microscopy technique

recently applied in the battery community has enabled the atomic observation of sensitive materials including metallic Li and SEI layer,⁴²⁴⁻⁴²⁷ which can be further extended to characterize sensitive biomass-derived battery materials (organic electrode materials, unstable electrochemical intermediates, electrode/electrolyte interphase, solid-state electrolyte, *etc.*).

Overall, biomasses have a high potential for building a “green battery” system and promoting the development of sustainable energy storage technologies, which will meet the demands of societal development. After figuring out the technique and material challenges, it is of great potential to harvest targeted green battery products from biomass with high plausibility for mass production (Table 5), which can deliver high performance as well as be comprehensively recycled and reused with the great benefits and low costs. Moreover, the “green battery” design and the associated green processing could be extended to broaden the green alkali-metal secondary batteries and even other energy storage devices.

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29

Fig. 1 Various biomasses and their extracts employed in battery chemistry, including electrode scaffolds (wood and bamboo-derived carbon),^{70,73} cathode (emodin)/anode (chitin) materials,^{71,79} binders (alginate, rubber, *etc.*),⁸² electrolyte additives (vitamin C, melanin, *etc.*),⁷⁵ conductive additives (activated carbon),^{76,81} separators (cellulose, silk, *etc.*),^{72,80} and solid-state electrolytes (starch).⁷⁷

Fig. 2 Hierarchical structure assembly of silk, cellulose, and chitin. Silk, wood, and exoskeletons of arthropods are formed following the same multiscale constructing principles. (a) Silk fibrils are composed modularly with the smallest units of highly repetitive core sequences of A-B domains (amino acids with hydrophilic and hydrophobic segments), which are flanked by terminal domains (N-terminal and C-terminal). The hydrophilic domains will assemble into random coils and/or helical structures, while the hydrophobic domains transforming into β -sheet structures. (b) Cellulose consists of a linear chain of β -(1,4)-linked D-glucose units. (c) Chitin consists of a long-chain polymer of (1,4)- β -N-acetylglucosamine. The nanocrystal size of the respective crystalline units, in general, is within several nanometers. The 2D laminar and 3D helicoidal architectures at the micrometer-scale in silk fibers, cell wall layers and exoskeletons can be further constructed by orientated fibrils (along the longitudinal axis) assembled by such nanocrystals. S is on behalf of the secondary wall layer. Reproduced with permission.⁴²⁸ Copyright 2018, Springer Nature.

Fig. 3 (a) Optical microscope image of pristine cellulose. (b) Schematic illustration for dissolution processes of the cellulose in alkali/urea aqueous solutions pre-cooled to $-10\text{ }^{\circ}\text{C}$. Reproduced with permission.¹¹² Copyright 2005, Wiley–VCH. (c) Digital photo of multifilament fibers produced by a pilot machine from cellulose. Inset is the SEM image of the regenerated cellulose fiber from the cross-section. (d) SAXS pattern of the dissolved and regenerated cellulose. Reproduced with permission.¹¹³ Copyright 2007, Wiley–VCH. (e) Optical microscope image of cellulose/PANI emulsion. Reproduced with permission.¹¹⁴ Copyright 2016, Wiley–VCH.

1
2 **Fig. 4** (a) Model of cocoon silk, containing sericin and fibroin, and the following hierarchical structures (from
3 left to the right): 1 Degummed silk, containing a bundle of silk microfibrils; 2 Single silk microfiber with a
4 width of about 1 μm ; 3 Silk nanofibrils with a width of about 30 nm in a microfibril; 4 Silk nanoribbons in a
5 nanofibril; 5 β -sheets and amorphous regions in the silk nanoribbons; 6 A single β -sheet; 7 A atomic-scale
6 model of the single β -sheet layer. Reproduced with permission.¹²⁰ Copyright 2018, American Chemical Society.
7 (b) Mechanism diagram for the liquid fabrication of silk fibers by exfoliation method. Reproduced with
8 permission.¹²² Copyright 2016, Wiley–VCH. (c) Mechanism diagram of the solvent-assisted sonication method
9 for preparing the ultrathin silk nanofibril membranes. (d) SEM image of a silk nanofibril membrane.
10 Reproduced with permission.¹²³ Copyright 2016, American Chemical Society.

Fig. 5 (a) An optical microscope image of *N. oculata* microalgae. (b) The fabrication process of $\text{MnO}_2/\text{microalgae}$ precursor. (c) SEM image of $\text{MnO}_2/\text{microalgae}$ precursor. Reproduced with permission.¹²⁶ Copyright 2013, American Chemical Society. (d) A digital photo of lotus. Inset is a lotus flower. (e) Schematic illustration of pretreatment of lotus pollen to stabilize its morphology. (f) SEM image of the carbonized pollen/NiO. (g) Rate performance of the carbonized pollen/NiO. Reproduced with permission.¹²⁷ Copyright 2012, The Royal Society of Chemistry.

Fig. 6 (a) Digital photo of a tree, and its SEM image from tree growing direction. And a mode for the microstructure of wood biomass composed of cellulose and lignin polymer. Reproduced with permission.¹³⁰ Copyright 2016, American Chemical Society. (b) Diagram illustration for the chemical and structural changes of natural wood after different treatments. (c,d) SEM images of wood composed of open channels (lumina) and cellulose nanofibers. Inset of c is the digital photo of natural wood. (e,f) SEM images wood sponge with a lamellar structure composed of multiple stacked layers and the cellulose nanofibers in the obtained wood sponge. Inset of e is the digital photo of wood sponge. Reproduced with permission.⁵⁷ Copyright 2018, Elsevier.

Fig. 7 (a) A digital photo of a wood livestock and a bulk of biochar, along with a table containing various biochar fabrication methods. HTC means the hydrothermal carbonization method. Reproduced with permission.¹⁴⁶ Copyright 2011, American Chemical Society. (b) Components of biomass at different charring intensity. (c) Yields for volatile matter, fixed carbon, and ash with the increasing of charring intensity. (d,e) Profiles that exhibit the relationship among temperature, product yield with component contents (volatile matter, fixed carbon, and ash), and the BET surface area for wood and grass biomasses, respectively. Reproduced with permission.¹⁴⁷ Copyright 2010, American Chemical Society.

Fig. 8 (a) Schematic diagram illustrating the fabrication of the PRC. (b) Optical images showing the morphology evolution of rice during the PRC preparation. (c) SEM image of porous PRC. (d) Cycling performance of Li-S batteries with the PRC/Ni, PRC, and 3D rGO hosts, respectively. Reproduced with permission.¹³⁵ Copyright 2017, Wiley–VCH. (e) Schematic diagram illustrating the fabrication of the nitrogen-doped double-shelled hollow carbon spheres (NDHCS) composites. (f) TEM image of NDHCS. (g) Rate

1 capability performances with G-NDHCS and graphene (G) hosts, respectively. Reproduced with permission.¹⁴⁹
 2 Copyright 2015, Wiley–VCH. (h) Schematic diagram introducing the *in situ* preparation of porous graphitic
 3 carbon and the C/S composite. Reproduced with permission. Copyright 2016,¹⁵¹ Springer Nature. (i)
 4 Mechanism diagram indicating the fabrication of 2D carbon hybrids from a metal-polymer framework. (j)
 5 SEM image of the obtained carbonaceous aerogel. (k) SEM image of Fe₃C/2D graphene-like carbon
 6 nanosheets. Reproduced with permission.¹⁵² Copyright 2018, Wiley–VCH.

9
 10 **Fig. 9** (a) SEM image showing the materials obtained from glucose by HTC method. Inset is the magnified
 11 image. Reproduced with permission.¹⁵³ Copyright 2011, The Royal Society of Chemistry. (b) SEM image of
 12 materials obtained from glucose by acrylic acid assisted HTC method. Reproduced with permission.¹⁵⁴
 13 Copyright 2009, American Chemical Society. (c) SEM image of HTC materials obtained from alginate after
 14 the addition of CaCl₂. Reproduced with permission.¹⁵⁶ Copyright 2011, Elsevier. (d) TEM image of silk fibroin-
 15 derived carbon quantum dots. (e) Mechanism diagram illustrating the fabrication of carbon quantum dots from
 16 biomasses. Reproduced with permission.¹⁶⁰ Copyright 2018, The Royal Society of Chemistry. (f) SEM image
 17 of carbon nanofibers. Reproduced with permission.¹⁶¹ Copyright 2012, Wiley–VCH. (g) Biochar prepared by

Fig. 10 (a) Mechanism diagram showing the carbonization and activation processes of wood. (b) SEM image of AWC. (c) A hierarchical pore model and corresponding SEM image of AWC. Reproduced with permission.¹⁷² Copyright 2017, The Royal Society of Chemistry. (d) A mechanism illustration for the activation effect of KOH. Reproduced with permission.¹⁷⁸ Copyright 2012, The Royal Society of Chemistry. (e) Digital

Fig. 11 (a) A SEM image showing the bamboo-derived HPC. (b,c) A TEM image showing the ZnO@HPC and ZnO nanoparticles. (d,e) SEM images showing the morphology difference between cycled bare Li foil and

1 ZnO@HPC optimized Li foil. Reproduced with permission.²⁰⁵ Copyright 2017, Elsevier. (f) Fabrication
2 diagram for the bacterial-derived Sn@C composite. (g) Cycling performance of Sn@C composite anode.
3 Insets are the SEM image, TEM image and elemental mappings for Sn@C composite. Reproduced with
4 permission.¹⁰² Copyright 2019, American Chemical Society. (h) Diagram illustrating the fabrication of
5 Sn@aCNT. (i,j) SEM and TEM images of the Sn@aCNT composite. Reproduced with permission.²²¹
6 Copyright 2016, Wiley–VCH. (k) SEM image of the bacterial cellulose. (l, m) SEM and TEM images of the
7 obtained PBC-SnO₂ composite. (n) Cycling performances of PBC-SnO₂ and SnO₂ nanoparticles over 100
8 cycles (100 mA g⁻¹). Reproduced with permission.²³⁷ Copyright 2013, Wiley–VCH. (o) SEM image showing
9 the yolk-shell structured Si/carbon composite (Si@void@C). (p) TEM image of Si@voids@carbon. Inset is
10 the corresponding SAED pattern. (q) Cycling performance of Si@voids@C at 1C for 1000 cycles. Reproduced
11 with permission.²⁴⁵ Copyright 2012, American Chemical Society.

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Fig. 12 (a) A high-resolution TEM image CSC-NPs, along with the illustration for electronic circuit configuration of CSC-NPs, and the rate performance of different LiMn_2O_4 cathodes. Reproduced with permission.²⁵⁷ Copyright 2012, Wiley–VCH. (b) Illustration of G and M in the sodium alginate and the gelation process. Cu ion could serve as the cross-linking ion to promote the formation of strong coordination bonds. The obtained mixture could be carbonized and fluorinated to collected the $\text{CuF}_2/\text{biochar}$ cathode materials. In addition, Cu could be replaced by other metals like Ca, Ni, Fe, Al, *etc.* Reproduced with permission.¹⁰¹ Copyright 2019, Wiley–VCH. (c-g) SEM, TEM images and elemental mappings of DHCSs. Reproduced with permission.²⁶⁸ Copyright 2012, Wiley–VCH. (h) SEM image showing the N/S doped cellulose-sulfur

1 composite cathode material. Inset is the self-assembled CNCs. (i) A polysulfide adsorption test of various
 2 materials, containing cellulose nanocrystal-derived carbon (CDC), NSC, Super P, Vulcan carbon, and
 3 commercial mesoporous TiO_2 toward polysulfide anions. (j) Cycling performance of NSC/S-70, N doped
 4 cellulose (NC)/S-70, CDC/S-70, and nonporous NSC (NP-NSC)/S-70. Reproduced with permission.²⁷⁴
 5 Copyright 2015, Wiley–VCH. (k) SEM images of $\text{Al}_2\text{O}_3/\text{C}$, CeO_2/C , $\text{La}_2\text{O}_3/\text{C}$, MgO/C and CaO/C composites,
 6 respectively (scale bar = 50 μm). (l) Cycling performance of various electrodes at 0.5 C. Reproduced with
 7 permission.⁴¹ Copyright 2016, Springer Nature. (m, n) SEM images of nitrogen and phosphorus-codoped TSC
 8 and the TSC/NbC scaffold. (o) Cycling performance of TSC/NbC-S and TSC-S test at 0.1 C. Inset is a digital
 9 photo of LED lights powered by the Li-S battery. Reproduced with permission.²⁷⁷ Copyright 2019, Wiley–
 10 VCH.

14 **Fig. 13** (a) Schematic diagram illustrating the Li- CO_2 battery with a flexible wood-based cathode. (b) A digital
 15 photo of the prepared flexible cathode. (c) Typical voltage profiles of Li- CO_2 batteries with the wood-based
 16 cathode. Reproduced with permission.²⁹⁰ Copyright 2018, The Royal Society of Chemistry. (d) Schematic
 17 diagram illustrating the Li- O_2 battery with the flexible wood-based cathode. (e) SEM image of the prepared
 18 wood-based cathode. Inset is the digital photo. Reproduced with permission.²⁹³ Copyright 2017, Wiley–VCH.

Fig. 14 (a) Template for preparing PMC. (b) TEM image of PMC. (c) Rate performance of PMC and graphite anode. Reproduced with permission.³⁰² Copyright 2013, The Royal Society of Chemistry. (d) Plot showing the capacity and initial Coulombic efficiency of various biomass-derived carbon anodes with different specific surface areas.^{47,96,294,296,301-303,429-432} (e) Schematic illustration of magnesio-planetary-milling process for reducing SiO_2 from rice husk to silicon. Reproduced with permission.³⁰⁵ Copyright 2016, American Chemical Society. (f, g) SEM images of diatom frustules before and after reduction. (h) STEM mapping of Si and C. (i) Rate performance of the Si anode derived from diatom frustules. Reproduced with permission.³⁰⁶ Copyright 2018, American Chemical Society.

Fig. 15 (a) Mussel derived polydopamine. (b) Stabilization energies of PDA unit according to DFT calculations at different stages. (c) The long-term cycling performance of PDA electrode. Reproduced with permission.³³¹ Copyright 2016, Wiley–VCH. (d) Molecular model of riboflavin (vitamin B2) derived electrode material (named as P3). Reproduced with permission.³³² Copyright 2016, Wiley–VCH. (e) Preparation of dilithium (2,5-dilithium-oxy)-terephthalate (Li₄-p-DHT) from D-glucose. Reproduced with permission.⁹⁸ Copyright 2016, The Royal Society of Chemistry. (f) Full-cell design based on renewable biomass-derived organic cathode and anode. Reproduced with permission.⁷¹ Copyright 2016, Wiley–VCH. (g–i) SEM images of fresh wd-NC, and wd-NC after discharge/charge process in Li-O₂ battery. Reproduced with permission.³⁴³ Copyright 2017, Springer Nature. (j, k) SEM images of SCC before and after discharge. Reproduced with permission.³⁴⁴ Copyright 2017, Springer Nature.

Fig. 16 (a) Young's modulus of Na-alginate in a wet state impregnated with electrolyte solvent. Inset is a digital photo of alga. (b) FT-IR spectra of nano Si powder, alginate, and nano Si electrode with alginate. (c) Cycling performance of Si anode with different binders. Reproduced with permission.¹⁰⁵ Copyright 2011, The American Association for the Advancement of Science. (d) An image showing the structure formula of Alg-C and PAA-C with the model of catecholic binder, and the architecture of designed Si anode. (e) Cycling performance of Si anodes with different binders. Reproduced with permission.³⁶³ Copyright 2013, Wiley-VCH. (f, g) Schematic diagram illustrating the composition and function of dynamic cross-linked polymeric binders

in Si anode. (h) Cycling performances of Si anodes with different binders. (i) SEM images of Si electrodes using β -CDp/6AD binders before and after cycles, respectively. Reproduced with permission.³⁶⁴ Copyright 2015, American Chemical Society.

Fig. 17 (a) A digital photo of the *Acacia Senegal* and the chemical formula of gum Arabic (GA). (b) Cycling performance of Li-S batteries with GA, PVDF, and gelatin binders. Reproduced with permission.³⁵⁵ Copyright 2015, Wiley-VCH. (c) Schematic illustration of the interaction between the sulfur cathode and DSM binder. (d) Calculated binding energy between the Li₂S and reduced DSM. Reproduced with permission.³⁶⁰ Copyright 2019, Wiley-VCH.

Fig. 18 (a) Schematic illustration showing the synthetic and structural features of C-LFP/C-PPy hybrid gel framework. (b) Cycling performance of C-LFP/C-PPy and C-LFP. Reproduced with permission.³⁷⁰ Copyright 2017, American Chemical Society. (c) Schematic illustration of the transporting mechanism for Li/Na ions in the PEO/carbon quantum dots nanocomposite polymer electrolyte (PEO/CQDs NPE). Reproduced with permission.³⁷¹ Copyright 2018, Wiley–VCH. (d) Schematic illustrating the fabrication process of CQDs from biomasses like chitin, chitosan, and glucose. Reproduced with permission.³⁷² Copyright 2015, Wiley–VCH.

Fig. 20 (a) Schematic diagram illustrating the fabrication process of bacterial cellulose supported composite gel polymer electrolyte named PMM-CPE. (b) Symmetric test of a battery using the PMM-CPE at various current densities. (c) Cycling performance of batteries using LiPF₆/EC-DMC electrolyte, LiODFB/PC electrolyte and PMM-CPE. (d) Left is 4.5-class LiCoO₂/Li cell design using the PMM-CPE. Middle is the flexible battery model. Right is a digital photo of a LED lighted by the flexible LiCoO₂/Li cell at its bent state. Reproduced with permission.⁴⁰⁰ Copyright 2018, The Royal Society of Chemistry. (e) Schematic diagram illustrating the interactions between BC chains and solvents. (f, g) SEM images showing the BC-based gel polymer electrolyte skeleton and the BC-GPE. (h) Temperature related voltage profiles for batteries using LE-

1 S and BC-GPE at 1C. Reproduced with permission.⁴⁰¹ Copyright 2018, The Royal Society of Chemistry. (k)
2 Digital photos of corn and corn starch. (i) Crosslinking reaction between starch and KH560. (j) Cycling tests
3 of Li-S batteries using the starch hosted electrolyte at 25 °C. Reproduced with permission.¹⁰³ Copyright 2016,
4 The Royal Society of Chemistry.

1 **Table 1** Summary of biomass-derived battery products for LSBs by various processing methods.

Processing method	Raw material	Product	Structure	Application	Capacity (mAh g ⁻¹)	Ref.
Activation	Silk	HPNC-NS	2D nano sheets	Anode	1865 at 0.1 A g ⁻¹	96
Magnesiothermic reduction	Rice husk	Si _{RH}	Nano porous structure	Anode	1554 at 2 A g ⁻¹	97
Catalytic synthesis and lithiation	Glucose	Li ₄ - <i>p</i> -DHT	NA	Cathode	110 at 25 mA g ⁻¹	98
Carbonization and activation	Wood	S@C-wood	Aligned channels	Cathode scaffold	1274 at 0.156 mA cm ⁻²	99
Chelation and carbonization	D-gluconic acid lactone	LFP/C	Nano plates	Cathode coating	167 at 17 mA g ⁻¹	100
Gelation and carbonization	Sodium alginate	Si@C@Cu	3D porous structure	Anode scaffold	1500 at 1 A g ⁻¹	101
Bio-concentration/carbonization	Bacteria absorbing Sn	Sn@C	Nanorods	Anode scaffold	560 at 1 A g ⁻¹	102
Crosslinking	Starch	Starch/LiTFSI AHM	NA	Polymer electrolyte	880 at 167.2 mA g ⁻¹	103
Electrospinning	Agarose	separators (LMO)	Nanofiber	Separator	110 at 1.52 mA cm ⁻²	104
Electrospinning	Silk fibroin	Fibroin interlayer (LTO anode)	Fiber	Interlayer	125 at 350 mA g ⁻¹	433
Adsorption	Collagen hydrolysate	CH@AGM (LMO)	NA	Interlayer	350 mA g ⁻¹	434
Solvothermal treatment	Eggshell membrane	TESM (LFP)	Membrane	Interlayer	120 at 1.8 mA cm ⁻²	412
Extraction	Seaweed	Na alginate (Si anode)	NA	Binder	150 at 170 mA g ⁻¹	105

2 HPNC-NS: hierarchical porous N-doped carbon nanosheet, Si_{RH}: rice husk-derived silicon, Li₄-*p*-
3 DHT: dilithium (2,5-dilithium-oxy)-terephthalate, S@C-wood: carbonized wood/sulfur composite,
4 LFP/C: carbon-coated LFP, Si@C@Cu: Cu particles embedded 3D multilayer silicon/carbon

1 composite, Sn@C: ultrafine Sn nanoparticles embedded in nitrogen and phosphorus co-doped porous
 2 carbon nanorods; starch/LiTFSI: electrolyte consisting of starch and LiTFSI salt, AHM separators:
 3 agarose-biofunctionalized, dual-electrospun heteronanofiber mat separators, CH@AGM: collagen
 4 hydrolysate coated on absorbed glass mat, TESM: trifluoroethanol modified eggshell membrane.

5 **Table 2** Characteristics of activated lignin by different activation agents with the highest BET surface
 6 areas at the corresponding temperatures. Reproduced with permission.¹⁸¹ Copyright 2000, Elsevier.

Activation agent	Temperature (°C)	BET surface area (m ² g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)
KOH	800	1500	0.12	0.60
K ₂ CO ₃	800	2000	0.2	0.76
NaOH	800	1320	0.14	0.56
Na ₂ CO ₃	800	760	0.08	0.32
ZnCl ₂	600	1300	0.06	0.52
H ₃ PO ₄	600	1000	0.04	0.42

7 **Table 3** Summary and comparison of Li-metal anodes accommodated with various scaffolds.

Scaffold	Maximum J (mA cm ⁻²)	Lifespan (hours)	Nucleation overpotential (mV)	CE (%)	Capacity of full cell (mAh g ⁻¹)	Capacity Retention (%)	Ref.
MgO@WC	15	~1600	10.3	98	LCO, 162	80 300 cycles	206
ZnO@HPC	2	800	30	97	LCO, 148	NA	205
Layered rGO	3	222	NA	NA	LCO, 130	NA	211
CC/CNT	5	500	125	97	LFP, 160	98/100 cycles	65
3D Nickel	5	200	NA	NA	LFP, 130	NA	210
NGCFs	2	1200	16	99	LFP, 130	90200 cycles	209
Cu-VAMCs	1	200	73	98	LFP, 134	90/100 cycles	212

8 J: current density, 1 C for LFP: 174 mA g⁻¹, 1 C for LCO: 280 mA g⁻¹.

9

1 **Table 4** Physical and electrochemical parameters of PP separator and biomass-derived separators.

Items	Method	Thickness (μm)	Uptake (%)	Young's modulus (MPa)	Thermal stability ($^{\circ}\text{C}$)	Ionic conductivity (mS cm^{-1})	Ref.
PP	Dry/wet process	25	125	260	165	0.65	379
Cellulose nonwoven	Electrosp -inning	25	340	NA	270	1.75	377
Cellulose/ PVDF-HFP	Electrosp -inning	27	280	960	300	1.04	377
FCCN separator	Paper making	40	270	690	300	2	379
Cellulose/P SA	Paper making	40	260	NA	300	1.2	378

2 **Table 5** Plausibility for mass production of battery materials from various kinds of biomasses.

Raw biomass materials	Selective target battery material	Plausibility score
	Conductive additive	3
Wood	Electrode scaffold	3
Bamboo	Separator/protective layer for electrodes	2
(cellulose)	Anode material	3
	Catalytic cathode	2
	Conductive additive	3
	Electrode scaffold	2
Straw	Separator/protective layer for electrodes	1
(cellulose)	Anode material	2
	Catalytic cathode	1
	Conductive additive	3
Cotton	Electrode scaffold	3
Kapok tree fruit	Separator/protective layer for electrodes	3
(cellulose)	Anode material	3
	Catalytic cathode	1
	Gel/polymer electrolyte	2
Bacteria cellulose	Electrode scaffold	2

(cellulose)	Separator/protective layer for electrodes	2
	Anode material	2
	Catalytic cathode	2
	Binder	3
Seaweed	Conductive additive	3
(cellulose/alginate)	Electrode scaffold	3
	Conductive additive	2
Pollen	Electrode scaffold	2
(amino acid/cellulose)	Anode material	2
Bacteria	Electrode scaffold	1
(protein/ polysaccharide)	Anode material	2
Corncob	Conductive additive	3
Coconut shell	Electrode scaffold	3
(cellulose/hemicellulose)	Anode material	3
	Gel/polymer electrolyte	2
Corn	Binder	2
Potato	Electrode scaffold	3
Soybean	Anode material	3
(starch/glucose)	Organic electrode	1
Herbal rhubarb (Emodin)	Organic electrode	2
	Organic electrode	2
Carrot	Binder	2
Tomato	Electrolyte additive	2
Beta vulgaris L.	Conductive additive	3
(natural	Electrode scaffold	3
pigments/polysaccharide)	Anode material	3
Fungus	Conductive additive	3
Wood	Electrode scaffold	3
(natural	Anode material	3

pigments/polysaccharide/lignin)	Organic electrode	2
	Conductive additive	2
	Electrode scaffold	3
Cocoon	Separator/protective layer for electrodes	3
(protein)	Anode material	3
	Catalytic cathode	2
	Conductive additive	3
	Electrode scaffold	3
Soybean	Separator/protective layer for electrodes	2
(protein)	Anode material	3
	Catalytic cathode	1
	Conductive additive	1
	Electrode scaffold	1
Eggshell membrane	Separator/protective layer for electrodes	2
(protein)	Anode material	1
	Catalytic cathode	2
Rice husk	Electrode scaffold	2
Diatom	Anode material	3
(biosilicone)		
Gum tree	Gel/polymer electrolyte	2
(natural gum)	Binder	3
Shrimp/crab shells	Gel/polymer electrolyte	2
(chitin)	Binder	3
Mussel	Binder	1
(adhesive protein)		

1 1: low plausibility, 2: medium plausibility, 3: high plausibility.

2

3

4

5

A glossary of abbreviations

Abbreviation	Item	Location
AAs	Activation agents	Page 24, line 11
ACs	Activated carbons	Page 8, line 9
AG	Agarose	Page 19, line 20
AHM separators	Agarose-biofunctionalized, dual-electrospun heteronanofiber mat separators	Page 101, line 6-7
Ala	Alanine	Page 11, line 15
ALG	Alginate	Page 49, line 15-16
Alg-C	Catechol groups modified Alg	Page 49, line 22
AWC	Activated wood carbon	Page 23, line 29
BC	Bacterial cellulose	Page 58, line 17
BC-GPE	BC-based polymer electrolyte	Page 59, line 2-3
BPPG-800-A	Banana peel pseudographite	Page 42, line 29
CA-wood/Ru	Carbonized natural wood loaded with Ru catalysts	Page 41, line 10
CC	Corncob carbon	Page 43, line 1
CC/CNT	CNTs modifying carbon cloth	Page 31, line 14-15
c-CNPs	Surface-carboxylated carbon nanoparticles	Page 42, line 28-29
CEI	Cathode electrolyte interphase	Page 52, line 21
Cellulose/PSA	Nonwoven separator composed of cellulose and PSA	Page 54, line 25

Cellulose/PVDF-HPF	Nonwoven separator composed of cellulose and PVDF-HPF	Page 54, line 24
CFs	Carbon fibers	Page 8, line 9
CH ₂ O	Formaldehyde	Page 13, line 2-3
CJS	Centrifugal jet-spinning	Page 56, line 2
CL	Carbonized leaf	Page 56, line 27
CMC	Carboxyl methyl cellulose	Page 35, line 29
CNF	Wood cellulose nanofibril	Page 55, line 10-11
CNSs	Carbon nanosheets	Page 8, line 9
C-PPy	Cross-linked polypyrrole	Page 52, line 11
CQDs	Carbon quantum dots	Page 21, line 25
CSC-NPs	Carbon coated single-crystal LiMn ₂ O ₄ nanoparticle	Page 37, line 21
CSEMs	Carbonized sucrose-coated eggshell membrane	Page 56, line 29
CSH	Cotton seed hull	Page 26, line 4
CSs	Carbon spheres	Page 8, line 9
CST	Carbonized cap skin tissue	Page 42, line 28
CTAC	Trimethylammonium cation	Page 22, line 12-13
Cu-VAMCs	Cu current collector with vertically aligned microchannels	Page 31, line 16
C-wood	Carbonized wood loaded with ZnO	Page 30, line 28
DHCS	Double-shelled hollow carbon spheres	Page 38, line 27-28
DSM	3D network binder	Page 50, line 24

Emodin	6-methyl-1,3,8-trihydroxyanthraquinone	Page 46, line 16-17
ESM	Eggshell membrane	Page 62, line 12
F127	Ploxamer	Page 22, line 12
FCCN separator	Flame-retardant cellulose-based composite nonwoven separator	Page 54, line 25
G	α -L-guluronic acid	Page 36, line 7
GA	Gum arabic	Page 50, line 13
GG	Guar gum	Page 49, line 28
Gly	Glycine	Page 11, line 15
G-NDHCS-S	Graphene wrapping N-DSHCS	Page 18, line 28
HAP	Hydroxyapatite nanowires	Page 55, line 17
HAP/CF	HAP/CF composite	Page 55, line 18
HFIP	Hexafluoroisopropanol	Page 12, line 2
HPC	Hierarchical porous carbon	Page 30, line 19
HPNC	Hierarchically porous nitrogen-rich carbon	Page 43, line 2
HPNC-NS	N-doped carbon nanosheets	Page 42, line 17
ILs	Ionic liquids	Page 9, line 23
KH560	γ -(2,3-epoxypropoxy)propyltrimethoxysilane	Page 60, line 6-7
LE-S	Liquid electrolyte-immersed separator	Page 59, line 4
LFP/C	Carbon coated LFP	Page 101, line 4
Li4-p-DHT	Dilithium (2,5-dilithium-oxy)-	Page 46, line 10-11

	terephthalate	
LiCl/DMAc	LiCl/N,N-dimethylacetamide	Page 9, line 23
LNPs	Lignin nanoparticles	Page 21, line 27
LSBs	Lithium secondary batteries	Page 1, line 14-15
M	β -D-mannuronic acid	Page 36, line 7
Mg15	MgO templated cotton-derived carbon	Page 43, line 2
MgO@WC	MgO modified wood carbon	Page 31, line 12
<i>N. oculata</i>	<i>Nannochloropsis oculata</i>	Page 13, line 22
N-doped fused CF	N-doped fused carbon fibers	Page 43, line 1
N-DSHCS	N-doped double-shelled hollow carbon spheres	Page 18, line 24
NGCFs	Nitrogen-doped graphitic carbon foams	Page 31, line 15
Ni ₂ P@NPC	NPC loaded with Ni ₂ P nanoparticles	Page 34, line 25-26
NMMO	N-methylmorpholine-oxide	Page 9, line 15
NPC	N and P dually-doped carbon nanosheets	Page 34, line 25
N-PCNFs-600	N-doped porous graphitic carbon nanofibers	Page 43, line 1
NSC	N and S dually-doped carbon	Page 39, line 7
NSC-S	Carbon/sulfur composite	Page 39, line 8
N-XG-GG	A 3D network binder	Page 50, line 16
OHC	Ox horn derived carbon	Page 43, line 3
P123	Polyethylene oxide-polypropylene	Page 22, line 11-12

	oxide-polyethylene oxide	
P3	Flavin polymer	Page 46, line 2-3
PAA	Poly(acrylic acid)	Page 49, line 22
PAA-C	Catechol groups modified PAA	Page 49, line 22
PANI	Polyaniline	Page 10, line 22
PBC	Pyrolyzed bacterial cellulose	Page 34, line 15
PBC-SnO ₂	Pyrolyzed bacterial cellulose/SnO ₂ composite anode	Page 34, line 16
PDA	Polydopamine	Page 33, line 13
PE	Polyethylene	Page 6, line 10
PEF	Poly(ethylene furanoate)	Page 6, line 24
PEO	Polyethylene oxide	Page 52, line 25
PEO-HPC	Poly(ethylene oxide)-2- hydroxypropylcellulose	Page 60, line 1-2
PET	Poly(ethylene terephthalate)	Page 6, line 25
PGC	3D porous graphitic carbon	Page 19, line 3-4
PI	Polyimide	Page 54, line 11
PLA	Poly lactide	Page 6, line 24
PMC	Protein derived mesoporous carbon	Page 42, line 11
PMM-CPE	Bacterial cellulose supported poly(methyl vinyl ether-alt-maleic anhydride) plus propylene carbonate/lithium difluoro(oxalato) borate	Page 58, line 18-19

PP	Polypropylene	Page 6, line 10
PRC	Puffed rice derived carbon	Page 18, line 12-13
PS	Polystyrene	Page 13, line 27
PSA	Polysulfonamide	Page 54, line 23
PVDF	Poly(vinylidene fluoride)	Page 49, line 5
PVDF-HPF	Poly(vinylidene fluoride-co-hexafluoropropylene)	Page 54, line 23
PVP	Polyvinylpyrrolidone	Page 36, line 1
RC	Rice husk derived carbon	Page 31, line 7
reDNA/ALG hybrid binder	Renatured DNA/Alginate	Page 49, line 15-16
rGO	Reduced graphene oxide	Page 18, line 18
rGO	Layered reduced graphene oxide	Page 31, line 14
S@C-wood	Carbonized wood embedded with sulfur	Page 101, line 3
SA	Sodium alginate	Page 36, line 5
SDCA	Sodium dihydrogen citrate	Page 56, line 12
SDS@TiO ₂	Anatase TiO ₂ -coated carbon microcapsules	Page 39, line 25-26
SEI	Solid-electrolyte interphase	Page 5, line 11-12
Ser	Serine	Page 11, line 15
Si@C@Cu	Si/C/Cu composite	Page 36, line 12
Si@SiO _x /C	Silicon nanoparticles with a thin layer of SiO _x and carbon	Page 35, line 26-27

Si@void@C	A yolk-shell structured Si/C	Page 35, line 20-21
SiO ₂ -coated PP	PP separator coated with SiO ₂	Page 56, line 16
Si _{IRH}	Rice husk derived silicon	Page 101, line 2
Sn@aCNT	Sn/amorphous carbon nanotube composite	Page 33, line 14
Sn@C	Ultrafine Sn nanoparticles embedded in nitrogen and phosphorus co-doped porous carbon nanorods	Page 32, line 28
SNRs	Silk nanoribbons	Page 11, line 25
SSA	Specific surface area	Page 16, line 22
TAC	Tomato activated carbon	Page 26, line 18
TSC	<i>Trichoderma</i> spore-derived carbon	Page 39, line 30
TSC/NbC	Carbon/NbC composite	Page 40, line 1
wd-NC	Wood-derived N-doped carbon	Page 47, line 15
XG	Xanthan gum	Page 50, line 17
ZnO@HPC	HPC modified with ZnO	Page 30, line 20-21
β-CDp/6AD	Dynamic cross-linked polymeric binders	Page 50, line 4
CH@AGM	Collagen hydrolysate coated on absorbed glass mat	Page 101, line 1
TESM	Trifluoroethanol modified eggshell membrane	Page 101, line 1

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For table of contents use

This review summarizes the employment of different biomass materials for green lithium secondary batteries.

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