Research Progress on Lignin-Based Carbon Electrode Materials in Rechargeable Batteries

Penghui Li, Shubin Wu,* and Yu Ding

*Corresponding author: shubinwu@scut.edu.cn

DOI: 10.15376/biores.19.2.Li

GRAPHICAL ABSTRACT

Research Progress on Lignin-Based Carbon Electrode Materials in Rechargeable Batteries

Penghui Li, Shubin Wu,* and Yu Ding

Lignin, with its carbon content of up to 60%, can be an ideal precursor for the preparation of carbon materials. Carbonaceous materials obtained from lignin can be transformed into porous and structural morphologies at different scales, providing a biomass approach to energy conversion and storage in batteries. Focusing on lignin-derived carbon materials, this paper summarizes the different morphologies and structures of lignin-based carbon obtained through different preparation methods, and the different electrochemical properties exhibited by these materials as electrode materials for rechargeable batteries (lithium-ion batteries, sodium-ion batteries, lithium-sulphur batteries, *etc*.). In addition, the development prospects and challenges of lignin-based carbon materials in the field of rechargeable batteries are summarized, providing ideas for the next step in the design and development of high-performance lignin-based carbon-based electrode materials.

DOI: 10.15376/biores.19.2.Li

Keywords: Lignin; Carbon; Electrode materials; Batteries

Contact information: State Key laboratory of Pulp and Paper Engineering, South China University of Technology, No. 381 Wushan Road, Guangdong Province, China;
** Corresponding author: shubinwu@scut.edu.cn*

INTRODUCTION

With the development of society, people have become more and more dependent on fossil energy. There has been a sharp decrease in fossil resources and there is rising pressure on the Earth's environment. To ensure the sustainable development of living standards, there is an urgent need to explore energy storage and energy conversion technology (Rois *et al*. 2022). At present, the rapid development of renewable resources as well as a large proportion of the specific wind energy, hydropower, solar energy, *etc*., but these renewable resources still are underutilized, not widely distributed, delayed in production, *etc*., and one of the main reasons is the high cost of development (Schirone *et al*. 2017). The large demand for electrode materials for energy storage has led to the development and design of inexpensive materials with high-power and high-energy. The most common source of carbon for electrode materials for energy storage is the factor that accounts for most of the cost of electrode materials for energy storage. This means that choosing a low-cost renewable and resourceful carbon-based material is of great significance for the development of sustainable.

In most energy storage devices, biomass-derived carbon-based electrode batteries can greatly reduce the cost of battery preparation and provide a clear path for the massive development of energy storage devices. Biomass has a unique porous, three-dimensional structure in comparison to traditional carbon-based materials, such that it can well serve as a carbon substrate for high-performance batteries. The abundance and unique structure of

biomass are advantages for battery electrodes (Sun *et al*. 2022). It is worth noting that the preparation of certain types of carbon destroys this specific structure.

Lignin is currently the second-largest natural polymer in terms of reserves on earth and is also a high displacement by-product of the pulp and paper industry. The carbon yield of lignin after pyrolysis is as high as 40 wt%. The high C content of lignin itself means that it can be used as an energy source for combustion, and these properties make lignin an excellent precursor for the manufacture of carbonaceous materials for electrodes (Culebras *et al*. 2019). Hard carbon materials display a lower average oxidation voltage due to their relatively low voltage plateau (below 100 mV), which is a good positive factor for high-energy density of the whole battery (Zhang *et al*. 2021). Lignin can be well converted to hard carbon materials due to its content of a large number of aromatic rings, and thus it is a preferred choice for high-quality carbon-based biomass materials. Current scholars are actively researching and reforming for the low initial coulombic efficiency and capacity decay caused by lignin-derived hard carbon (Elena *et al*. 2018; Chen *et al*. 2020). With this, lignin-derived carbon materials are gaining attention as emerging energy storage materials, mainly including electrode materials for supercapacitors (Li *et al*. 2022a,b), lithium-ion (Xi *et al*. 2020; Jiang *et al*. 2019), and sodium-ion batteries (Wang *et al*. 2022; Jin *et al*. 2023). Although the performance of lignin-derived carbon materials for energy storage has been comparable to that of some commercial batteries, some morphology modulation and preparation methods of lignin-based carbon materials still need to be explored and discussed, and they have also been summarized and commented upon by scholars from different perspectives (Baloch *et al*. 2021; Chen *et al*. 2022; Jung *et al*. 2022; Li *et al*. 2023; Liu *et al*. 2021).

LIGNIN-CARBON-BASED MATERIALS AND THEIR PROPERTIES

The extended network of lignin is constructed from monomers of coniferyl alcohol, sinapyl alcohol, and *p*-coumarin alcohol in random order through intermolecular C-O and C-C bonds (Yue *et al*. 2016; Shao *et al*. 2017; Feghali *et al*. 2018; Du *et al*. 2023). In nature, lignin is produced by free radical polymerization of three aromatic alcohols, with different lignocellulosic species, then varying the proportions of *p*-coumaryl, pinacol and mustelol (Rinaldi *et al*. 2016; Ralph *et al*. 2019). Lignin is a polymer with carbon-carbon and ether bonds, of which about 2/3 to 3/4 of the phenylpropane units are ether-bonded and the rest are carbon-carbon bonded (Li *et al*. 2023c). β-O-4' accounts for half of such bonding types in lignin, which is much higher than the other ether bonds (Liu *et al*. 2021; Kirui *et al*. 2022; Li *et al*. 2022a).

As lignin has become better understood and increasingly exploited, the applications of lignin have been expanding. There were 7,144 publications on lignin alone in 2022, which is an almost seven-fold increase as compared to the number of publications in 2003, which was 1,038. Currently, lignin-based materials have applications in medicine, agriculture, military, energy, and fine chemicals (Yadav *et al*. 2023). When searching for "lignin" and "battery" in Web of Science's core database, keywords such as "hierarchical porous carbon", "hard carbon", and "anode" are relevant, and the morphology of lignin carbon has been the focus of research on lignin-based batteries (see Fig. 1a). The number of publications such as lignin research articles exceeded 5000/year in 2019 alone. The research publications on lignin have been increasing in the years 2003 to 2022, where lignin carbon materials have increased significantly only in 2015 until the number increased to

1670 or 23.4% in 2022. It is noted that the number of publications on lignin carbon-based materials for batteries also reached 71 in 2022 (see Fig. 1b).

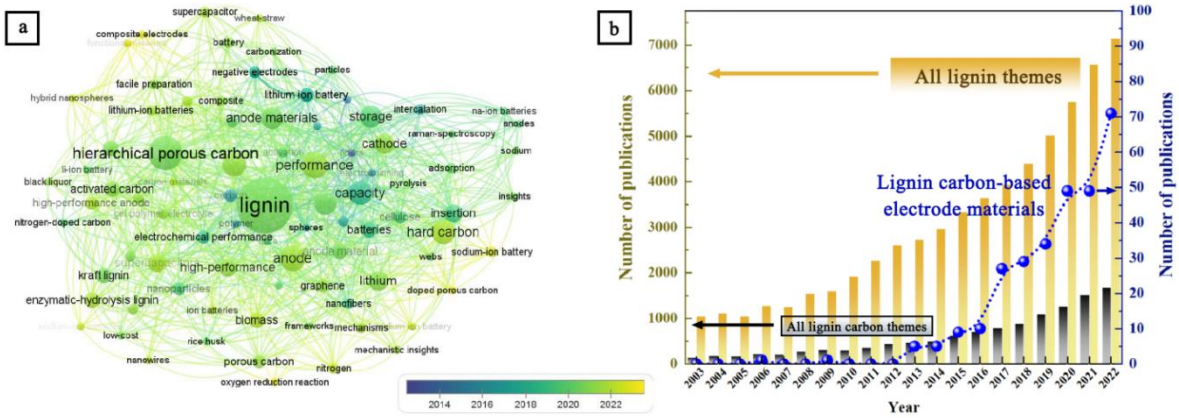

Fig. 1. Links between the keywords "lignin" and "carbon" based on the Web of Science's core database between 2013 and 2023 (calculated by VOSviewer software); (b) total number of publications on lignin, total number of publications on lignocarbon and total number of publications on lignocarbon-based batteries in the last two decades (Web of Science's core database)

Lignin carbon-based materials have good application prospects in adsorbent materials, catalytic conversion carriers, electrode materials, and so on. Most of the electrode materials for batteries are carbon materials, but the cost is high and the production process is complicated. Lignin has high carbon content and has a high content of oxidized benzoquinone groups, which have good electron transfer ability. Oxygen-containing functional groups in lignin and on lignin-derived carbon have irreplaceable roles in electrode materials. For example, oxygen-containing functional groups can form complexes with lithium ions, which undoubtedly facilitates the transport of lithium ions and also increases the capacity and cycle life of batteries. The process of lignin forming carbon-based products at high temperature is shown in Fig. 2. In addition, lignin can be prepared into different morphologies through different processes, such as porous carbon, carbon fiber, carbon aerogel, and carbon nanotubes. The specific preparation process will be discussed in the following classification (Liu et al. 2015).

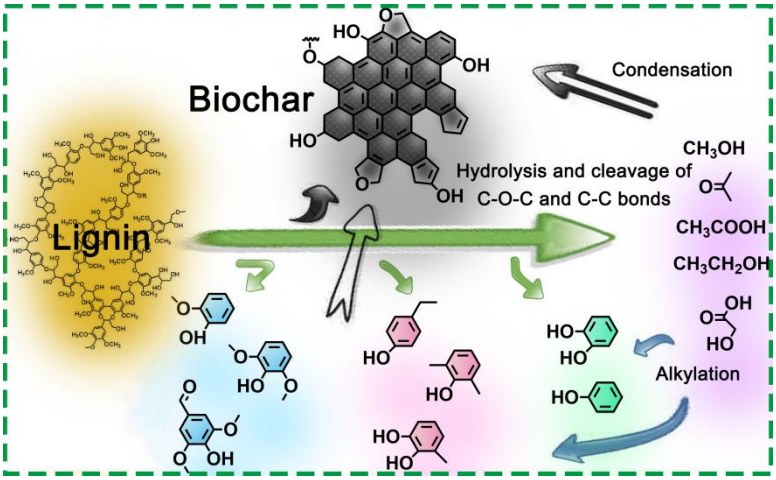

Fig. 2. Mechanism of lignin pyrolytic carbonization process

Lithium-ion Batteries

Lithium-ion batteries (LIBs) are currently used as a rechargeable batteries. They have many good characteristics, such as environmental friendliness, good charging and discharging performance, and high energy density. Especially at a time when traditional fossil fuels are becoming increasingly depleted and environmental pressure issues are surfacing, the development of LIBs has been exceptionally rapid (Wei *et al.* 2013). The reaction mechanism diagram of a typical lithium-ion battery device is shown in Fig. 3.

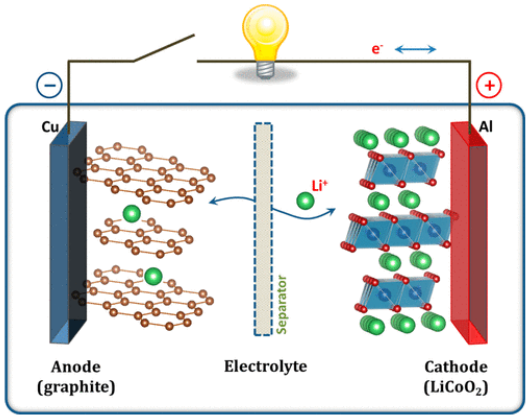

Fig. 3. Schematic diagram of the ion transport mechanism of a lithium-ion battery (Goodenough and Park 2013; Permission granted by ACS)

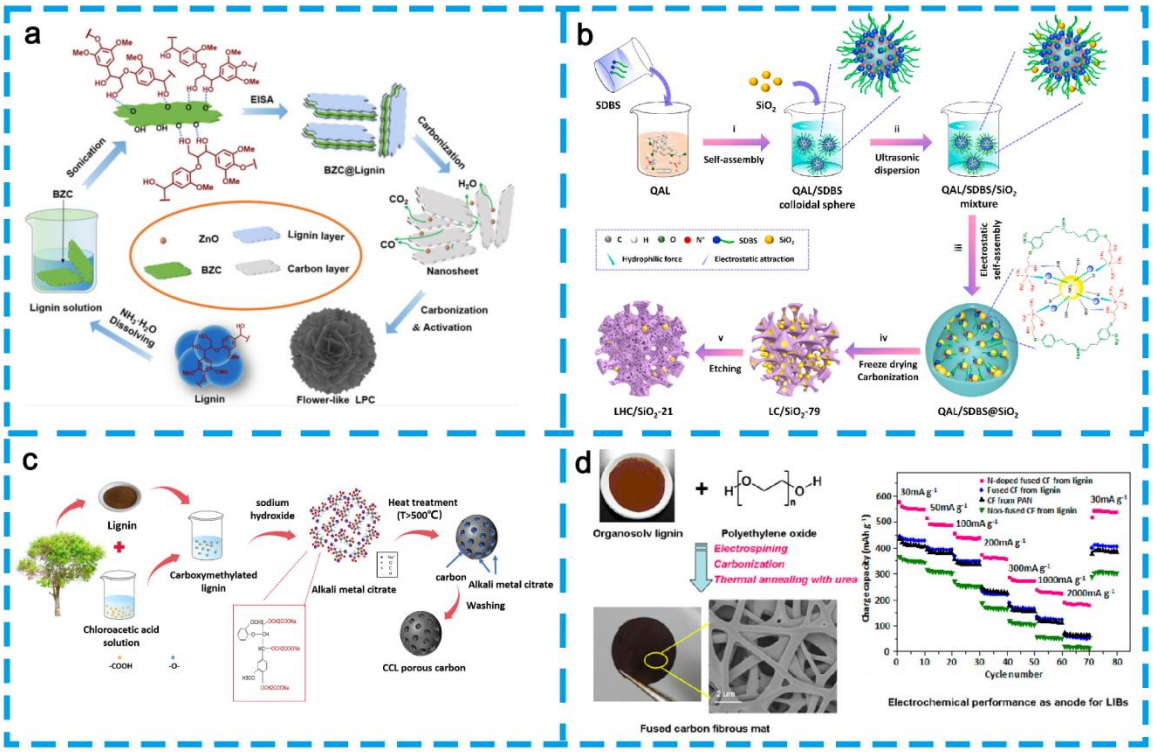

Fig. 4. (a) Schematic route for the preparation of three-dimensional flower-like lignin-based porous carbon (Wu *et al*. 2023; Permission granted by Elsevier); (b) Schematic route for the preparation of three-dimensional lignin-derived honeycomb carbon/silica composites (Huang *et al*. 2021; Permission granted by Elsevier); (c) Schematic route for the preparation of chloroacetic acid modified lignin-based porous carbon microspheres (Li *et al*. 2022; Permission granted by Elsevier); (d) Schematic route for the preparation of nitrogen-doped lignin-poly (ethylene oxide) carbon fibres (Wang *et al*. 2013; Permission granted by ACS)

Lignin contains mostly benzene rings in its structure, which makes it easy to prepare carbon-based materials. While lignin is directly used for carbonization, its porosity is underdeveloped and its specific surface area is small. The porosity and specific surface area of the electrode material affect the electrochemical performance of the resulting battery. A large specific surface area can improve the electrochemical activity of the electrode and increase the discharge capacity of the battery. This is conducive to maintaining a higher voltage level when the battery is discharged at a high rate, and also it can improve the cycle life of the battery. Generally speaking, the specific surface area of electrode materials is relatively large for batteries with high discharge capacity and a need for high numbers of cycles. However, when the specific surface area is too large, the hardness of the material cannot be guaranteed and the internal resistance of the battery increases, thus affecting the life and cycle performance of the battery. There should be a balanced relationship between the specific surface area, the cycle life of the battery, and the preparation cost. The size of the specific surface area is also related to the type of the battery and the environment in which the battery is used, so we will consider the selection of the lignin-based carbon materials through the preparation method, the size of the specific surface area, and the electrochemical performance of the battery comprehensively. Zhang *et al*. (2015) prepared lignin-based multistage porous carbon with three-dimensional macroporous network by using KOH as an activator and template. Further, the product was applied as an anode material for lithium-ion batteries, and a capacity of 470 mAh/g was obtained by charging and discharging 400 times at a current density of 0.2 A/g. The results showed a high capacity of 470 mAh/g. The cycle stability and rate capability are also comparable. This method is simple and efficient, and lays the foundation for the application of lignin-based carbon materials in the production of lithium-ion batteries.

Enzymatic hydrolysis of lignin is another important source of lignin. Xi *et al*. (2018) prepared lignin-based carbon materials by setting different potassium compounds activated enzymatically hydrolyzed lignin. It was found that the magnitude of the specific surface area was in the order of K_2CO_3 > KOH > $K_2C_2O_4$ > K_3PO_4, and that K_2CO_3 could easily improve the pore structure and increase the specific surface area. At the temperature of 900 ℃, the product obtained after K_2CO_3 activation can be applied to lithium-ion batteries with better performance. After 200 times of charging and discharging at a current density of 0.2 A/g, it can still maintain a reversible capacity of 494 mAh/g, and the coulombic efficiency reaches 99%. Even at 1 A/g, the button cell can maintain a specific capacity of 260 mAh/g.

Li *et al*. (2019) treated lignin from rice husk waste liquid with neutral zinc chloride as an activator, and the carbon material prepared by one-step carbonization at 500 °C was applied as an anode material for lithium-ion batteries, with good electrochemical performance. The specific capacity after 100 cycles was 469 mAh/g, with good cycling stability (higher than the theoretical capacity of graphite). The unique porous structure of the lignin-derived carbon material results in a shorter diffusion distance for lithium ions and a larger contact area between the electrode and the electrolyte. Li *et al*. (2022) utilized the addition of chloroacetic acid to modify lignin and then coordinated metal ions to it, which subsequently resulted in the expansion of the pores with carbonates. The lignin of the three-dimensional network of biomass macromolecules can sufficiently scatter metal ions and obtain homogeneous pore positions. The specific surface area of the carbon material can reach 233 m^2/g, and when electrochemical tests were performed, the specific capacity was 500 mAh/g (0.05 A/g). From the above work, it can be seen that lignin treated with different activators will obtain different morphology and structure. Selection of

suitable activators is important for increasing specific surface area and enhancing electrochemical properties. Wu *et al*. (2023) synthesized carbon materials with flower-like structures using basic zinc carbonate activator, which is recyclable. The authors proposed ethanol fractionation to build the microstructure of the material. The material maximized the interlayer spacing and specific surface area to improve the diffusion control and capacitive contribution of specific capacity for lithium-ion storage. When testing its specific capacity, it was found that the unique 3D flower-like morphology could achieve a reversible capacity of 528 mAh/g (current density of 0.2 A/g for 200 cycles), which is also 60% higher compared to graphite.

Lignin can be prepared into carbon fiber structures. Wang *et al.* (2013) used an electrostatic spinning technique to mix lignin with poly (ethylene oxide) (PEO) 9:1, carbonized and synthesized fused carbon fiber mats, in addition to doping urea as a nitrogen source. The electrochemical properties were tested, and it was found that the undoped urea fused carbon fibers exhibited a high specific capacity of up to 445 mAh/g (current density of 30 mA/g). When doped with a nitrogen source, the capacitance was enhanced to 576 mAh/g. With a current density of 2 A/g, the performance capacity was 200 mAh/g.

Similarly, Culebras *et al*. (2019) prepared carbon fibers by electrostatic spinning using polylactic acid (PLA) or polyurethane mixed with lignin. The fiber porosity could be altered by the miscibility/immiscibility rule between lignin and the two polymers. The mixing of PLA with lignin resulted in a porous structure, and the addition of PLA at 50% gave carbon fiber electrodes with a specific capacitance of 611 mAh/g after 500 cycles.

Nowak *et al*. (2023) synthesized lignocellulosic carbon materials with carbon fiber morphology at high temperatures (1000 to 1700 °C) designed with the oxidative thermal stability of pure melt-spun lignin. The microstructure of the material is mostly amorphous carbon, and the strength and stiffness of the material decreases with increasing temperature. At a carbonization temperature of 1000 °C, the carbon fibers exhibited a stiffness of 37 GPa and a strength of 628 MPa. In lithium-ion battery applications, the material has a capacity of 335 mAh/g and excellent cycling stability. It is because of the material's good mechanical integrity and conductivity that conductive additives, binders and collectors are eliminated. On a deeper level, it has a high-energy density by weight compared to graphite.

The emergence of lignin carbon fibers was inevitable. The precursors are cheap, but need to be blended with other polymers or the process is demanding. In addition, the mechanical integrity of lignin converted into carbon material, electrical conductivity still needs to be improved.

Lignin is obtained by conventional carbonization methods, and the morphology of carbon materials is rather irregular. Thus, the manner of obtaining porous carbon materials with unique and homogeneous structure is crucial. Xi *et al*. (2021) prepared lignin/silica composites by in-situ self-assembled co-precipitation of lignin with sodium silicate by using the principle of electrostatic force. In addition, the lignin was a quaternary ammonium lignin, which rendered the carbon materials successfully doped with nitrogen. The material exhibited a hollow porous framework structure. It exhibited a reversible specific capacity of 480 mAh/g when used as an anode in lithium-ion batteries, after 200 cycles at 0.2 A/g. The material has been used as an anode in lithium-ion batteries, and it has been used as an anode in lithium-ion batteries. Of course, lignin can also be distributed in other types of skeletons to prepare carbon materials. Li *et al*. (2023) used a metal organic framework as a template, in which the lignin particles were uniformly dispersed, and the final material obtained was rich in mesopores, which facilitates the transfer of Li^+ transport afterward. In terms of electrochemical performance, after 300 cycles, it showed a specific

capacity of 420 mAh g at 0.2 a/g with a capacity retention rate of more than 99%. After 1000 charge/discharge cycles, its capacity retention was still above 85%.

Silicon has a specific capacitance that exceeds that of graphite by several digits, and it is particularly used as electrode materials for lithium-ion batteries. Combining lignin carbon materials with silicon-based materials is also one of the promising prospects for developing novel materials. Silicon and silica can be combined with lignin as well as lignin-carbon materials in a various of ways. Rios *et al*. (2014) prepared a carbon-silicon composite with a fibrous morphology for electrodes, with 10-nm-thick uniform silica particles on the surface of the silica, which were then filled with lignin-derived carbon fiber material, making it difficult to swell the silicon. The specific capacity of the complex exceeds 700 mAh/g and the coulombic efficiency is close to 99.5%. The lignin's carbon fiber structure provides for unstable volume expansion of the silicon-based material.

Table 1. Partial Research Progress of Lignin-based Carbon Materials for the Preparation of Anode Materials for Lithium-ion Batteries

Precursor	Activator	Electrochemical Performance		Reference
		Current density	Specific capacity after (n) cycles	
N-doping lignin	$Ni(NO_3)_2{\cdot}6H_2O$	300 mA/g	248 mAh/g (300)	Yang *et al*. 2018
Kraft lignin-based carbon fibers	None	37 mA/g	348 mAh/g (3)	Nowak *et al*. 2018
Alkali-based carbon nanofibers	$Mg(NO_3)_2{\cdot}6H_2O$	2 C	1065 mAh/g (100)	Wang *et al*. 2022
Enzymatic hydrolysis lignin	Dual CO/CO_2 exfoliation and ZnO templating	1 A/g	323 mAh/g (650)	Wang *et al*. 2022
Fractionated lignin	$3Zn(OH)_2{\cdot}2ZnCO_3$	200 mA/g	528 mAh/g (200)	Wu *et al*. 2023
Lignin-based azo polymers	None	60 mA/g	225 mAh/g (50)	Zhao *et al*. 2016
Enzymatic hydrolysis lignin	K_2CO_3	200 mA/g	490 mAh/g (200)	Xi *et al*. 2019
Enzymatic hydrolysis lignin	K_2CO_3	200 mA/g	494 mAh/g (200)	Xi *et al*. 2018
Enzymatic hydrolysis lignin	$ZnCO_3$	200 mA/g	550 mAh/g (200)	Xi *et al*. 2020
Si@C-alkali lignin-azo-NO_2	None	200 mA/g	882 mAh/g (150)	Du *et al*. 2018
Sodium lignosulfonate	$Ni(OH)_2$	100 mA/g	863 mAh/g (100)	Zhou *et al*. 2018
Alkali lignin-derived carbon encapsulated SiO_2	Alkali etching	1 A/g	921 mAh/g (50)	Huang *et al*. 2021

Carbon-based materials are not only carbon fiber materials, but porous carbon is also a common structure of carbon materials. Huang *et al*. (2021) prepared lignin-based porous carbon to be used for capping SiO_2 by using a dual-template-assisted self-assembly method, which has a high pore volume (2.2 cm^3/g), allowing for faster diffusion of lithium ions and more lithium-ion storage sites. When assembled into a lithium-ion battery, the

button cell exhibited good multiplicative performance and a reversible capacity of 1109 mAh/g (Li *et al*. 2023a). Li *et al*. (2023a) also carried out research on capped silicon, in which a lignin-based phenolic resin was prepared using lignin as a precursor, and then Si nanoparticles were capped with the lignin-based phenolic resin. The carbon layer was uniformly encapsulated on the surface of Si nanoparticles. It was also found that the lignin-doped phenolic resin exhibited better electrochemical properties, with the tested initial specific capacity reaching 782 mAh/g. Coating Si-based materials with lignin-based carbon effectively prevents problems such as large volume changes during charging and discharging and poor cycle life.

Li-X Battery

Most portable devices on the market use lithium-ion batteries, which are the mainstream energy storage system in modern society. The low-energy density is a bottleneck for large-scale applications (Geng *et al*. 2021). Following lithium-ion batteries, lithium-sulfur batteries have received very widespread attention, because they can provide higher theoretical energy density by weight (2500 Wh/kg) and energy density by volume (2800 Wh/L), as well as a capacity that is an order of magnitude higher than that of conventional lithium-ion batteries (1675 mAh/g) (Yeon *et al*. 2020). Unlike the insertion/withdrawal mechanism of conventional lithium-ion batteries, S-S bonds can be broken and formed during the charging/discharging process of lithium-sulfur batteries and some intermediates are generated (Zhou *et al*. 2022). The reaction mechanism diagram of a typical lithium sulfur battery device is shown in Fig. 5 (Kang *et al*. 2016).

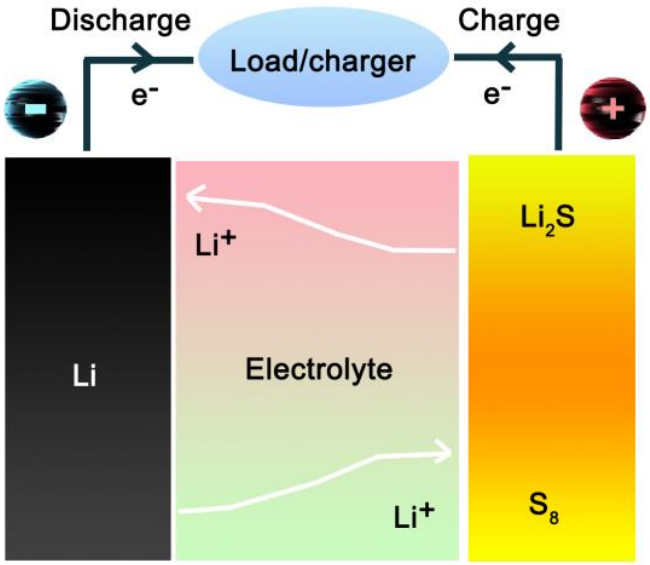

Fig. 5. Schematic diagram of the ion transport mechanism of a lithium-sulfur battery

Liu *et al*. (2018) investigated a film of lignin fibre/carbon nanotubes and graphene and used it as a substrate for active materials in lithium-sulphur batteries. The electrode maintained a high reversible capacity of 668.8 mAh/g (capacity retention of 91.5%) at a sulphur loading of 9.2 mg/cm^2 after 100 cycles at 0.5 C. Yu *et al*. (2017) designed a macro/microporous sulfur-loaded carbon-based material with lignin as the carbon skeleton, and the synthesized material had a specific surface area of 1212 m^2/g. The total sulphur

content of the composite was as low as 50.0 wt% (44.8% in the micropores) when the sulphur loading time was 10 h. The electrode then had a high reversible discharge capacity of 1240 mAh/g. Similarly, Xu *et al*. (2021) prepared lignin-based porous carbon using a NaCl template to load sulphur into the carbon material (high sulphur utilization of 66 wt%), which was able to provide a stable cycle life when used as a cathode for lithium-sulphur batteries, with an initial specific capacity of 1066 mAh/g at 1 C (capacity maintained at 99.9% after 400 cycles). Xu *et al*. (2019) turned their attention to enzymatically degraded lignin, using carbonization and other methods to investigate the residual lignin after enzymatic degradation. The material has a large specific surface area and the carbon substrate promotes uniform dispersion of the sulphur particles. It was assembled into a lithium-sulfur battery with cathode specific capacities of 1238, 1085, and 1035 mAh/g at 0.1, 0.2, and 0.5 C, respectively, with excellent multiplication capacity. After 200 cycles at 0.5 C, 596 mAh/g was retained with a coulombic efficiency of 92%. In conclusion, to design and develop high-performance cathode materials for lithium-sulfur batteries, in addition to the structural properties of lignin-based porous carbon, the optimization of sulfur loading time and the chemical bonding between the carbon-based materials and sulfur (especially the morphology of lignin-based carbon and the reason for the porosity) should also be considered.

In carbon substrates, nitrogen doping may lead to an improvement in electrochemical performance because of the confinement of S in the micropores, and N doping inhibits polysulfide solubilization and efficient utilization of S. Yeon *et al*. (2020) prepared nitrogen-doped porous carbon substrate materials by hydrothermal carbonization reaction, and the as-prepared nitrogen-doped materials have a large surface area (2070 m^2/g) and high nitrogen content (3.47%). The lithium-sulfur battery was prepared by loading S into the carbon substrate to achieve an initial discharge capacity of 1296 mAh/g (0.1 C). After 600 cycles, the electric capacity of 647 mAh/g was maintained, and the electrode also exhibited excellent cycling stability (0.05% capacity decay per cycle over 900 cycles at 1 C). The reason for such phenomena is the electrochemical and thermal stabilization of S due to the strong restriction of S in the N-doped micropores, providing different redox environments. Liu *et al*. (2020) also prepared lignocellulosic carbon matrices using cyanuric acid as a nitrogen source using spray-drying technique to obtain N-doped hollow porous carbon spheres, which, due to the N-type doping (especially pyrrolidinic acid-N), led to a strong Li_2S_x-N chemisorption force and effectively suppressed the insolubility of the polysulphides in the Li-S batteries and the "shuttle effect".

In addition, selenium exhibited higher conductivity (1×10^{-3} S/m) and almost the same volumetric capacity (3265 mAh/cm^3) compared to sulfur (5×10^{-28} S/m, 3467 mAh/cm^3). Lu *et al*. (2021) engineered lignin-derived multistage porous carbon as a novel highly loaded support for use in high-capacity and long-term-cycling lithium selenium batteries selenium hosts. The porous carbon doped with heteroatoms such as sulfur and oxygen exhibited a large specific surface area of 1696 m^2/g, which is favorable for a stable selenium host. Applied to lithium-selenium battery cathode exhibits excellent cycling stability with 92% retention after 500 cycles at 0.5 C.

Zhang *et al*. (2017) also prepared lignin-based lithium-selenium batteries. The specific process was alkaline lignin was first carbonized to obtain a carbon-based material, which was later loaded with selenium to obtain a composite material with well-developed pores and good electronic conductivity. It was then assembled into a lithium-selenium battery. The composite electrode exhibited a reversible capacity (at 0.5 C) of 596.4 mAh/g, and a capacity retention rate of 453.1 mAh/g. The capacity retention was 453.1 mAh/g in

the second cycle. The composite electrode exhibited excellent performance (363.2 mAh/g) at 4 C due to its excellent microporous properties.

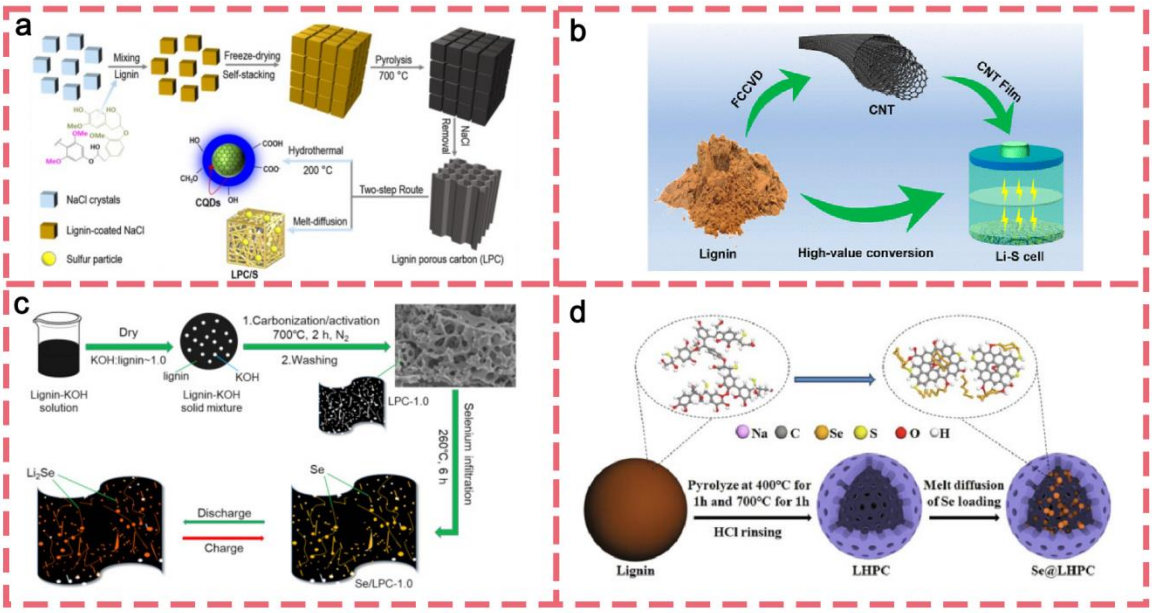

Fig. 6. (a) Schematic diagram of the preparation process of lignin porous carbon loaded S composites with NaCl as template (Xu *et al*. 2021; Permission granted by Elsevier); (b) Schematic diagram of the preparation process of lignin carbon nanotube film loaded S composites (Liu *et al*. 2023; Permission granted by ACS); (c) Schematic diagram of the preparation process of lignin porous carbon loaded Se composites (Zhang *et al*. 2017; Permission granted by Elsevier); (d) Composites of lignin hollow carbon microspheres loaded Se Schematic diagram of the preparation process (Lu *et al*. 2021; Permission granted by Elsevier)

Sodium Ion Battery

Sodium-ion batteries (SIBs) are likely to gradually replace lithium-ion batteries due to their low cost and environmental reasons. Developing anode materials for sodium-ion batteries still faces a relatively large number of challenges, such as low initial coulombic efficiency and capacity. Hard carbon shows a price advantage over graphite, while biomass is a more efficient and cheaper precursor, and biomass carbon will also be beneficial in improving the stability of hard carbon electrodes with electrolytes. Hard carbon is non-graphitizable carbon, which has high sodium ion uptake and excellent stability, and it has stacked graphite layers in the range of 3 to 5, with a larger *d*-spacing (0.36 to 0.4 nm) than graphite (0.335 nm), with predominantly turbo-layered graphite regions embedded in amorphous carbon domains and micropores (Susanti *et al*. 2020). Hard carbon with multilevel pore structure and large interlayer lattice space will enable the unobstructed transport of Na^+ and is more conducive to the storage of Na^+, which greatly improves its electrochemical performance. Hard carbon derived from lignin, which precisely meets this condition, has made lignin-based hard carbon materials loved by research scholars (Irisarri *et al*. 2015; Wang *et al*. 2015).

Lignin is abundant and it is also a polymer with a three-dimensional structure, so it holds promise as a hard carbon material for SIB anodes. In practice, the poor electrochemical performance of lignin-derived hard carbon has led to its hindered application. In nature, tree species such as pine and spruce produce lignocellulose, which exists together with cellulose and hemicellulose. Jin *et al*. (2023) utilized lignin combined

with cellulose or hemicellulose in a two-way combination to obtain high-performance and low-cost hard carbon. The conversion of lignin to hard carbon results in a higher content of oxygen-containing functional groups and a relatively well-posed porosity, which in turn inhibits the effective diffusion of Na^+. In comparison, the capacity of lignin hard carbon material with added cellulose was increased. The capacity of lignin hard carbon material with added hemicellulose was stabilized quite considerably, both in terms of long cycling and high current density.

The electrochemical performance of lignin-derived hard carbon obtained by direct carbonization is poor; however, the electrochemical performance of sodium-ion batteries can be improved by modulation of physical morphology and surface microstructure, which results in a microporous fine structure of the hard carbon anode (Wang *et al*. 2021). Ghimbeu *et al*. (2019) used two different sources of lignin (kraft lignin, lignosulfonate) to prepare SIB hard carbon anode materials. The two different lignin types exhibit similar physical structures at temperatures up to 1200 °C, but they have different pore sizes and very different surface morphologies. The reasons for this difference are the different sources of lignin. The groups and molecular weights of the lignin are distinctly different, the purity of lignin from different sources is also different, and the impurities also affect the surface morphology at high temperature. Lignosulfonate-derived hard carbon has a high specific surface area with a reduced capacity, especially under long cycling tests. The authors designed an improved method for this purpose, purifying the lignin and improving the heating method, which resulted in a reduction of impurities and a decrease in the specific surface area. The results was an improvement in the electrochemical performance (both the initial irreversible capacity and the reversible capacity were increased), which has led to the prospect of lignosulfonate-derived hard carbon materials for industrial applications. Alvin *et al*. (2019) enriched the theory of Na storage mechanism in lignin-based hard carbon by probing more deeply into the physical structure, such as the degree of graphitization, interlayer spacing, and specific surface area. The authors propose that at the beginning of the sodiation process (1 to 0.2 V), Na^+ adsorbs on surface defects and edge sites, and then it fills micropores in the discharge-tilted region between 0.2 and 0.1 V. The authors suggest that the Na^+ is stored in the surface defects of the lignin-based hard carbon. Then, the graphite layer below 0.1 V will also have Na^+ adherence. At the final cutoff potential (0.05 V), the concentration in the micropores is already high enough for Na^+ to be adsorbed, at which point the morphology becomes clustered.

The morphology of hard carbon greatly affects the electrochemical performance of sodium ion batteries as well. The more popular ones applied to sodium ion batteries are: carbon microspheres, carbon fibers, and layered carbon. As shown in Fig. 7, different morphologies of hard carbon can be applied to sodium-ion batteries. Hard carbon microspheres are one of the most common structures of lignin-based derived carbon. Li *et al*. (2020) synthesized a kind of hard carbon microspheres with a small specific surface area and a large interlayer spacing using lignosulfonate, and with fewer defects in this morphology, it can be applied to the anode of sodium-ion batteries to obtain a very high capacity, and the reversible capacity is very considerable. A large part of the synthesis of carbon microspheres can be obtained from spherical carbon structures formed by carbonization of phenolic resins. Zhang *et al*. (2019) synthesized lignin-based resin nanospheres by the principle of phenol-formaldehyde, followed by solvent evaporation and resinization. The carbon microsphere microcrystals obtained exhibited a larger size and the interlayer distance was increased, which makes it advantageous for sodium storage. Their application to sodium-ion batteries resulted in a reversible capacity of up to 347 mAh/g as

well as an initial coulombic efficiency of 74%, with excellent electrochemical performance. The carbon microspheres doped with heteroatoms may also lead to a substantial improvement in the battery performance. For example, Fan *et al*. (2021) synthesized a nitrogen atom doped carbon microspheres with 3-aminophenol as the nitrogen source, which yielded carbon microspheres in a better spherical state and with a large number of active sites attached, with a pore structure with ultra-micropores (< 0.7 nm). In the preparation of sodium-ion batteries, the specific capacity can reach 374 mAh/g (25 mA/g), the initial coulombic efficiency is as high as 85%, and 223 mAh/g can be maintained after 300 charges and discharges at a current density of 0.1 A/g. The reason for this result is the additional defects brought by nitrogen atoms and the large number of ultra-microporous morphology of the carbon microspheres. Another important point is that the interlayer spacing is large. These are the main factors in improving the capacity. Similarly, Zhang *et al*. (2021) doped two heteroatoms, nitrogen and phosphorus, and they prepared lignin into nanoporous N,P co-doped hard carbon microspheres using solvent evaporation. The Na^+ diffusion coefficients in the electrodes were up to 10^{-9} cm^2/s. The cells exhibited quite excellent and balanced sodium-storage properties, such as low-pressure capacities (up to 229 to 246 mAh/g), high initial coulombic efficiencies (78.7 to 82.4%), good multiplicative performance, and stable charge/discharge capability. In summary, it has been found that the large layer spacing and multi-atom doping of hard carbon microspheres are favorable for the platform capacity, and the preparation of carbon microspheres can be done by simple steps such as solvent evaporation, which will provide an easy way to implement the exploitation of lignin in high value-added applications.

Another major form factor in the application of lignin-based hard carbon materials for sodium-ion batteries is carbon fibers. Compared to polymers such as polyacrylonitrile (PAN), lignin generally has a low molecular weight and very poor electrospinnability. To improve the ability of lignin to prepare fibers, it is generally chemically modified and combined with other polymers. Jia *et al*. (2018) prepared nanofibers by electrostatic spinning of a mixture of kraft lignin and cellulose acetate in an inert gas at a high temperature of 1000 °C. Carbonization formed a unique carbon nano-network structure, and the product had an oxygen content of 13.26%, a wider broad face spacing (0.384 nm), and large specific surface area (541 m^2/g). The electrode exhibited a reversible capacity of 340 mAh/g (50 mA/g) when used as an anode material for sodium-ion batteries, and after 200 charge/discharge cycles, the high-multiplier capacity was still achievable up to 103 mAh/g when the current density was increased to 400 mA/g. As mentioned earlier, pure kraft lignin-derived porous carbon produces a large microscopic morphology, which makes electrochemical performance poorer (Jin *et al*. 2014). Currently, most lignin-based electrostatically spun carbon fibers for SIBs are prepared by blending lignin with other polymers. The technology of pure lignin-based electrostatically spun carbon fibers is still not perfected, and a pure lignin base would be beneficial for cost reduction, so it needs to be continued to be explored. Peuvot *et al*. (2019) prepared lignin-based electrostatic spun carbon fibers with a high specific capacity of 310 mAh/g and an initial coulombic efficiency of 89%. The authors also found that the carbonization temperature would be the main factor affecting the cycling stability. Wang *et al*. (2022) designed lignin-based carbon nanofiber anodes using gas-electric blending method. The material can be used directly in Na-ion batteries, and the binder can be omitted. In electrochemical performance tests, it showed good specific discharge capacity, high multiplicity performance and long cycle stability. In summary, the production of lignin-based carbon fibers for application in sodium-ion batteries requires electrostatic spinning technology, which is also the preferred

method for controllable structures and the most effective method in nanofibers. Nevertheless, the technology of preparing carbon fibers from pure lignin still needs to be discovered and explored.

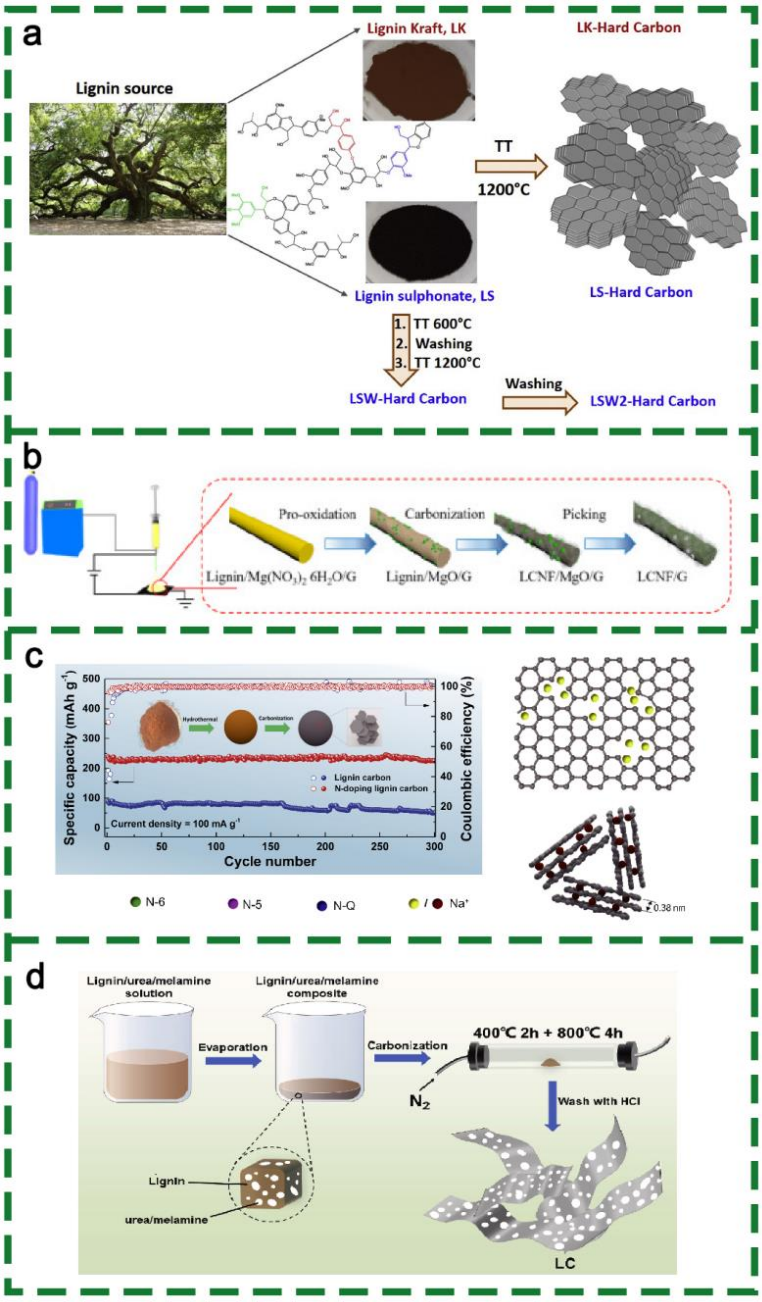

Fig. 7. (a) Roadmap for the preparation of two lignin-based hard carbon materials, kraft lignin, and lignosulfonate, by direct carbonization with two-step carbonization by water washing (Ghimbeu *et al*. 2019; Permission granted by Elsevier); (b) Roadmap for the preparation of lignin-based porous carbon nanofibers (Wang *et al*. 2022; Permission granted by Elsevier); (c) Roadmap for the preparation of nitrogen-doped lignin-based carbon microspheres (Fan *et al*. 2021; CC BY-NC-ND 4.0 Deed); (d) Roadmap for the preparation of porous nitrogen-doped lignin-based ultrathin layered carbon (Chen *et al*. 2020; Permission granted by Elsevier)

In addition to the classical morphology structures such as hard carbon microspheres and carbon fibers, layered carbon can also perform well electrochemically in sodium-ion

batteries. Chen *et al*. (2020) synthesized nitrogen-doped thin layered carbon using melamine and urea as nitrogen sources. The synthesized material showed large surface area and pore volume, and the nitrogen-doped ultrathin graphitic carbon made the active sites for sodium storage abundant. Further, it was used as an anode material for sodium-ion batteries, which could reach an initial capacity of 320 mAh/g (current density of 3 mA/g) in the voltage range of 0.01 to 3 V, and a capacity of up to 139 mAh/g at 150 mA/g, with virtually no capacity degradation after 4000 cycles. Such a high electrochemical performance may be due to the structural defects caused by doped N atoms, which will favor its capacity. The porous and ultrathin structure of layered carbon improves the Na ion storage kinetics, resulting in excellent multiplicity performance with stable cycling performance. This study also illustrates the feasibility of lignin-based layered carbon as a high-multiplication-rate carbon anode material for sodium-ion batteries.

Other Types of Batteries

Potassium ion batteries (PIBs) have been recognized in recent years as the preferred choice for energy storage in mainstream grids due to their high energy density and affordable price. Potassium ions can reduce their (de)-solvation energy at the electrode/electrolyte interface due to its small Stokes radius (3.6 Å compared to 4.6 Å for sodium ions and 4.8 Å for lithium ions) (Zhang *et al*. 2021). Hard carbon is the preferred choice for PIBs anode materials, probably because the material structure and K-ion storage mechanism still need to be further explored. Lignin serves as a rich source of hard carbon, and the molecular weight of lignin plays a major role in the formation of hard carbon structures. Wu *et al*. (2022) prepared hard carbon materials by carbonizing lignin of different molecular weights, and the carbonization of lignin of medium molecular weight (9660 g/mol) at a temperature of 700 °C yielded a hard carbon material with the maximum interlayer distances and amorphous structure of graphite-like nanocrystals. These structures maximize the native insertion and surface adsorption mechanisms for K-ion storage. At optimal carbonization conditions, the lignin-based hard carbon material exhibits a reversible specific capacity of ~300 mAh/g at 50 mA/g. Jiang *et al*. (2021) reconstructed the lignin using graphene oxide, and the reconstructed lignin had fewer defects, 86% lower oxygen functionality, and 82% fewer micropores compared to direct carbonization. When prepared as PIBs, the modified lignin provides enhanced capacity in the low potential range and exhibited better properties at high current densities. The authors found that the voltage hysteresis in K storage was much more severe than in Na storage. In practical applications, the voltage hysteresis of K-ion batteries will be an important aspect of electrode material design.

Sodium-selenium batteries are gradually gaining attention because of their sustainability and low cost, and they are also promising energy storage media to drive smart portable devices and electric vehicles. However, the slow kinetics at the Se cathode and the unpredictable metal electrodeposition of Na at the anode remain key challenges. Zeng *et al*. (2022) loaded Fe onto lignin-derived porous carbon material composites with reduced graphene oxide to encapsulate Se in a lignin-derived flexible porous carbon matrix and assembled them as sodium-selenium batteries, which were tested to show that at 2 A/g with a high reversible capacity of 213 mAh/g. This study expands the application of lignin in batteries in a new direction and provides a low-cost and sustainable method to solve the preparation of anode for future sodium-selenium batteries.

CHALLENGES AND OUTLOOK

Lignin as a carbon source for the preparation of carbon-based electrode materials has many advantages, such as a wide range of sources, low cost, a large number of aromatic ring structure, high carbon content, renewable, a large number of by-products of the paper industry, environmentally friendly and non-polluting, and high tensile strength (see Fig. 8). However, in the author's opinion, lignin carbon-based electrode materials are still far from large-scale industrial applications, specifically because the supply system of high-purity and high-molecular-weight lignin raw materials has not yet been formed (lignin fractionation is currently generally small-scale and costly), and it is difficult for lignin spinning and molding in the preparation of carbon fibers. Porous carbon produced by directly carbonizing alkali lignin, enzymatic lignin and kraft lignin will have low specific surface area, and the pretreatment step will be cumbersome.

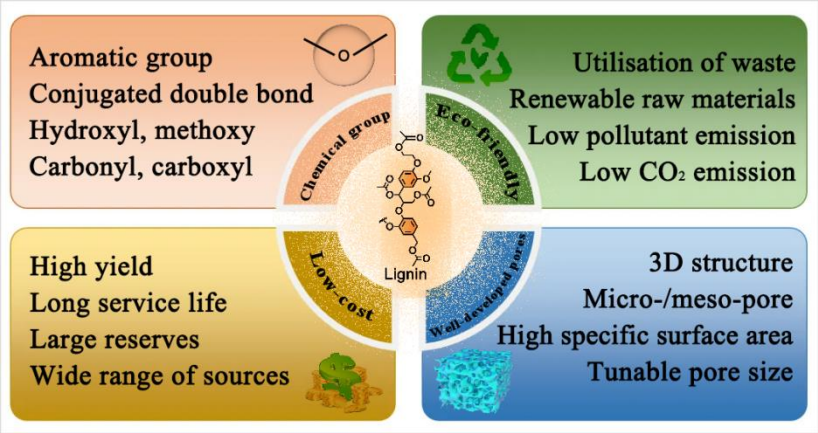

Fig. 8. Generalized map of the advantages and characteristics of lignin as a precursor for carbon materials

Different sources of lignin have different molecular weights, activities, polydispersities and degrees of heterogeneity. Carbon fibers and carbon microspheres prepared from different lignin species have different process characteristics and applicability. More deeply, the process and synthesis methods of lignin carbon materials are cumbersome and demanding, and further optimization is needed in controlling the porosity of lignin-based porous carbon materials, and the porosity requirements of lithium-ion batteries and sodium-ion batteries are not the same, so it is necessary to choose the optimal process conditions for a specific battery.

Within lignin-based carbon materials, is relatively easy to form microporous less than 2 nm, which is favorable for the electrolyte ions/electrons. But the wettability is poor, and the transmission path has been impeded. For lithium-ion batteries, carbon material specific capacity of the improvement of the negative factors, but of course, this will be beneficial to a certain extent to the sodium-ion batteries, the production of hard carbon materials.

Heteroatom doping can improve the inherent electrochemical properties of lignin-based carbon materials, but the choice of heteroatom or the combination of heteroatoms remains to be demonstrated. Particularly, lignosulfonate itself contains sulfur, which has a unique advantage over alkali lignin and enzymatic lignin.

In the hard carbon material for sodium ion batteries, the small molecular weight of alkali lignin is unfavorable to the formation of hard carbon, while the black liquor of papermaking is alkaline, which can reduce the use of KOH reaming agent to a certain extent. The specific process conditions remain to be explored.

CONCLUSIONS

This paper has reviewed and discussed the benefits, preparation, and properties of lignin-derived carbon-based electrode materials for small rechargeable battery energy storage devices and recent advances. Lignin – a renewable bio-resource – can be a potential candidate material for high-performance energy storage systems due to its cost suitability and environmental friendliness. The results show that lignin is a potential electrode material for rechargeable devices, and it can serve as a precursor for the production of porous carbon materials (*e.g.*, hard carbon, carbon microspheres, carbon fibres, porous carbon). The utilization of industrial lignin for the production of lignin-based carbon materials can "turn waste into treasure", which has important resource and environmental significance. Currently, the development of lignin-based electrode materials is in a "blowout" stage, and a large number of studies have made it possible to transform lignin into high-value energy storage materials.

ACKNOWLEDGMENTS

The authors greatly acknowledge the support of National Natural Science Foundation of China (No. 32271807).

REFERENCES CITED

Alvin, S., Yoon, D., Chandra, C., Cahyadi, H. S., Park, J. H., Chang, W., Chung, K. Y., and Kim, J. (2019). "Revealing sodium ion storage mechanism in hard carbon," *Carbon* 145, 67-81. DOI: 10.1016/j.carbon.2018.12.112

Balocha, M., and Labidi, J. (2021). "Lignin biopolymer: The material of choice for advanced lithium-based batteries," *RSC Advances* 11, 23644-23653. DOI: 10.1039/D1RA02611A

Chen, M., Luo, F., Liao, Y., Liu, C., Xu, D., Wang, Z., Liu, Q., Wang, D., Ye, Y., Li, S., and Wang, H. (2022). "Hard carbon derived for lignin with robust and low-potential sodium ion storage," *Journal of Electroanalytical Chemistry* 919, article 116526. DOI: 10.1016/j.jelechem.2022.116526

Chen, S., Feng, F., and Ma, Z. (2020). "Lignin-derived nitrogen-doped porous ultrathin layered carbon as a high-rate anode material for sodium-ion batteries," *Composites Communications* 22, article 100447. DOI: 10.1016/j.coco.2020.100447

Chen, W.-J., Zhao, C.-X., Li, B.-Q., Yuan, T.-Q., and Zhang, Q. (2022). "Lignin-derived materials and their applications in rechargeable batteries," *Green Chemistry* 24, 565-584. DOI: 10.1039/D1GC02872C

Culebras, M., Geaney, H., Beaucamp, A., Upadhyaya, P., Dalton, E., Ryan, K. M., and Collins, M. N. (2019). "Bio-derived carbon nanofibres from lignin as high-

performance li-ion anode materials," *ChemSusChem* 12(19), 4516-4521. DOI: 10.1002/cssc.201901562

Du, L., Wu, W., Luo, C., Zhao, H., Xu, D., Wang, R., and Deng, Y. (2018). "Lignin derived Si@C composite as a high performance anode material for lithium ion batteries," *Solid State Ionics* 319, 77-82. DOI: 10.1016/j.ssi.2018.01.039

Du, X., Wu, S., and Li, P. (2023). "Catalytic hydrogenolysis lignin to obtain phenols: A review of selective cleavage of ether bonds," *BioResources* 18(2), 4231-4261. DOI: 10.15376/biores.18.2.Du

Fan, L., Shi, Z., Ren, Q., Yan, L., Zhang, F., and Fan, L. (2021). "Nitrogen-doped lignin based carbon microspheres as anode material for high performance sodium ion batteries," *Green Energy and Environment* 6(2), 220-228. DOI: 10.1016/j.gee.2020.06.005

Feghali, E., Torr, K. M., Van De Pas, D. J., Ortiz, P., Vanbroekhoven, K., Eevers, W., and Vendamme, R. (2018). "Thermosetting polymers from lignin model compounds and depolymerized lignins," *Topics Current Chemistry* 376(4), 32. DOI: 10.1007/s41061-018-0211-6

Geng, X., Lin, R., Gu, X., Su, Z., and Lai, C. (2021). "Water reducer: A Highly dispersing binder for high-performance lithium-sulfur batteries," *Chinese Journal of Chemistry* 39(6), 1523-1530. DOI: 10.1002/cjoc.202000702

Ghimbeu, C. M., Zhang, B., Martinez de Yuso, A., Réty, B., and Tarascon, J. M. (2019). "Valorizing low cost and renewable lignin as hard carbon for Na-ion batteries: Impact of lignin grade," *Carbon* 153, 634-647. DOI: 10.1016/j.carbon.2019.07.026

Goodenough, J. B., and Park, K. S. (2013). "The Li-ion rechargeable battery: A perspective," *J. Am. Chem. Soc.* 135, 1167-1176. DOI: 10.1021/ja3091438

Huang, S., Yang, D., Zhang, W., Qiu, X., Li, Q., and Li, C. (2021). "Dual-templated synthesis of mesoporous lignin-derived honeycomb-like porous carbon/SiO_2 composites for high-performance Li-ion battery," *Microporous and Mesoporous Materials* 317, article 111004. DOI: 10.1016/j.micromeso.2021.111004

Irisarri, E., Ponrouch, A., and Palacin, M. R. (2015). "Review–hard carbon negative electrode materials for sodium–ion batteries," *Journal of the Electrochemical Society* 162(14), A2476-A2482. DOI: 10.1149/2.0091514jes

Jia, H., Sun, N., Dirican, M., Li, Y., Chen, C., Zhu, P., Yan, C., Zang, J., Guo, J., Tao, J., Wang, J., Tang, F., and Zhang, X. (2018). "Electrospun kraft lignin/cellulose acetate-derived nanocarbon network as an anode for high-performance sodium-ion batteries," *ACS Applied Materials and Interfaces* 10(51), 44368-44375. DOI: 10.1021/acsami.8b13033

Jiang, G., and Xie, S. (2019). "Preparation and electrochemical properties of lignin porous carbon spheres as the negative electrode of lithium-ion batteries," *International Journal of Electrochemical Science* 14(6), 5422-5434. DOI: 10.20964/2019.06.36

Jiang, K., Tan, X., Zhai, S., Cadien, K., and Li, Z. (2021). "Carbon nanosheets derived from reconstructed lignin for potassium and sodium storage with low voltage hysteresis," *Nano Research* 14, 4664-4673. DOI: 10.1007/s12274-021-3399-7

Jin, J., Yu, B., Shi, Z., Wang, C., and Chong, C. (2014). "Lignin-based electrospun carbon nanofibrous webs as free-standing and binder-free electrodes for sodium-ion batteries," *Journal of Power Sources* 272, 800-807. DOI: 10.1016/j.jpowsour.2014.08.119

Jin, Q., Tao, L., Feng, Y., Xia, D., Spiering, G. A., Hu, A., Moore, R., Lin, F., and Huang,

H. (2023). "Agricultural wastes for full-cell sodium-ion batteries: Engineering biomass components to maximize the performance and economic prospects," *ACS Sustainable Chemistry and Engineering* 11(2), 536-546. DOI: 10.1021/acssuschemeng.2c04750

Jung, H. Y., Lee, J. S., Han, H. T., Jung, J., Eom, K., and Lee, J. T. (2022). "Lignin-based materials for sustainable rechargeable batteries," *Polymers* 14(4), 673. DOI: 10.3390/polym14040673

Kang, W. M., Deng, N. P., Ju, J. G., Li, Q. X., Wu, D. Y., Ma, X. M., Li, L., Naebe, M., and Cheng, B. W. (2016). "A review of recent developments in rechargeable lithium-sulfur batteries." *Nanoscale* 8,16541-16588. DOI: 10.1039/C6NR04923K

Kirui, A., Zhao, W. C., Deligey, F., Yang, H., Kang, X., Frederic Mentink-Vigier and Tuo Wang. (2022). "Carbohydrate–aromatic interface and molecular architecture of lignocellulose," *Nature Communications* 13, 538. DOI: 10.1038/s41467-022-28165-3

Li, C., Sun, Y., Wu, Q., Liang, X., Chen, C., and Xiang, H. (2020). "A novel design strategy of a practical carbon anode material from a single lignin-based surfactant source for sodium-ion batteries," *Chemical Communications* 56, 6078-6081. DOI: 10.1039/D0CC01431A

Li, P., Ren, J., Jiang, Z., Huang, L., Wu, C., and Wu, W. (2022a). "Review on the preparation of fuels and chemicals based on lignin," *RSC Advances* 12, 10289-10305. DOI: 10.1039/D2RA01341J

Li, P., Yang, C., Wu, C., Wei, Y., Jiang, B., Jin, Y., and Wu, W. (2022b). "Bio-based carbon materials for high-performance supercapacitors," *Nanomaterials* 12, article 2931. DOI: 10.3390/nano12172931

Li, P., Miao, C., Yi, D., Wei, Y., Chen, T., and Wu, W. (2023a). "Pomegranate like silicon–carbon composites prepared from lignin-derived phenolic resins as anode materials for lithium-ion batteries," *New Journal of Chemistry* 47, 16855-16863. DOI: 10.1039/D3NJ02547K

Li, P., Yang, C., Yi, D., Li, S., Wang, M., Wang, H., Jin, Y., and Wu, W. (2023b). "Preparation of spherical porous carbon from lignin-derived phenolic resin and its application in supercapacitor electrodes," *International Journal of Biological Macromolecules* 252, article 126271. DOI: 10.1016/j.ijbiomac.2023.126271

Li, P., Yu, J., Wang, M., Su, W., Yang, C., Jiang, B., and Wu, W. (2023c). "Preparation of symmetrical capacitors from lignin-derived phenol and pani composites with good electrical conductivity," *International Journal of Molecular Sciences* 24, article 8661. DOI: 10.3390/ijms24108661

Li, S., Jiang, Z., Liu, A., Lu, J., Du, J., Tao, Y., Cheng, Y., and Wang, H. (2022). "A porous carbon based on the surface and structural regulation of wasted lignin for long-cycle lithium-ion battery," *International Journal of Biological Macromolecules* 222(Part A), 1414-1422. DOI: 10.1016/j.ijbiomac.2022.09.269

Li, S., Luo, W., He, Q., Lu, J., Du, J., Tao, Y., Cheng, Y., and Wang, H. (2023). "A lignin-based carbon anode with long-cycle stability for li-ion batteries," *International Journal of Molecular Sciences* 24(1), 284. DOI: 10.3390/ijms24010284

Li, W., and Shi, J. (2023). "Lignin-derived carbon material for electrochemical energy storage applications: Insight into the process-structure-properties-performance correlations," *Frontiers in Bioengineering and Biotechnology* 11, article 1121027. DOI: 10.3389/fbioe.2023.1121027

Li, Y., Huang, Y., Song, K., Wang, X., Yu, K., and Liang, C. (2019). "Rice husk lignin-derived porous carbon anode material for lithium-ion batteries," *ChemistrySelect*

4(14), 4178-4184. DOI: 10.1002/slct.201900401

Liu, F., Feng, P., Yuan, M., Zhai, G., Innocent, M. T., Xiang, H., Wu, Q., Lu, Y., and Zhu, M. (2023). "Continuous preparation of a flexible carbon nanotube film from lignin as a sulfur host material for lithium–sulfur batteries," *ACS Sustainable Chemistry and Engineering* 11(46), 16544-16553. DOI: 10.1021/acssuschemeng.3c04368

Liu, H., Xu, T., Liu, K., Zhang, M., Liu, W., Li, H., Du, H., and Si, C. (2021). "Lignin-based electrodes for energy storage application," *Industrial Crops and Products* 165, article 113425. DOI: 10.1016/j.indcrop.2021.113425

Liu, T., Sun, S., Song, W., Sun, X., Niu, Q., Liu, H., Ohsaka, T., and Wu, J. (2018). "A lightweight and binder-free electrode enabled by lignin fibers@carbon-nanotubes and graphene for ultrastable lithium-sulfur batteries," *Journal of Materials Chemistry A* 6, 23486-23494. DOI: 10.1039/C8TA08521H

Liu, W., Jiang, H., and Yu, H. (2015). "Thermochemical conversion of lignin to functional materials: a review and future directions," *Green Chemistry* 2015, 17, 4888-4907. DOI: 10.1039/C5GC01054C

Liu, Y., Guo, H., Zhang, B., Wen, G., Vajtai, R., Wu, L., Ajayan, P. M., and Wang, L. (2020). "Sustainable synthesis of N-doped hollow porous carbon spheres *via* a spray-drying method for lithium-sulfur storage with ultralong cycle life," *Batteries and Supercaps* 3(11), 1201-1208. DOI: 10.1002/batt.202000143

Liu, Z. H., Hao, N. J., Wang, Y. Y., Dou, C., Lin, F., Shen, R., Bura, R., Hodge, D. B., Dale, B. E., Ragauskas, A. J., Yang, B., and Yuan, J. S. (2021). "Transforming biorefinery designs with 'Plug–In Processes of Lignin' to enable economic waste valorization," *Nature Communications* 12, article 3912. DOI: 10.1038/s41467-021-23920-4

Lu, P., Liu, F., Zhou, F., Qin, J., Shi, H., and Wu, Z.-S. (2021). "Lignin derived hierarchical porous carbon with extremely suppressed polyselenide shuttling for high-capacity and long-cycle-life lithium–selenium batteries," *Journal of Energy Chemistry* 55, 476-483. DOI: 10.1016/j.jechem.2020.07.022

Nowak, A. P., Hagberg, J., Leijonmarck, S., Schweinebarth, H., Baker, D., Uhlin, A., Tomani, P., and Lindbergh, G. (2018). "Lignin-based carbon fibers for renewable and multifunctional lithium-ion battery electrodes," *Holzforschung* 72(2), 81-90. DOI: 10.1515/hf-2017-0044

Peuvot, K., Hosseinaei, O., Tomani, P., Zenkert, D., and Lindbergh, G. (2019). "Lignin based electrospun carbon fiber anode for sodium ion batteries," *Journal of The Electrochemical Society* 166, A1984. DOI: 10.1149/2.0711910jes

Ralph, J., Lapierre, C., and Boerjan, W. (2019). "Lignin structure and its engineering," *Current Opinion in Biotechnology* 56, 240-249. DOI: 10.1016/j.copbio.2019.02.019

Rois, M. F., Sasono, S. R. A., Widiyastuti, W., Nurtono, T., and Setyawan, H. (2022). ""High-performance electrocatalyst made from lignosulfonate nanofiber composited with manganese dioxide without carbonation process," *Advanced Powder Technology* 33(5), article 103572. DOI: 10.1016/j.apt.2022.103572

Rios, O., Martha, S. K., McGuire, M. A., Tenhaeff, W., More, K., Daniel, C., and Nanda, J. (2014). "Monolithic composite electrodes comprising silicon nanoparticles embedded in lignin-derived carbon fibers for lithium-ion batteries," *Energy Technology* 2(9-10), 773-777. DOI: 10.1002/ente.201402049

Rinaldi, R., Jastrzebske, R., Clough, M. T., Ralph, J., Kennema, M., Bruijnincx, P. C. A., and Weckhuysen, B. M. (2016). "Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis," *Angewandte Chemie–*

international Edition 55, 8164-8215. DOI: 10.1002/anie.201510351

Schirone, L., and Pellitteri, F. (2017). "Energy policies and sustainable management of energy sources," *Sustainability* 9(12), article 2321. DOI: 10.3390/su9122321

Shao, Y., Xia, Q. N., Dong, L., Liu, X., Han, X., Parker, S. F., Cheng, Y., Daemen, L. L., Ramirez-Cuesta, A. J., and Yang, S. (2017). "Selective production of arenes *via* direct lignin upgrading over a niobium–based catalyst," *Nature Communications* 8, article 16104. DOI: 10.1038/ncomms16104

Stojanovska, E., Pampal, E. S., Kilic, A., Quddus, M., and Candan, Z. (2019). "Developing and characterization of lignin-based fibrous nanocarbon electrodes for energy storage devices," *Composites Part B: Engineering* 158, 239-248. DOI: 10.1016/j.compositesb.2018.09.072

Sun, Y., Shi, X. L., Yang, Y. L., Suo, G., Zhang, L., Lu, S., and Chen, Z. G. (2022). "Biomass-derived carbon for high-performance batteries: From structure to properties," *Advanced Functional Materials* 32(24), article 2201584. DOI: 10.1002/adfm.202201584

Susanti, R. F., Alvin, S., and Kim, J. (2020). "Toward high-performance hard carbon as an anode for sodium-ion batteries: Demineralization of biomass as a critical step," *Journal of Industrial and Engineering Chemistry* 91, 317-329. DOI: 10.1016/j.jiec.2020.08.016

Wang, C., Yang, D., Zhu, Y., Xi, Y., Zhang, W., Yan, M., Qin, Y., Qi, X. (2022). "Pyrolytic gas exfoliation and template mediation inducing defective mesoporous carbon network from industrial lignin for advanced lithium-ion storage," *Industrial Crops and Products* 180, article 114748. DOI: 10.1016/j.indcrop.2022.114748

Wang, H., Hu, P. F., Yang, J., Gong, G., Guo, L., and Chen, X. (2015). "Renewable–juglone–based high–performance sodium–ion batteries," *Advanced Materials* 27(14), 2348-2354. DOI: 10.1002/adma.201405904

Wang, S.-X., Yang, L., Stubbs, L. P., Li, X., and He, C. (2013). "Lignin-derived fused electrospun carbon fibrous mats as high performance anode materials for lithium ion batteries," *ACS Applied Materials and Interfaces* 5(23), 12275-12282. DOI: 10.1021/am4043867

Wang, X., Li, X., Lu, Z., Liu, J., Bai, L., Dong, J., and Nan, D. (2022). "Constructing porous lignin-based carbon nanofiber anodes with flexibility for high-performance lithium/sodium-ion batteries," *Materials Today Sustainability* 20, article 100234. DOI: 10.1016/j.mtsust.2022.100234

Wang, Y., Wang, K., Yong, B., Deng, L., and Zhang, P. (2021). "Constructing advanced high-performance sodium-ion batteries anode materials *via* the morphology tuning strategy of lignin-derived carbon," *Journal of Materials Research* 36, 3460-3471. DOI: 10.1557/s43578-021-00378-0

Wei, H., Xu, D., Chen, W., Liu, X., Zhang, Z., Dai, L., Hu, H., and Yu, X. (2022). ""Low-temperature hydrothermal activation-catalytic carbonation boosting porous Si/SiOx@C composites derived from bamboo leaves for superior lithium storage performance," *Applied Surface Science* 584, article 152580. DOI: 10.1016/j.apsusc.2022.152580

Wu, K. L., Zhang, W. W., Jiang, T. B., Wu, M., Liu, W., Wang, H. M., and Hou, Q. X. (2023). "Structure regulated 3D flower-like lignin-based anode material for lithium-ion batteries and its storage kinetics," *International Journal of Biological Macromolecules* 227, 146-157. DOI: 10.1016/j.ijbiomac.2022.12.095

Wu, Z., Zou, J., Zhang, Y., Lin, X., Fry, D., Wang, L., and Liu, J. (2022). "Lignin-derived

hard carbon anode for potassium-ion batteries: Interplay among lignin molecular weight, material structures, and storage mechanisms," *Chemical Engineering Journal* 427, article 131547. DOI: 10.1016/j.cej.2021.131547

Xi, Y., Liu, X., Xiong, W., Wang, H., Ji, X., Kong, F., Yang, G., and Xu, J. (2021). "Converting amorphous kraft lignin to hollow carbon shell frameworks as electrode materials for lithium-ion batteries and supercapacitors," *Industrial Crops and Products* 174, article 114184. DOI: 10.1016/j.indcrop.2021.114184

Xi, Y., Huang, S., Yang, D., Qiu, X., Su, H., Yi, C., and Li, Q. (2020). "Hierarchical porous carbon derived from the gas-exfoliation activation of lignin for high-energy lithium-ion batteries," *Green Chemistry* 22(13), 4321-4330. DOI: 10.1039/D0GC00945H

Xi, Y., Yang, D., Qiu, X., Wang, H., Huang, J., and Li, Q. (2018). "Renewable lignin-based carbon with a remarkable electrochemical performance from potassium compound activation," *Industrial Crops and Products* 124, 747-754. DOI: 10.1016/j.indcrop.2018.08.018

Xi, Y., Yang, D., Wang, Y., Huang, J., Yan, M., Yi, C., Qian, Y., and Qiu, X. (2020). "Effect of structure of technical lignin on the electrochemical performance of lignin-derived porous carbon from K_2CO_3 activation," *Holzforschung* 74(3), 293-302. DOI: 10.1515/hf-2019-0107

Xu, J., Liu, B., Wu, L., Hu, J., Hou, H., and Yang, J. (2019). "A waste-minimized biorefinery scenario for the hierarchical conversion of agricultural straw into prebiotic xylooligosaccharides, fermentable sugars and lithium-sulfur batteries," *Industrial Crops and Products* 129, 269-280. DOI: 10.1016/j.indcrop.2018.12.002

Xu, J., Zhou, P., Yuan, L., Liu, X., Ma, J., and Zhang, C. (2021). "Dual lignin valorization enabled by carbon quantum dots and lithium-sulfur cathode," *Industrial Crops and Products* 170, article 113801. DOI: 10.1016/j.indcrop.2021.113801

Yadav, R., Zabihi, O., Fakhrhoseini, S., Nazarloo, H. A., Kiziltas, A., Blanchard, P., and Naebe, M. (2023). "Lignin derived carbon fiber and nanofiber: Manufacturing and applications," *Composites Part B: Engineering* 255, article 110613. DOI: 10.1016/j.compositesb.2023.110613

Yang, Z., Guo, H., Li, F., Li, X., Wang, Z., Cui, L., and Wang, J. (2018). "Cooperation of nitrogen-doping and catalysis to improve the Li-ion storage performance of lignin-based hard carbon," *Journal of Energy Chemistry* 27(5), 1390-1396. DOI: 10.1016/j.jechem.2018.01.013

Yeon, J. S., Park, S. H., Suk, J., Lee, H., and Park, H. S. (2020). "Confinement of sulfur in the micropores of honeycomb-like carbon derived from lignin for lithium-sulfur battery cathode," *Chemical Engineering Journal* 382, article 122946. DOI: 10.1016/j.cej.2019.122946

Yu, F., Li, Y., Jia, M., Nan, T., Zhang, H., Zhao, S., and Shen, Q. (2017). "Elaborate construction and electrochemical properties of lignin-derived macro-/micro-porous carbon-sulfur composites for rechargeable lithium-sulfur batteries: The effect of sulfur-loading time," *Journal of Alloys and Compounds* 709, 677-685. DOI: 10.1016/j.jallcom.2017.03.204

Yue, F. X., Lu, F. C., Ralph, S., and Ralph, J. (2016). "Identification of 4–O–5–units in softwood lignins *via* definitive lignin models and NMR," *Biomacromolecules* 17(6): 1909-1920. DOI: 10.1021/acs.biomac.6b00256

Zeng, L., Zhu, J., Wang, J., Huang, L., Liu, X., Lu, W., and Yu, X. (2022). "A lignin-derived flexible porous carbon material for highly efficient polyselenide and sodium

regulation," *Nanoscale* 14, 11162-11170. DOI: 10.1039/D2NR01727J

Zhang, H., Jia, D., Yang, Z., Yu, F., Su, Y., Wang, D., and Shen, Q. (2017). "Alkaline lignin derived porous carbon as an efficient scaffold for lithium-selenium battery cathode," *Carbon* 122, 547-555. DOI: 10.1016/j.carbon.2017.07.004

Zhang, H., Zhang, W., and Huang, F. (2021). "Hard carbon microsphere with expanded graphitic interlayers derived from a highly branched polymer network as ultrahigh performance anode for practical sodium-ion batteries," *ACS Applied Materials and Interfaces* 13(51), 61180-61188. DOI: 10.1021/acsami.1c19199

Zhang, S., Teck, A. A., Guo, Z., Xu, Z., and Titirici, M. M. (2021). "Carbon composite anodes with tunable microstructures for potassium-ion batteries," *Batteries and Supercaps* 4(4), 663-670. DOI: 10.1002/batt.202000306

Zhang, J., Duan, J., Zhang, Y., Chen, M., Ji, K., and Wang, C. (2021). "Facile synthesis of N,P-codoped hard carbon nanoporous microspheres from lignin for high-performance anodes of sodium-ion batteries," *ChemElectroChem* 8(18), 3544-3552. DOI: 10.1002/celc.202100795

Zhang, Y., Zhu, Y., Zhang, J., Sun, S., Wang, C., Chen, M., and Zeng, J. (2020). "Optimizing the crystallite structure of lignin-based nanospheres by resinification for high-performance sodium-ion battery anodes," *Energy Technology* 8(1), article 1900694. DOI: 10.1002/ente.201900694

Zhao, H., Wang, Q., Deng, Y., Shi, Q., Qian, Y., Wang, B., Lü, L., and Qiu, X. (2016). "Preparation of renewable lignin-derived nitrogen-doped carbon nanospheres as anodes for lithium-ion batteries," *RSC Advances* 6, 77143-77150. DOI: 10.1039/C6RA17793J

Zhou, G., Chen, H., and Cui, Y. (2022). "Formulating energy density for designing practical lithium–sulfur batteries," *Nature Energy* 7, 312-319. DOI: 10.1038/s41560-022-01001-0

Zhou, Z., Chen, F., Kuang, T., Chang, L., Yang, J., Fan, P., Zhao, Z., and Zhong, M. (2018). "Lignin-derived hierarchical mesoporous carbon and NiO hybrid nanospheres with exceptional Li-ion battery and pseudocapacitive properties," 274, 288-297. DOI: 10.1016/j.electacta.2018.04.111

Article submitted: November 10, 2023; Peer review completed: November 27, 2023; Revised version received: March 1, 2024; Accepted: March 13, 2024; Published: March 26, 2024.
DOI: 10.15376/biores.19.2.Li