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# Biomass-derived nanostructured porous carbons for lithium-sulfur batteries

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**ABSTRACT Biomass has been utilized as an energy source for thousands of years typically in the form of wood and charcoal. Technological advances create new methodologies to extract energy and chemicals from biomass. The biomass-derived nanostructured porous carbons (BDNPCs) are the most promising sulfur hosts and interlayers in rechargeable lithium-sulfur (Li-S) batteries. In this article, a comprehensive review is provided in the synthesis of nanostructured porous carbon materials for high-performance rechargeable Li-S batteries by using biomass. The performances of the Li-S batteries dependent on the porous structures (micro, meso and hierarchical) from BDNPCs are discussed, which can provide an in-depth understanding and guide rational design of high-performance cathode materials by using low-cost, sustainable and natural bio-precursors. Furthermore, the current existing challenges and the future research directions for enhancing the performance of Li-S batteries by using natural biomass materials are also addressed.**

**Keywords:** biomass, lithium-sulfur battery, porous carbon, cathode, sulfur hosts, interlayers

## INTRODUCTION

Carbon is an essential constituent of the universe and all living organisms, which is the 4th most abundant element in the universe and the 2nd most common element in human body with a percentage of 18.5% by mass [1]. It has many forms or allotropes, which are widely used in many fields. Among them, porous carbon has been well developed and extensively utilized in modern industrial society due to its porous microstructure with immense surface area [2–4], high porosity along with good physiochemical stability [5,6], large adsorption capacity [7] and excellent reactivity [8–10]. However, the fabrication of such porous carbon faces some challenges as it is a complex and expensive synthesis process, involving high temperature and non-renewable precursors consequently limiting its commercial applications. Therefore, the importance of finding facile and cost-effective routes for obtaining porous carbon is a high priority. Due to the fact that naturally available materials have hierarchically nano-structures with inorganic/organic composites, the derivation of functional materials from naturally available resources has always been very attractive for academic researchers and industrial applications in order to obtain environmentally friendly materials with facile techniques [11]. For example, biomass-derived nanostructured porous carbons (BDNPCs) have been used in many applications such as adsorbents, $CO_2$ storage, catalytic supports or catalysts [12,13]. Very recently, they have also been widely employed in the energy storage devices such as rechargeable lithium-sulfur (Li-S) battery.

Li-S battery is one of the most promising candidates to satisfy commercialized electrochemical power storage sources due to its high theoretical capacity and energy density of 1,675 mA h $g^{-1}$ and 2,500 W h $kg^{-1}$, respectively. However, Li-S batteries suffer many issues including low sulfur utilization, poor long-term cycling stability, large volumetric expansion and low columbic efficiency, as detailed in next section, which has greatly limited their practical use. Various attempts have been made to overcome the above mentioned problems such as the use of

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composites of sulfur with graphene or graphene oxide [14–16], carbon nanotubes/nanowires/nanofibers and porous carbons [6,15,17–19]. Among various materials, porous carbons have attained most considerable attention due to their porous structure and high conductivity, large surface area, pore volume and strong adsorption ability in attempts to overcome the problems associated with Li-S batteries. As mentioned above, BDSPCs have also been well developed with an aim at overcoming these challenges. The use of BDSPCs plays a key role in the enhancement of performance of Li-S batteries.

In this mini review, biomass-derived nanostructured porous carbons for Li-S batteries are summarized and prospected. General synthetic methods for nanostructured porous carbon are presented. By analyzing the working principles and the current challenges for Li-S batteries especially with regard to sulfur cathodes, a detailed and comprehensive overview of advances involving utilization of BDSPCs in Li-S batteries in recent years and the influence of porous structure of BDSPCs on the battery performance are discussed. Furthermore, current challenges and approaches are introduced for addressing the shortages from the perspective of the use of natural biomass materials as precursors.

## PRINCIPLE AND FUNDAMENTALS OF LI-S BATTERIES

For Li-S batteries, the electrodes consist of a lithium metal anode and a sulfur cathode, which are separated by a separator filled with electrolyte [15,20]. Sulfur has a theoretical specific capacity of 1675 mA h $g^{-1}$. The average voltage of the Li-S cell is 2.15 V with a theoretical energy density of 2500 W h $Kg^{-1}$ or 2800 W h $L^{-1}$ [21,22]. Fig. 1 shows a schematic configuration of a typical Li-S cell. The electrical energy is stored/released through a reversible redox reaction during charge/discharge operation [20]. The reaction starts from discharge, because sulfur is in a charged state [15]. On discharge, the Li metal at the anode is oxidized to produce Li ions and electrons. The Li ions and electrons produced travel to the cathode via the electrolyte and through the external circuit, respectively. As a result, sulfur is converted to lithium sulfide. The reverse reaction occurs during the charging process. The anode and cathode reactions are expressed as follows [21]:

$$16Li \rightarrow 16Li^{+} + 16e^{-} \text{(anode reaction)} \quad (1)$$

$$S_8 + 16Li^{+} + 16e^{-} \rightarrow 8Li_2S \text{ (cathode reaction)} \quad (2)$$

It is widely accepted that the discharge of S proceeds through multiple steps [20,21,23]:

$$S_8 + 2Li^{+} + 2e^{-} \rightarrow Li_2S_8 \quad (3)$$

$$3Li_2S_8 + 2Li^{+} + 2e^{-} \rightarrow 4Li_2S_6 \quad (4)$$

$$2Li_2S_6 + 2Li^{+} + 2e^{-} \rightarrow 3Li_2S_4 \quad (5)$$

$$Li_2S_4 + 2Li^{+} + 2e^{-} \rightarrow 2Li_2S_2 \quad (6)$$

$$Li_2S_2 + 2Li^{+} + 2e^{-} \rightarrow 2Li_2S \quad (7)$$

A typical charge/discharge profile in a Li-S cell is illustrated in Fig. 1 [22]. Two voltage plateaus at 2.4 and 2.0 V during discharge correspond to the reduction of long chain and short chain polysulfides, respectively. During the charge cycle, two plateaus at 2.2 and 2.5 V are observed. The five steps of the discharge procedure can be divided into two parts [24,25]. The initial three steps which occur at high voltage plateaus exhibit fast reaction kinetics, corresponding to the formation of long chain lithium polysulfides ($Li_2S_x$, $x \geq 4$) which are readily dissolved in the liquid electrolyte. In the latter two steps (low and long voltage plateaus), insoluble Li polysulfides ($Li_2S_x$, $x \leq 4$) are formed which precipitate out at the cathode. The kinetics of the latter two steps are much slower due to liquid $Li_2S_4$/solid $Li_2S_2$ and solid $Li_2S_2$/$Li_2S$ interfaces, and the conversion from $Li_2S_2$ to $Li_2S$ is difficult due to the sluggish kinetics as a result of the solid-state reactions [20–23,26,27].

Despite the considerable advantages for the Li-S cell, there are also many challenges. Of these, the first one is the

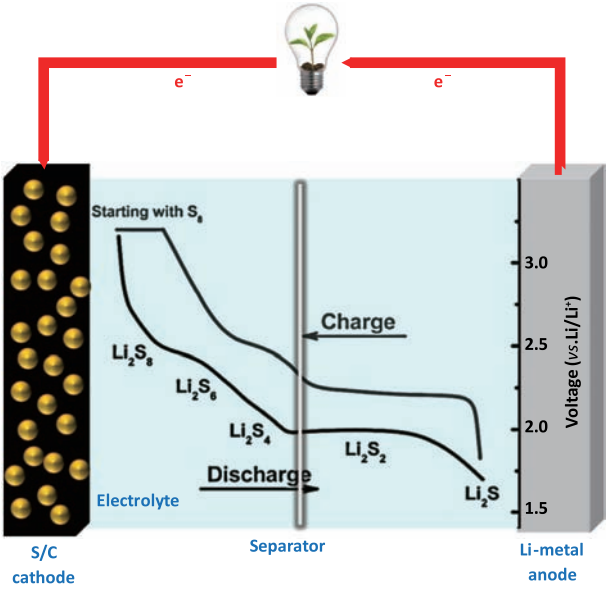


**Figure 1** Schematic configuration, typical charge/discharge profile and chemistry of sulfur cathode in a traditional liquid Li-S cell.

poor intrinsic conductivity of sulfur ($5\times10^{-30}$ S cm$^{-1}$) [27] and the insulating nature of $Li_2S$, which results in low utilization of the active material and gives rise to limited rate capability. The second one is the volumetric change which occurs during the charge/discharge process. Due to the difference between the densities of sulfur (2.03 g cm$^{-3}$) and $Li_2S$ (1.66 g cm$^{-3}$), the volume changes by up to 80% during the conversion between sulfur and $Li_2S$ [21]. This large volume change may deteriorate the architecture of electrode, leading to the degradation of the active material, and hence to poor mechanical stability and severe capacity fade. Thirdly, the high-order polysulfides are soluble in the electrolyte. These dissolved polysulfide anions can freely be transported between the anode and cathode, which is the so-called shuttle effect [15,21]. The high-order polysulfides diffuse to the surface of the Li anode and are reduced to insoluble low-order polysulfides. Then these low-order polysulfides return to the cathode and are oxidized to high-order polysulfides. This results in the loss of active material, self-discharge behavior, passivation of the Li-metal surface with insoluble product, and an increase in impedance and decrease in columbic efficiency [20,21,27,28].

To address these issues, developing sulfur/carbon composite cathodes with sulfur embedded into the conductive carbon frameworks has been proven as one of the most promising perspectives over the past decade for improving the performance of Li-S batteries. By creating composites of sulfur with carbon, the poor conductive properties of sulfur can be constrained within the carbon frameworks resulting in great enhancement of the conductivity of the sulfur electrode, and the solubility losses of the intermediate sulfur species in the liquid electrolyte can be restrained owing to the excellent sorption properties of the carbon. Both factors lead to a much improved electrochemical performance of Li-S batteries. Although numerous nanoporous carbon-based materials, including carbon nanospheres, carbon nanotubes, graphene nanosheets, etc., show good performance in Li-S batteries, most of these require a complex synthesis process, using expensive and non-renewable precursors. Fortunately, many biomass materials in the nature can be efficiently transformed into various nanostructured porous carbons. The preparation and cost of these BDSPCs are much easier and cheaper than the above-mentioned nanoporous carbon-based materials. Numerous literatures have reported the use of BDSPCs in Li-S batteries as sulfur host materials that exhibit excellent electrochemical properties. In the coming sections, the synthesis strategy of nanostructured porous carbon is introduced, and the advance made by using low-cost and eco-friendly biomass materials in Li-S batteries to achieve high utilization of active material, good cycling stability, high columbic efficiency and large power density is presented.

## SYNTHESIS OF NANOSTRUCTURED POROUS CARBONS FROM BIOMASS

Biomass from agricultural crop residues, forest crops and other renewable resources could be converted into nanostructured porous carbons with high surface area and pore volume by well-developed facile methods [29]. Thermochemical conversion technologies, such as pyrolysis or hydrothermal carbonization (HTC) are widely used to derive carbon from biomass. In pyrolysis, the biomass is thermo-chemically degraded at elevated temperatures, normally in the range of 300–650°C under inert atmosphere whereas the HTC converts the biomass into carbon by utilizing water as a carbonization medium in a milder temperature range (180–260°C) under autogenic pressure [30–36]. HTC is advantageous because of the relatively high yields of carbonaceous solids and the elimination of energy intensive pre-drying [32]. However, both pyrolysis and HTC cannot fulfill all of the required properties of nanostructured porous carbons because they produce materials with limited surface area and porosity [37]. In general, high surface area, large pore volume and well defined pore size distribution are the key parameters to obtain excellent electrochemical performance in Li-S batteries. Hence, many researchers have implanted the nano-template into the biomass precursor before the pyrolysis, followed by removal of template, which can generally be denoted as sacrificial template method (STM) [29,30]. Compared to the direct pyrolysis or HTC, the STM prepared carbon not only owns a higher surface area, but also has a well-uniformed pore size distribution determined by the parameter of the sacrificial template. Nevertheless, to achieve the best required battery performance, the carbon obtained from the above-mentioned method must be subjected to an activation process that can further tune the carbon structure and morphology [37,38].

The tuning of pore size distribution and surface area after pyrolysis or HTC of biomass is carried out by physical or chemical activation. In physical or thermal activation, the pyrolyzed carbon is exposed to an oxidizing atmosphere (such as $CO_2$, steam or a mixture of both) in the temperature range of 600–1200°C and the porosity is developed by partial etching of the carbon. On the other hand, in chemical activation the carbon precursor is mixed with some chemicals such as NaOH [39], KOH [40–48], $ZnCl_2$

[5,49–51], $H_3PO_4$ [52–54] and $H_2SO_4$ [3,55], and then carbonization and activation are accomplished simultaneously at a slightly lower temperature ranged within 300–950°C. Of the activating agents, KOH is the most promising because it can produce nanostructured porous carbons with higher yields at lower temperature, and produce materials with ultrahigh specific surface area up to 3000 $m^2 g^{-1}$ with a well-defined pore size distribution. The activation by KOH is a convoluted process and involves many chemical reactions. Generally, the reaction between KOH and carbon commences as solid-solid reaction and proceeds through solid-liquid reactions [56,57]. Marsh *et al.* [58] described the activation by KOH and suggested that two main processes lead to the chemical activation. In the first process, the alkali metal act as a catalyst and carbon is consumed by oxygen, and as a result CO and $CO_2$ is produced. In the second process, hydroxide is reduced to give free potassium metal, and this free metal penetrates into the carbon lattice. As a result of this penetration carbon lattice is expanded and the speedy removal of free metal from carbon occurs. Otowa *et al.* [57] described the KOH activation of petroleum coke by various simultaneous/consecutive reactions. They proposed that below 700°C $H_2O$, $H_2$, CO, $CO_2$, $K_2O$ and $K_2CO_3$ were the main products and above 700°C the formation of metallic potassium and activation process occurs (Fig. 2). Thus, the carbon activated by KOH shows high surface area and porosity due to the synergetic effect of physical and chemical activation, and intercalation of metallic K into the carbon lattice [38]. The degree of activation can be controlled by two parameters: the amount of KOH and the activation temperature [59]. However, the reactivity of the various carbon sources along with these activation parameters also play significant role in determining the pore structure and surface chemistry. In general, lower surface area and pore volume are obtained with higher pre-carbonization temperature whereas high KOH/Carbon ratio and activation temperature result in high porosity [38]. Despite the fact that both physical and chemical activation can produce carbons with a porous network, chemical activation has the advantage over physical activation because it produces nanostructured porous carbons at lower temperature, shorter time, with a higher surface area and a more uniform pore size distribution [12,13,29,33,37,38,60–66].

## BIO-DERIVED CARBON AS SULFUR HOST IN Li-S BATTERIES

The bio-derived carbons are of much interest due to low cost, high availability and good product yield of the bio-sources. These sources can be synthesized to green, energy efficient and cost effective carbons. Bio-carbon with particular categories of shapes and pores can be obtained by employing modern carbonization techniques. Moreover, considering the fact that surface chemistry is important especially for Li-S batteries, inherent doped carbon can also be produced from these cheap resources. The carbons produced from bio-sources have high surface area and pore volume which when employed in energy storage devices, showed excellent electrochemical properties. The carbons obtained from biomass which are applied as sulfur hosts in Li-S batteries, can be divided into microporous, mesoporous, hierarchically porous and other nanostructured carbons according to the structure of the carbon obtained. In the following sections, the important progress in such carbon materials as sulfur hosts in Li-S batteries is summarized.

### Bio-derived microporous carbon

According to the International Union of Pure and Applied Chemistry (IUPAC), a microporous carbon contains pores with size less than 2 nm [20]. The sulfur composite with microporous carbon is a good choice to immobilize the sulfur and to avoid polysulfide dissolution [18]. Although many works have been done on S/microporous carbon composites, researchers continue to show much interest in utilizing bio-derived carbons in Li-S batteries due to their facile synthesis, low cost and high availability and sustainability.

Gu *et al.* [67] used bamboo-derived carbon as host of sulfur for Li-S battery. They activated the bamboo carbon

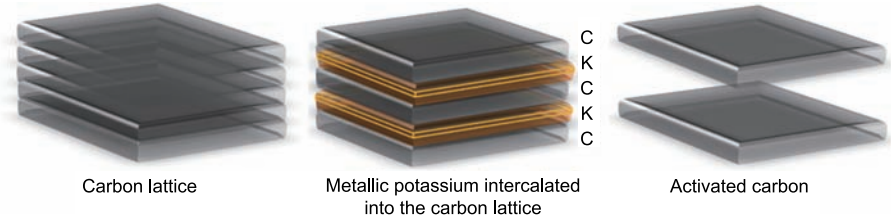


**Figure 2** The activation process above 700°C, intercalation of carbon lattice by metallic K, expansion of carbon lattice and rapid removal of intercalated metallic K from the carbon matrix. Reprinted with permission from Ref. [59], Copyright 2012, Institute of Physics.

with KOH and annealed it at 700°C to create microporous structure which enhanced the surface area by up to 14 times and pore volume to almost 8 times. The sulfur was infiltrated into the treated carbon to achieve the S/bamboo carbon composites with S loadings of 40, 50 and 60 wt.%. Excellent electrochemical properties, such as high initial capacity (1295 mA h $g^{-1}$) and Columbic efficiency (≥ 95%) were attained in the sample with 50 wt.% S loading. Yang *et al.* [68] employed a facile and bio-inspired safe technique to synthesize activated carbons with a high product yield of 40.7 wt.% from waste apricot shells. The apricot shell was firstly pyrolyzed at 750°C and then mixed with KOH and heated at 750°C to obtain activated porous carbon. The obtained porous carbon showed large pore volume (1.05 $cm^3$ $g^{-1}$) and surface area (2269 $m^2$ $g^{-1}$) with irregular particles that were widely distributed from several up to tens of micrometers. The sulfur was infiltrated into the porous carbon through capillary action and the pore size distribution (0.6–2.0 nm) of the as-prepared porous carbon allowed sulfur to be loaded in a highly dispersed state. The obtained S/porous carbon composite showed excellent electrochemical performance due to the different pore sizes and partially graphitized structure. It was able to effectively inhibit the shuttle of polysulfides, enhance the conductivity and facilitate gain or loss of electrons. Its discharge capacity was as high as 613 mA h $g^{-1}$ after 200 cycles at 1 C.

It has been stated that the microporous carbon can confine only small sulfur molecules due to the space limitation and hence the formation of soluble polysulfides can be avoided. However, there are still some questions regarding this hypothesis since no solid evidence has been reported till now [69]. Helen *et al.* [70] demonstrated the direct transformation of sulfur to smaller sulfur molecules ($Li_2S_2$/$Li_2S$) by using ultra-microporous carbon (Fig. 3) as sulfur host and carbonate-based electrolyte. Coconut shell derived ultra-microporous carbon was synthesized by carbonization at 600°C with KOH as activating agent. The S/ultra-microporous carbon composite with 45.8 wt.% S loading was obtained by vacuum assisted melt-diffusion. The lithiation/delithiation and capacity fading mechanism of the composite was analyzed by using X-ray photoelectron spectroscopy (XPS) sputter profiling, which demonstrated the direct transformation from S to $Li_2S_2$/$Li_2S$ during cycling. Since there is no direct contact between S and the liquid electrolyte, the reaction is of quasi solid-state and thus S can be directly transformed to $Li_2S_2$/$Li_2S$. The capacity fade in the composite can be ascribed to the encapsulated sulfur within the narrow pores of ultra-microporous carbon and discharge products. The absence of higher

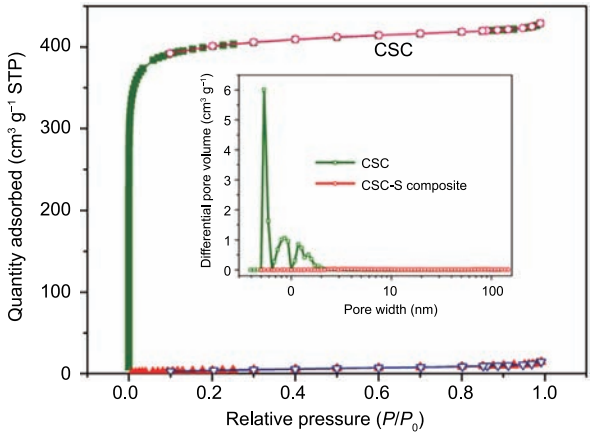


**Figure 3** $N_2$ adsorption/desorption isotherm for coconut shell derived ultra-microporous carbon (CSC) and CSC-S composite. Inset shows the distribution of pore size. Reprinted with permission from Ref. [70], Copyright 2015, Nature Publishing Group.

polysulfides in the electrolyte, on the surface and in the subsurface of the composite gives rise to a sustainable cycling performance of over 400 Cycles with Columbic efficiency of 99.6%.

In addition to the tuning of pore sizes and volume, the surface chemistry of porous carbon materials is also very important for Li-S batteries. Since the carbon is non-polar whereas Li polysulfides are inherently polar molecules, the cathodes which make up this non-polar host still face fast capacity decay over long-term cycling because it can only permit adsorption of polysulfides up to diffusion limitations [71,72]. Surface properties of the porous carbon can be altered by functionalization such as doping with N or B. Doping carbon with N or B is an effective way to enhance the intrinsic properties of porous carbon materials as it may facilitate the chemisorption of Li polysulfides at the surface [16,73–76]. By considering the fact that N-doping can improve the performance of Li-S batteries, Yu *et al.* [77] synthesized an inherently N-doped microporous carbon from human hair by carbonization and NaOH activation at 900°C (Fig. 4). XPS showed that inherent doping of N significantly changed the electrical properties and provided additional adsorption sites for Li polysulfides. The S/C composite with 69 wt.% S loading showed Columbic efficiency higher than 98.6% for 200 cycles at 0.2 C. Further wrapping this composite with reduced graphene oxide provided considerably improved electrochemical properties with a high reversible capacity of 989 mA h $g^{-1}$ and a Columbic efficiency of 99.8% after 300 cycles. The superior performance of cathode was attributed to the porous structure of carbon with inherent N-doping and graphene

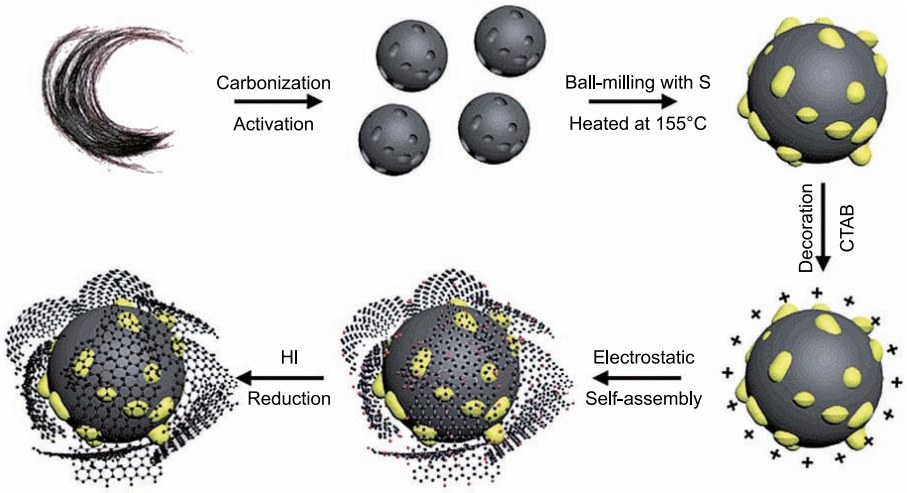


**Figure 4** Schematic illustration of the hair derived carbon, and g-C/S composite preparation process. Reprinted with permission from Ref. [77], Copyright 2015, Royal Society of Chemistry.

protection.

Some characteristics of the microporous carbons derived from biomass and the resulting properties obtained for Li-S batteries are summarized in Table 1. The microporous C/S composites exhibit unprecedented electrochemical behavior because of the smaller sulfur entities, $S_{2\text{-}4}$, as starting material. Thus, the higher order polysulfides are not formed during the reaction and the shuttle effect can be avoided. As an outcome, excellent cycling stability, high rate capability and electrolyte compatibility are obtained.

**Bio-derived mesoporous carbon**

Mesoporous carbon with a pore diameter between 2 and 50 nm has reasonable pore volume, which can permit high S loading and improve ionic/electronic and electrolyte transportation [78,79]. Pioneering work on the use of mesoporous carbon in Li-S batteries was performed by Nazar's group in 2009 [79], in which high S loading and large initial capacity were attained. Subsequently, many researchers have developed low-cost bio-derived mesoporous carbons instead of the commercially-available mesoporous carbon to achieve high-performance Li-S batteries.

The direct pyrolysis of naturally derived biomass materials can efficiently be used to prepare the mesoporous carbons. For example, Cheng *et al.* [80] utilized bamboo charcoal as a sulfur host and attained 57.7 wt.% S loading by a melt-diffusion technique. The charcoal with pore size of about 4 nm exhibited a surface area of 57.8 $m^2 g^{-1}$ and pore volume of 0.05 $cm^3 g^{-1}$. They obtained a very stable composite with the reversible capacity of 414 mA h $g^{-1}$ after 500 cycles at 0.5 C. A mesoporous carbon microtube was prepared by pyrolysis of poplar catkins at 800°C by Zhang *et al.* [81] and employed as a sulfur host in Li-S batteries. The carbon microtubes showed a Brunauer-Emmett-Teller (BET) surface area of 186 $m^2 g^{-1}$ and a pore volume of 0.287 $cm^3 g^{-1}$. At 0.1 C, after 100 cycles the composite delivered reversible capacity of 810 mA h $g^{-1}$ and initial discharge capacity of 1173 mA h $g^{-1}$. The excellent electrochemical properties of the composite were due to the mesoporous surface that provided good electrical conductivity and trapped the polysulfides intermediates. However, the carbon prepared by this method has limited surface area and pore volume, which cannot fulfill the requirements of Li-S batteries with high energy density.

To improve the surface area and pore volume, the use of biomass material along with STM can develop outstanding mesoporous carbons. Brun *et al.* [82] prepared the carbon material from biomass via an environmentally friendly and cost effective HTC route. They used glucose and xylose as carbon precursors and nanosized silica spheres as hard templates to obtain hollow carbon spheres (HCS). The as-prepared HCS showed an average shell thickness of 5–8 nm. The glucose-derived HCS had a smaller surface area and thicker carbon walls as compared to the xylose-derived one. Sulfur was encapsulated into the HCS by melt-diffusion method and the composites were examined as electrode for Li-S batteries. The same group also synthesized *N*-doped carbon aerogels (NCA) by catalyst-free hydrothermal treatment from glucose, *D*-glucosamine and/or *N*-acetyl-*D*-glucosamine and phenolic compounds [83]. They applied the obtained NCA as metal-free oxygen reduction catalyst. Followed their own work, Brun *et al.*

**Table 1** Microporous, mesoporous and hierarchical porous carbons derived from biomass used as electrode materials and their properties for Li-S batteries

| Biomass source | Obtained structure | Activating agent | Surface area ($m^2\ g^{-1}$) | Pore volume ($cm^3\ g^{-1}$) | Initial capacity (mA h $g^{-1}$) | Capacity retention (mA h $g^{-1}$) | Cycle number | Rate (C) | S (wt.%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Bamboo biochar | Microporous biochar | KOH | 791.8 | 0.38 | 1295 | 756 | 50 | 0.1 | 50 | [67] |
| Apricot shells | Microporous | KOH | 2269 | 1.05 | 1193 | 613 | 200 | 1 | 53.3 | [68] |
| Coconut shells | Ultra microporous | KOH | 1600 | 0.66 | 1458 | 411 | 400 | 0.2 | 45.8 | [70] |
| Hair | N-doped microporous carbon | NaOH | / | / | 1113 | 989 | 300 | 0.2 | 69 | [77] |
| Monosaccharides | Mesoporous hollow carbon spheres | / | 296 | 0.65 | 1000 | 600 | 50 | 1 | 50 | [82] |
| Glucose etc. | Mesoporous hydrogel and hollow spheres | / | NCA* = 130<br>HCS** = 296 | NCA = 0.23<br>HCS = 0.65 | 1500 | 700 | 25 | 0.1 | 50 | [84] |
| Sodium alginate | Mesoporous carbon spheres | / | 1270 | 4.1 | 1388 | 857 | 100 | 0.2 | 60 | [87] |
| Sucrose | Mesoporous carbon | / | 1980 | 3.1 | 1038 | 736 | 80 | 0.1 | 72 | [85] |
| Starch | Mesoporous carbon | / | 949.9 | 3.14 | 922 | 683 | 100 | 0.5 | 81.3 | [86] |
| Bamboo charcoal | Mesoporous | / | 57.8 | 0.05 | 685 | 414 | 500 | 0.5 | 57.7 | [80] |
| Litchi shell | Mesoporous | KOH | 3164 | 1.88 | 790 | 403 | 800 | 0.5 | 60 | [88] |
| Poplar catkin | Mesoporous carbon microtube | / | 186 | 0.287 | 1173 | 810 | 100 | 0.1 | / | [81] |
| Biomass waste (gelatin) | N-doped mesoporous carbon | KOH | 2892.6 | 2.8 | 1209 | 600 | 200 | 1 | 53.3 | [89] |
| Cotton | Hierarchical micro-macropores | KOH, Urea | 1286 | 1.15 | 1017 | 760 | 200 | 0.20 | 68 | [90] |
| Pomelo peel | Hierarchically meso/micropores | KOH | 1533 | 0.837 | 1258 | 750 | 100 | 0.20 | 60 | [91] |
| Olive stones | Hierarchical microporous and meso | Steam | 587 | 0.333 | 930 | 670 | 50 | 0.06 | 80 | [93] |
| Coconut shells | Hierarchical micro with small meso | KOH | 2258.7 | 2.246 | 1233 | 929 | 100 | 0.12 | 62 | [95] |
| Fish scales | Hierarchical micro-mesopores | KOH | 2441 | 1.69 | 1400 | 1100 | 20 | 0.10 | 59 | [96] |
| Glucose | Hierarchical porous carbon spheres: meso and micro | KOH | 699.76 | 0.47 | 1253.5 | ~850 | 50 | 0.10 | 70 | [97] |
| Sucrose, glucose and xylose | Hierarchically porous carbon monoliths | / | 1426 | 3.097 | 1305 | 469 | 25 | 0.10 | 75 | [98] |
| Pig bone | Hierarchical meso/micro/macro | KOH | 2157 | 2.26 | 1265 | 643 | 50 | 0.24 | 63 | [100] |
| Glucose and colloidal silica spheres | Hierarchical porous honeycomb carbon (Meso/micro/macro) | / | 614.4 | 1.34 | 923 | 564 | 100 | 2.00 | 66 | [101] |
| Silk cocoons | Hierarchical porous carbon (Meso/micro/macro) | KOH | 3243 | 2.1 | 1443 | 804 | 80 | 0.50 | 48 | [102] |

* N-doped carbon aerogels, ** Hollow carbon spheres

[84] studied the synergistic effect of carbohydrate derived HCS and NCA for improving performance in Li-S battery. Compared with the previously-reported results of HCS/S [82], the S composite with mixed NCA and HCS exhibited a surprisingly higher specific capacity of more than 700 mA h $g^{-1}$ with a low capacity fading over 25 cycles.

Based on the reactive carbochlorination etching of $TiO_2$ nanoparticles inside dense carbon matrix, Kaskel's group prepared a type of highly mesoporous carbon material called Kroll-carbons by using sucrose as a carbon precursor [85]. The Kroll carbon with a specific surface area of 1980 $m^2$ $g^{-1}$ and pore volume of 3.1 $cm^3$ $g^{-1}$ showed high performance as a sulfur host with initial specific capacity of approximately 1400 mA h $g^{-1}$. Li *et al.* [86] reported a facile, chemical activation-free method to prepare highly porous carbon derived from starch and colloidal silica as templates through sol-gel method. The as-synthesized porous carbons contained uniform mesopores with a large pore volume of 3.14 $cm^3$ $g^{-1}$ and a surface area of 949.85 $m^2$ $g^{-1}$. Sulfur was infiltrated by melting-infusion and a very high S loading (81.3 wt.%) was achieved. At 0.5 C, the composite exhibited an initial capacity of 922 mA h $g^{-1}$ and a high reversible capacity of 483 mA h $g^{-1}$ was still maintained after 300 cycles at 1 C. They suggested that these excellent electrochemical properties of the sulfur cathode were due to the uniform and appropriate structure of porous carbons. Sodium alginate (a biopolymer from seaweed) was subjected to carbonization at 900°C for 5 h with colloidal silica as pore directing template and produced mesoporous carbon spheres with hierarchical pores (3–30 nm) [87]. Carbon spheres with surface area of 1270 $m^2$ $g^{-1}$ and pore volume of 4.1 $cm^3$ $g^{-1}$ were obtained by tuning the ratio of sodium alginate and pore directing agent. Sulfur was infiltrated by a one-step autogenetic high-pressure method, and Li-S cell based on this composite maintained a capacity of 857 mA h $g^{-1}$ after 100 cycles at 0.2 C.

As mentioned above, the KOH activated porous carbon has ultrahigh specific surface area with excellent porous structure. Zhang *et al.* [88] utilized waste litchi shells as precursor along with KOH activation at 900°C to prepare porous carbon. The nature of channel-like macropores in waste litchi shells can be efficiently introduced with KOH into the internal channel, which is beneficial to activation and creation of more porosity with high surface area. The synthesized activated porous carbon owned a large pore volume of 1.88 $cm^3$ $g^{-1}$ and ultrahigh surface area of 3164 $m^2$ $g^{-1}$. The carbon was employed as host matrix for sulfur and the composite was fabricated by simple melt-diffusion process with 60 wt.% S loading. The high surface area and pore volume of carbon ensured the fine dispersion and high content of sulfur in a conducting network. Due to the excellent structural parameters of litchi-derived porous carbon, very promising electrochemical results were obtained. The available nanopores effectively suppressed the dissolution of polysulfides. An initial discharge capacity of 1105 mA h $g^{-1}$ was attained at a current density of 200 mA $g^{-1}$. At 800 mA $g^{-1}$, the composite showed long-term capacity retention of 51% after 800 cycles.

In addition, based on the reports that N-doping could further improve the electrochemical properties via enhanced surface affinity to Li polysulfides [16,73,74,76], Qu *et al.* [89] synthesized ordered N-rich mesoporous carbon by pyrolysis of gelatin (biomass waste) as a carbon source and SBA-15 as hard template. The N-rich mesoporous carbon was activated with KOH and the surface area increased to 2892.6 $m^2$ $g^{-1}$ with a pore volume of 2.80 $cm^3$ $g^{-1}$. The obtained carbon showed acceptable S loading (53.3 wt.%) and a stable framework to sustain the volume expansion and suppress the shuttle phenomenon. Due to the increased surface adsorption via N-doping (9.74 at.%), the diffusion of polysulfides was further inhibited. The composite exhibited stable cycling performance and high rate capability, as it maintained the discharge capacity of 600 mA h $g^{-1}$ after 200 cycles at 1 C.

Various bio-derived mesoporous carbons and their corresponding properties used as hosts in Li-S batteries are summarized in Table 1. The large pore volume with high S loading makes the mesoporous carbons excellent contenders as hosts for Li-S batteries. The mesoporous carbons not only facilitate sulfur encapsulation but also improve the ionic/electronic and electrolyte transportation as well as an increase in voltage plateau. However, due to the large pore size compared to microporous carbons, they cannot avoid the dissolution of polysulfides. The modified surface of mesoporous carbon with nitrogen assists in avoiding the shuttling effect because N-doping provides enhanced chemical adsorption and increases the electronic conductivity of carbon. A coating of conducting polymer on the surface of mesoporous carbon/sulfur composite can also provide improved performance by limiting the transport of polysulfides within the carbon matrix.

**Bio-derived hierarchical porous carbon**

In order to obtain high performance in Li-S batteries, a carbon material is required to provide a suitably high pore volume for a high S loading, suppress the shuttle effect, ensure good electrolyte penetration and facilitate electronic/ionic transport. According to the previous studies, an individ-

ual material such as macro-, meso- or microporous carbon cannot fulfill all of these requirements for a sulfur host. Therefore, by accepting the advantage of each category of pores, consistent efforts have been made in an attempt to fabricate hierarchical porous carbons (HPC). HPCs contain at least two categories of pores, which take the advantages of micro-, meso- and macro-pores. Combining the benefits of different categories of pores to load sulfur is an alternative methodology to achieve better performance for Li-S batteries [78].

Bimodal porous carbon can provide dual advantage of pores. Bimodal mesoporous carbon has many advantages to achieve high performance Li-S batteries without sacrificing capacity and cycle life. Wang *et al.* [90] presented a simple approach for synthesizing micro/macro-porous carbon with cotton as a carbon source. Chemical activation was carried out by using KOH. Two samples were studied: one treated with KOH/urea and the other with KOH alone. They found that the former treatment of carbon led to only micropores, but the later produced a material featuring micro-macropores. The micro/macro-porous carbon displayed a surface area of 1286 $m^2$ $g^{-1}$. A simple heating method was employed to infiltrate the sulfur into the as-prepared carbon and attained an S loading of 68 wt.%. The composite exhibited an excellent electrochemical performance in which micropores adequately trapped the polysulfides whereas macropores enhanced the efficient transportation of electrons/ions and electrolyte. A good rate capability and a large capacity of 760 mA h $g^{-1}$ at 0.2 C after 200 cycles were obtained.

Previously prepared activated carbon featured a pore size distribution ranging from micro to macropores, and due to limited electronic contact of sulfur within the macropores, significant polarization could occur. To overcome these issues, Zhang *et al.* [91] prepared a 3D carbon material from pomelo peels by KOH assisted carbonization at 600°C. They synthesized a highly porous carbon foam (mirco/meso porosity) with a surface area and pore volume of 1533 $m^2$ $g^{-1}$ and 0.837 $cm^3$ $g^{-1}$, respectively. The obtained carbon foam was applied as binder-free and free-standing support for a sulfur electrode. The sulfur was loaded up to 60.1 wt.% via a solution approach to fabricate the S/carbon foam. Due to the 3D structure of the carbon foam, the initial discharge capacity of 1258 mA h $g^{-1}$ at 0.2 C and Columbic efficiency of 96% were attained. Olive stone, a by-product of olive oil production, was used as a carbon precursor to synthesize activated carbon at 700°C under steam activation [92–94]. Moreno *et al.* [93] used the obtained carbon with the surface area of 587 $m^2$ $g^{-1}$ and pore volume of 0.333 $cm^3$ $g^{-1}$ as sulfur host. The investigation on pore size distribution indicated the availability of micro and mesopores. The activated carbon/S composite was fabricated by *in situ* deposition and a high sulfur loading of 80% was obtained. The microporous texture of the activated carbon adequately trapped the polysulfides during the redox reaction. On cycling, the composite showed excellent capacity retention and delivered a capacity of 670 mA h $g^{-1}$. Coconut-shells were utilized by Liu *et al.* [95] to synthesize a carbon structure with micropores and a low number of mesopores (average pore size of 2.246 nm). After loading with 62 wt.% sulfur, the material gave a retained discharge capacity of 929 mA h $g^{-1}$ after 100 cycles at 0.12 C. Following recent interest in using cost-effective approaches, Zhao *et al.* [96] employed fish scales to synthesize bimodal porous carbon mainly containing micro and mesopores. The fish scales were activated with KOH and calcined at 900°C. The as-prepared carbon had a very high surface area of 2441 $m^2$ $g^{-1}$ and a pore volume of 1.69 $cm^3$ $g^{-1}$. The composite displayed various benefits such as high active site density due to high surface area, accommodation of volume expansion, suppression of shuttle effect and conductive path for Li ions. As a consequence of the benefits of hierarchically structure, the cathode showed high initial discharge capacity of 1039 mA h $g^{-1}$ at 1 C and excellent cycling stability of 1023 mA h $g^{-1}$ after 70 cycles.

A variety of monosaccharide and disaccharides have been utilized as green carbon precursors for many years. By applying modern carbonization techniques, high quality carbon materials with special categories of pores and shapes can be obtained [6,82,84,85,97–99]. Porous carbon spheres were developed by Park *et al.* [97] using glucose as the carbon precursor and KOH as the activating agent. The 3D interconnected micro and mesoporous carbon spheres provided a large surface area and a porosity which allowed sulfur to be stored in the mesopores and on the surface of carbon spheres. Compared with the porous carbon hosts, the shape of porous carbon spheres provided the advantage of featuring enhanced packing density of electrode. Thus high energy density and stability of cathode were achieved. Eco-friendly hydrothermal nanocasting was used by Yu *et al.* [98] to obtain HPC monoliths from sucrose. The template used for this purpose was hierarchically meso-macroporous silica monolith. After removing the silica template by hydrothermal treatment at 180°C for 6 h, the carbon structure was soft and flexible so that the HTC chains curled up, blocked the pores and led to the low porosity. The porosity and conductivity were increased by post treatment at 950°C, and the surface

area and pore volume of 1426 $m^2 g^{-1}$ and 3.097 $cm^3 g^{-1}$, respectively, were attained. Due to high porosity, the S/C composite with a mass ratio of 3:1 was achieved. At 0.1 C, the composite exhibited a high initial discharge capacity of 1305 mA h $g^{-1}$.

The unique characteristics of each different kind of pores in the composite have urged scientists to pursue hierarchical micro-meso-macro architectures for improved sulfur utilization. Wei *et al*. [100] prepared an HPC with high surface area from pig bone which was activated with KOH. They also investigated the effect of activation temperature on the surface area and pore volume, and found that HPC exhibited the highest pore volume (2.26 $cm^3 g^{-1}$) and specific surface area (2157 $m^2 g^{-1}$) at 850°C (Fig. 5a). The pig-bone derived HPC showed high structural stability even at high temperatures. The HPC structure contained interconnected macro-, meso- and micro-pores, in which macro/mesopores provided appropriate ion transfer path while micropores prevented capacity fading during cycling (Fig. 5b). As an electrode with sulfur, the HPC/S composite exhibited a high initial capacity of 1265 mA h $g^{-1}$. Qu *et al*. [101] designed a 3D hierarchically porous honeycomb carbon from glucose and colloidal silica spheres as removable templates. The honeycomb carbon possessed a surface area of 614 $m^2 g^{-1}$ with the major contribution being micropores and with a pore volume of 1.34 $cm^3 g^{-1}$. The honeycomb carbon contained internally connected macro/meso/micropores that efficiently infiltrated the sulfur, providing good electronic/ionic conductivity and suppressing the shuttle effect. The composite with 66.3 wt.% S loading exhibited an initial discharge capacity of 923 mA h $g^{-1}$. In particular, a long-term cycling stability up to 300 cycles was observed at 1.5 C. Zhang *et al*. [102] synthesized HPC microfiber from silk cocoon (a bio-polymer widely available in nature) by carbonization at 900°C assisted with KOH activation. The carbon microfiber possessed a very high surface area of 3243 $m^2 g^{-1}$ and large pore volume of 2.1 $cm^3 g^{-1}$ (Figs 5c and d). The sulfur was encapsulated into the carbon microfiber and used as an electrode in the Li-S cell. From the electrochemical properties, they observed that carbon microfiber/S cathode could trap the polysulfides and boost the reutilization of sulfur due to very high surface area and electronic conductivity. The carbon microfiber/S composite with 48.4% sulfur exhibited a high initial discharge capacity of 1443 mA h $g^{-1}$ and Columbic efficiency of up to 92% after 80 cycles (Fig. 5e).

Various HPCs derived from biomass used to prepare electrode materials for Li-S batteries are compared in Table 1. The HPCs retain the advantages of macro/meso/micropores that can efficiently encapsulate the sulfur, provide good ionic and electronic conductivity and sufficiently suppress the shuttle effect. In HPCs, micropores bring high cycle performance due to the space confinement effect and inhibit the dissolution of polysulfides. The macropores allow fast electrolyte ingress and while the mesopores give good sulfur loading and promote the electronic/ionic transport. The combined effect of all these pores makes HPC an acceptable candidate for hosting sulfur and obtaining Li-S batteries with excellent cycling stability and rate capability.

**Bio-derived carbon nanostructures**

Another approach to obtain high performance in Li-S battery is to encapsulate sulfur within the carbon nanostructures. Bio-template method for the synthesis of nanostructures is most attracting for the researchers of bionanotechnology, chemistry, physics and materials science field. Exploiting the diversity, sustainability and cost-effectiveness of biomass, Yao *et al*. [103] utilized a natural composite crab shell with a Bouligand pattern as a bio-template to fabricate hollow carbon nanofiber. Sulfur was introduced by thermal infusion to prepare the crab shell-templated carbon-sulfur composites. Crab shell template based carbon showed very interesting features such as high electrode activity due to its high surface area of nanochannels and the volume buffer capacity due to the availability of empty spaces within the nanochannels, facilitating the diffusion and fast transport of Li ions. The prepared cathode exhibiting a high specific capacity of 1230 mA h $g^{-1}$ and 60% capacity was retained over 200 cycles. They also fabricated crab shell-templated carbon/silicon composites by chemical vapor deposition (CVD) method and obtained excellent electrochemical properties. Inspired by the fish scale structure, Tao *et al*. [104] designed scale-like carbon nanotiles using an inexpensive and widely available biomass kapok fibers as a carbon precursor. They synthesized scale-like kapok fiber carbon nanotiles via facile calcination (700°C) and grinding procedure. As sulfur host, the scale-like carbon nanotiles displayed a very high sulfur loading (93.2 wt.%), and the S/carbon nanotiles composite exhibited noteworthy electrochemical performance. They hypothesized that the scale-like carbon nanotiles successfully suppressed the shuttling of polysulfides, accommodated volume expansion and made the sulfur particles electrically conducting during the $Li^+$ insertion/extraction process. At 0.4 C, the composite showed a reversible capacity of 524 mA h $g^{-1}$ with capacity retention of 95.4% after

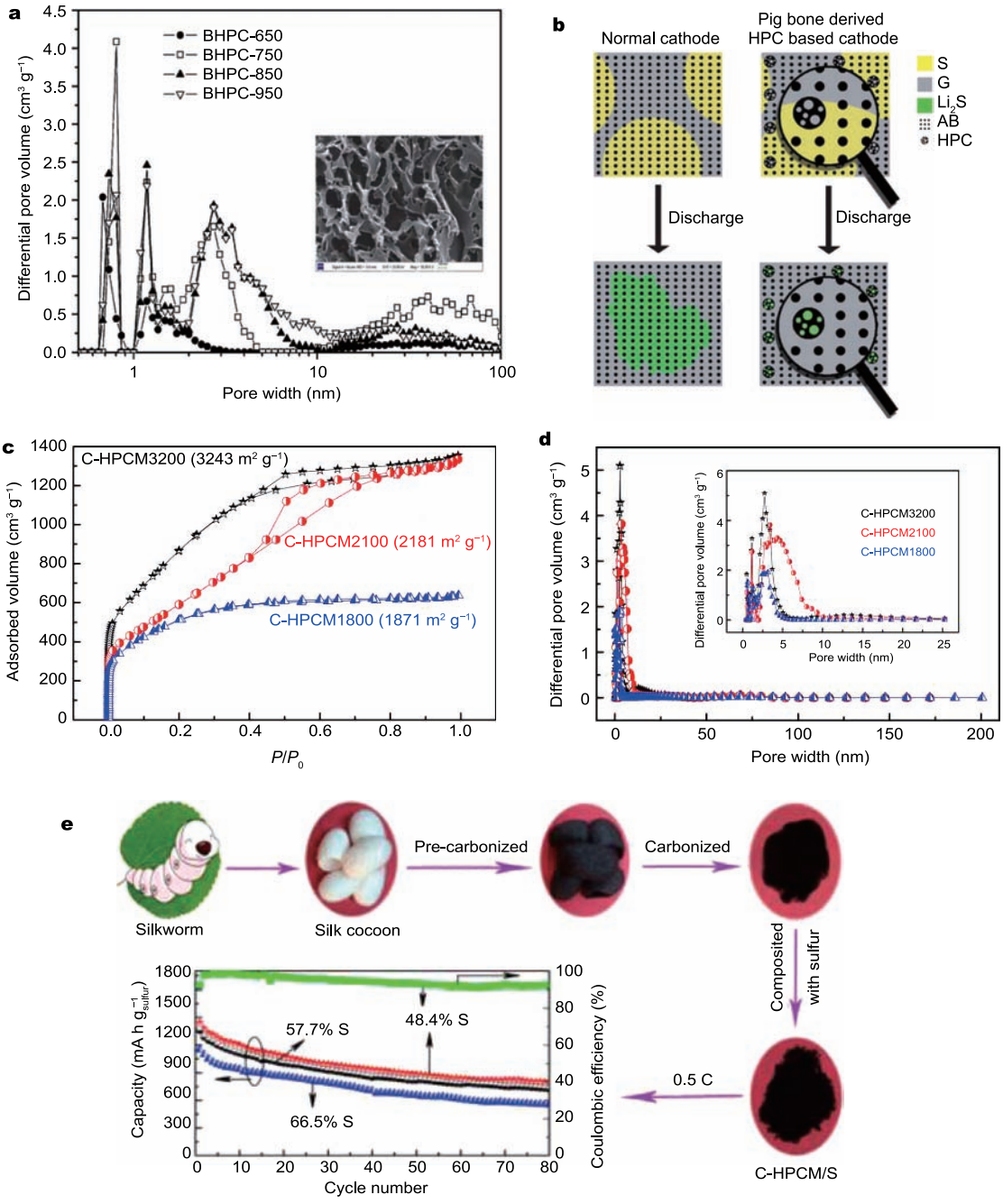


**Figure 5** (a) Pore size distribution curves at different activation temperatures. The inset in (a) is a scanning electron microscopy image of the pig bone based HPC at activation temperature of 850°C. (b) Illustration of normal cathode and pig-bone derived HPC based cathode. The AB and G represent acetylene black and gelatin (Reprinted with permission from Ref. [100], Copyright 2011, Royal Society of Chemistry). (c and d) $N_2$ adsorption-desorption isotherms, specific surface area and pore size distribution of C/HPCMs (hierarchically porous carbon materials). (e) Schematic preparation for C/HPCMs composites and cycle performance (Reprinted with permission from Ref. [102], Copyright 2014, American Chemical Society).

90 cycles.

The dissolution of lithium polysulfides, agglomeration of insulated sulfur and corrosion of the lithium anode are some of the main reasons for the low utilization of sulfur. Yang *et al*. [99] combined the chemical bonding and envelopment for high utilization of sulfur. They prepared a carbon precursor by carbonizing sucrose using concentrated $H_2SO_4$ and the resultant precursor was deoxygenated to obtain the carbon matrix. It was observed that the prepared carbon matrix was comprised of large lamellas. The syn-

thesized C/S composite contained a carbon coating outside and C–S bond which was promoted due to deoxygenation of the carbon precursor. The obtained structure showed improved electrochemical properties compared with acetylene black and sulfur composite because of the high utilization of sulfur during charge/discharge. The coating of carbon and C–S bonding can hold the sulfur and maintain contact between the sulfur and conductive carbon.

In pursuit of a cheap and abundant carbon source to obtain the desirable morphology for rapid electron and ion transportation as sulfur host, Guo *et al.* [105] utilized corncob as the carbon source. They obtained a bimodal porous carbon with 2D nano-sheet structure by carbonization and activation with KOH. The as-synthesized carbon exhibited a large surface area of 1198 $m^2\ g^{-1}$ with pore volume of 0.672 $cm^3\ g^{-1}$. The C/S composite was prepared by conventional melt-diffusion technique. The 2D structure of carbon provided excellent pathways for electron/ion transportation and restricted polysulfides within the electrode. Due to the large surface area, high sulfur utilization was observed with the initial discharge capacity of 1600 mA h $g^{-1}$ and the reversible capacity of 554 mA h $g^{-1}$ after 50 cycles.

Table 2 lists the biomass-derived nanostructured carbons used as host materials in Li-S batteries. Biomass-derived nanostructured porous C/S composites represent an excellent method for improving cathode performance in Li-S batteries, as demonstrated in the above examples. The use of bio-template instead of nano-templating provides a cheap, effective and green route to fabricate nanostructured carbons and has been proven to be effective to overcome the problems for Li-S batteries. From the reports discussed, it is obvious that rational biomass derived nanostructures are promising for addressing the numerous challenges for high-performance Li-S batteries.

According to the above mentioned examples, the pore structure of bio-derived carbon has great influence on the performance of the Li-S batteries. Microporous carbon can facilitate the immobilization of sulfur and inhibit the shuttle effect, leading to a long cycling stability. However, the limited sulfur loading and lower discharge plateau in microporous carbon/sulfur composite has dramatically reduced the capacity and the energy density of the battery, respectively. Compared with microporous carbon, mesoporous carbon has a higher sulfur loading due to its larger pore size and higher pore volume, and meanwhile the composite also shows a higher voltage plateau. Thus, mesoporous carbon/sulfur composite shows higher capacity and energy density in comparison with microporous carbon. Nevertheless, the cycling stability of mesoporous carbon should be further improved because it cannot efficiently avoid the dissolution of polysulfides. Macroporous carbon has been little reported because its large open structure results in poor inhibition of polysulfides. However, macroporous carbon permits fast electrolyte ingress and diffusion for enhanced ion-transport kinetics, and offers large volume space for high sulfur loading. As discussed, the individual porous carbon cannot satisfy all the requirements of sulfur host in Li-S batteries. Considering the unique characteristics of each kind of pores, to balance their advantages and disadvantages, the hierarchical bio-derived carbon architectures have been well developed and exhibited an optimum performance in Li-S batteries as mentioned above. In hierarchical carbon, micropores can efficiently encapsulate the sulfur, suppress the shuttle effect, and macropores and mesopores can allow fast electrolyte ingress as well as higher sulfur loading. Therefore, the use of hierarchical carbon, due to its combined effect, as a host for sulfur in Li-S batteries has been considered the best strategy.

## BIO-DERIVED CARBON AS INTERLAYERS IN Li-S BATTERIES

As we know, the so-called "shuttle effect" is due to dissolution of polysulfides in the electrolyte and their free diffusion between the anode and cathode. To explore a more effective and facile strategy to inhibiting the shuttling mechanism, Manthiram's group introduced a series of papers on a new concept of inserting a carbon interlayer between the cathode and separator [106,107]. This interlayer carbon can block polysulfides within the electrode, enhance the utilization of the active material and further boost the conductivity. By considering the importance of bio-derived materials, Manthiram and co-workers prepared sucrose-coated chicken eggshell membrane followed by carbonization at 800°C [108]. The as-prepared membrane contained both micro and macropores for trapping the active mass and also functioned for continuous electron path. A sandwich electrode was fabricated in which the bottom membrane acted as a current collector and encapsulated the active mass, whereas the top membrane played the role of inhibitor. The sandwiched membrane cathode permitted the dissolved polysulfides to be localized and stabilized the electrochemical reaction. As a result, an excellent discharge capacity of 1327 mA h $g^{-1}$ was achieved. The same group recently employed tree leaves to form a free-standing carbon film by carbonization at 800°C [109]. To maintain the natural structure, they rinsed the carbonized leaves with deionized water only and without any alkali/acid treatment. The as-prepared naturally carbonized leaves were then

**Table 2** Biomass derived nanostructured carbons and their electrochemical properties in Li-S batteries

| Biomass source | Obtained structure | Activating agent | Surface area ($m^2 g^{-1}$) | Pore volume ($cm^3 g^{-1}$) | Initial capacity (mA h $g^{-1}$) | Capacity retention (mA h $g^{-1}$) | Cycle number | Rate (C) | S (wt.%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Crab shells | Hollow carbon nanofiber | / | / | / | 1230 | 810 | 200 | 0.2 | ~65 | [103] |
| Kapok fiber | Carbon nanotiles | / | 282 | 0.157 | 549 | 524 | 90 | 0.4 | 93 | [104] |
| Sucrose | Lamellar carbon | $H_2SO_4$ | / | / | 1266 | 886 | 100 | 0.1 | 57 | [99] |
| Corncob | Nanosheet microporous | KOH | 1198 | 0.672 | 1600 | 554 | 50 | 0.1 | 44 | [105] |

**Table 3** Summary of bio-derived carbons and their application as interlayers in Li-S batteries

| Biomass source | Obtained structure | Activating agent | Surface area ($m^2 g^{-1}$) | Pore volume ($cm^3 g^{-1}$) | Initial capacity (mA h $g^{-1}$) | Capacity retention (mA h $g^{-1}$) | Cycle number | Rate (C) | S (wt.%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Natural carbonized leaf | Micro/mesoporous | Interlayer | 390 | 0.34 | 1320 | 1013 | 100 | 0.1 | 70 | [109] |
| Cassava | Hierarchical porous architecture | Interlayer | 13.8 | 0.015 | 1318 | 811 | 100 | 0.5 | 60 | [110] |
| Filamentous fungi | Meso/macropores carbon fiber monolith | Interlayer | 20.8 | 1.45 | ~970 | 650 | 100 | 0.5 | 60 | [111] |
| Bamboo sticks | Macro/micropore structures | Interlayer | 776 | 0.33 | 907.8 | 605.7 | 300 | 1 | 70 | [112] |
| Bacterial cellulose | 3D carbon nanofiber | S host + interlayer | 375 | 5.29 | ~1060 | 700 | 400 | 0.24 | 81 | [113] |
| Eggshell membrane | Macro/micropores | S host + current collector + interlayer | 429 | 0.36 | 1327 | 1000 | 100 | 0.1 | 3.2 mg $cm^{-2}$ | [108] |

used as a polysulfide inhibitor in sulfur batteries, which efficiently suppressed polysulfide shuttling due to the availability of micro-mesoporous adsorption sites and inherent moisture retention sites. The conductivity of cell was improved, and as a result, the Li-S cell showed high discharge capacity of 1320 mA h $g^{-1}$, and long-term cycling stability with a discharge/charge efficiency of 98% and a low capacity fading of 0.18% per cycle.

A high yield tropical crop cassava was carbonized at 800°C by Qin *et al.* [110] to obtain cassava carbon material. The cassava-derived carbon sheet was employed as an interlayer for a Li-S battery. Such interlayer contained macroporous structure to provide accommodation and reutilization of polysulfides, and availability of active material to the electrolyte with enhanced electronic and ionic conductivity. The Li-S cell with the interlayer exhibited excellent rate performance and rate capability. A reversible capacity of 811 mA h $g^{-1}$ was kept after 100 cycles at 0.5 C, and discharge capacity of 640 mA h $g^{-1}$ was obtained at high rate (4 C). Zhang *et al.* [111] reported the sustainable synthesis of highly porous carbon fiber monolith from filamentous fungi by filtration and subsequent pyrolysis. Fungi were cultured, followed by subsequent filtration and drying to achieve fungi aerogel. Intact carbon fiber monolith was formed via pyrolysis. Doping carbon monolith with N and O produced materials with surface areas of 305 and 20 $m^2$ $g^{-1}$, respectively. This carbon monolith was employed as interlayer for Li-S battery and promising electrochemical properties were attained with a capacity of 650 mA h $g^{-1}$ after 100 cycles. Recently, Gu *et al.* [112] utilized bamboo sticks to prepare bamboo carbon fibers by treating with KOH solution and calcination at 800°C. The as-synthesized carbon fibers were interwoven to form a carbon-fiber-membrane and used as an interlayer between C/S cathode and separator. The carbon-fiber-membrane significantly suppressed the shuttle effect by retaining the polysulfides (Fig. 6a). It also provided efficient electrolyte and ion transportation along with a good conductive network. The Li-S battery with carbon-fiber-membrane showed a high sulfur loading of 70 wt.%, a superb Columbic efficiency of 98% and a stable cyclability with capacity fading of only 0.11% per cycle (Fig. 6b).

Recently carbonized bacterial cellulose has received attention. Huang *et al.* [113] derived a low-cost and eco-friendly 3D carbonaceous aerogel from bacterial cellulose for Li-S batteries. With the carbonized aerogel as sulfur host, a 81 wt.% S loading was attained. Meanwhile, the cellulose aerogel was thin enough to be directly used as an

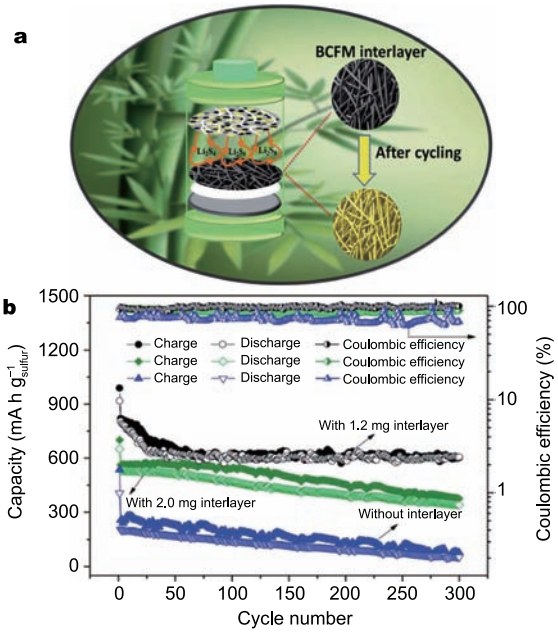


**Figure 6** (a) Cell configuration with the bamboo carbon fiber membrane (BCFM) interlayer. (b) Cycle life of cells at 1 C. Reprinted with permission from Ref. [112], Copyright 2015, Royal Society of Chemistry.

interlayer. The highly interconnected nanofibrous macroporous structure of the carbonized cellulose aerogel brought structural stability and fast diffusion of Li ions through the electrolyte. A high specific capacity based on total mass of electrode can be achieved due to the binder and current collector-free cathode, while the interlayer can successfully reduce the electrode resistance and effectively adsorb the migrated polysulfides. The cell exhibited a discharge capacity as high as 1134 mA h $g^{-1}$ (based on elemental sulfur) at 200 mA $g^{-1}$ and an average Columbic efficiency of 98.3% over 400 cycles, which should be ascribed to the combined and rational configuration of bacterial cellulose aerogel.

Table 3 summarizes bio-derived carbons and their application as interlayers in Li-S batteries. The carbon interlayer provides a high utility of active material by blocking polysulfides within the electrode system and thus gives rise to high cycling stability. Although this novel approach is very effective for high sulfur utilization, it should also be noted that the carbon interlayer is usually electrochemically inactive and affects sulfur content in a cell system, which ultimately decreases the energy density of the cell. It is proposed to reduce the weight or thickness of the interlayer though this strategy weakens its dual function [114]. Therefore, it is necessary to modify the structure of the carbon interlayer to obtain high porosity with modified pore size distribution. By using naturally available precursors,

advanced interlayers can be obtained to maintain high energy density for Li-S batteries.

## CONCLUSIONS AND REMARKS

This review is intended to provide the readers an overview of recent progress in bio-derived carbon materials used as sulfur hosts and interlayers in high-performance Li-S batteries. We highlight various preparation methods from different biomass precursors for carbons with microporous, mesoporous, hierarchical porous and some other nanostructured morphologies, and demonstrate the importance of using biomass to achieve green, cost-effective and energy efficient synthesis. Furthermore, the effects of preparation methods and microstructures of the bio-derived carbons on the electrochemical performances of Li-S batteries have been systematically discussed. Although in the recent years substantial progresses in Li-S batteries have been made by using nanostructured porous carbons based on their novel physicochemical properties, many challenges such as cycling stability, energy density and safety are still faced for commercial application. The energy density is closely associated with the sulfur content in the cathode, the cycling stability is mainly due to the shuttling effect, and the safety is related with the Li anode.

It should be noted that the main advantage of Li-S batteries is their high energy density. However, additives such as binders, additional carbon black conductive and current collectors may weaken this advantage. Therefore, in order to make a practicable Li-S battery, a carbon material is needed to provide: (1) appropriate porosity for high sulfur loading, (2) excellent conductive framework, and (3) efficient utilization without binder and current collector. As discussed, the individual carbon cannot provide high loading capability as well as inhibition of polysulfides. Therefore, an optimal hierarchically porous carbon architecture containing micropores outside and meso/macropores inside could be the best choice, in which the micropores serve as polysulfides inhibitor and the meso/macropores guarantee high sulfur loading as well as fluent ion and electrolyte transport. In addition, a free-standing carbon electrode is desirable because it does not involve the binders, conductive additives and current collectors needed to achieve high sulfur loading and hence ultimately high energy density.

One of the main reasons for the shuttle effect is the sulfiphobic nature of the carbon hosts that limits them to physically adsorb polysulfides. Since the lithium polysulfides are inherently polar molecules, they do not engage in strong interactions with typical non-polar carbons. To maximize the bonding between carbon and lithium polysulfides, the sulfiphobic surface of carbon material should be functionalized to induce sulfiphilic characteristics. A new strategy is to design a sulfur host that can utilize chemisorption and thus prevent lithium polysulfides from shuttling (Fig. 7) [71,72,115]. The surface chemistry of carbon can be modified by functionalization by heteroatom-doping. These modified carbonaceous materials can enhance polar-polar interaction with lithium polysulfides. Thus there is a need to find a biomass source that has inherently heteroatom-doping, which can naturally enhance the chemical interactions between sulfur and carbon to meet the demands of Li-S batteries. The surface modification of C/S composite with different conductive materials, polymers and metal hydroxides such as graphene [116], polyethylene glycol [117], PEDOT:PSS [118], polyaniline [119] and $Ni(OH)_2$ [120] has also been proven to be a good choice for obtaining high cycling stability since they can effectively trap the shuttling polysulfides during cycling. Therefore, the key to utilizing biomass-derived porous carbons to achieve commercially viable high energy density with improved cyclability is to develop the advanced hybrid nanostructures as described above.

We hope that this review can pave the avenues and inspire more researchers and scientists to work towards developing the next-generation biomass porous carbons to achieve low-cost, sustainable and green Li-S batteries for practical commercialization.

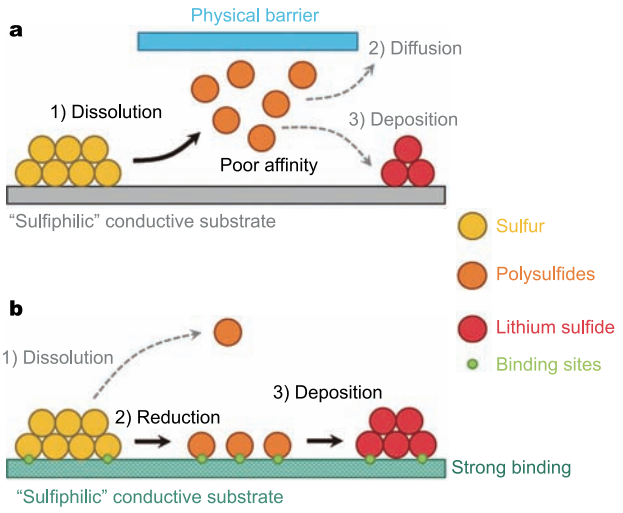


**Figure 7** (a) Physical confinement of polysulfides by a sulfiphobic conductive surface (for example, carbonaceous materials); and (b) enhanced affinity of polysulfide intermediates for the surface by polar adsorbents as sulfiphilic conductive substrates (for example, N-doped carbon materials). Reprinted with permission from Ref. [72], Copyright 2015, John Wiley and Sons.

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**Conflict of interest** The authors declare that they have no conflict of interest.

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## 源自于生物质的纳米多孔炭在锂硫电池中的应用

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**摘要** 在人类发展的几千年中, 生物质材料被广泛应用于能源领域, 例如木材和木炭. 基于生物质材料便宜、来源广泛、可持续发展的优点, 采用先进的科学技术将生物质材料转换为功能化的纳米多孔碳材料, 并将其作为锂硫电池的正极材料和隔膜展现出了非常好的应用前景. 因此, 本综述介绍了以生物质为原料制备的纳米多孔碳材料及其在锂硫电池中的应用, 并针对不同方法制备的生物质纳米多孔炭材料的孔结构(包括微孔、介孔及分级孔)及其作为正极材料对于锂硫电池性能的影响进行了全面的总结, 这对合理利用生物质制备纳米多孔碳材料进一步提升锂硫电池的性能具有很好的指导作用. 最后, 本文指出了当前锂硫电池的问题及挑战, 并对进一步提升锂硫电池性能提供了有价值的观点和策略.