

Review

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From laboratory to mass production: mechanistic insights and optimization of eco-friendly carbon-based anodes from biomass for potassium-ion batteries

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How to cite this article: Liu, Z.; Chen, J.; He, K.; Fang, Z.; Zhang, H.; Gong, Z.; Ding, S.; Wang, T.; Zhang, G.; Liu, Q. From laboratory to mass production: mechanistic insights and optimization of eco-friendly carbon-based anodes from biomass for potassium-ion batteries. *Energy Mater.* 2025, 5, 500051. <https://dx.doi.org/10.20517/energymater.2024.154>

Received: 2 Sep 2024 **First Decision:** 8 Oct 2024 **Revised:** 6 Nov 2024 **Accepted:** 19 Nov 2024 **Published:** 25 Feb 2025

Academic Editors: Ho Seok Park, Yuping Wu **Copy Editor:** Ping Zhang **Production Editor:** Ping Zhang

Abstract

Biomass-derived carbon-based materials with high performance are expected to become the frontrunners in anodes for potassium-ion batteries because of cost-effectiveness, non-toxic, and ecological compatibility. Herein, this review systematically explores critical parameters during the application of biomass-derived carbon as anodic electrodes for potassium-ion batteries, highlighting material selection, preparation methods, and electrochemical performance. Biomass sources such as plant organs, plant straw, and animal bones offer a cost-effective and renewable route to produce carbon anodes, with unique structural advantages for potassium storage. Key preparation techniques (including pyrolysis, chemical activation, templating, hydrothermal carbonization and microwave-assisted pyrolysis) allow for precise tuning of porosity, surface area, and heteroatom doping, enhancing reversible capacity, rate property, and cycling stability. We further analyze the potassium storage mechanisms,



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providing insights into the intercalation and adsorption processes that occur during battery operation. However, the mass production before application of these materials is constrained by material selection, preparation processes, and reaction mechanisms. The review also identifies critical challenges for scaling up production, such as consistency in material properties and energy efficiency, and outlines potential solutions, including process optimization and sustainable synthesis techniques. Future research will focus on enhancing the properties of bio-derived carbon anodes through structural and compositional optimization to catch the increasing demands of electrochemical energy storage technologies.

Keywords: Potassium-ion batteries, anode, carbon, biomass-derived, ion storage mechanism

INTRODUCTION

As the economy rapidly advances, there is a growing consensus on the need to promote innovation in green, clean and low-carbon technologies while cultivating a modern energy system based on renewable energy, which promotes the progress of stable large-scale energy storage^[1-3]. Electrochemical energy storage devices provide high flexibility and adaptability, and their demand share is increasing annually^[4-6]. Supercapacitors are critical components in energy storage systems due to their excellent power density, fast charge/discharge cycles, and long lifespan^[7]. Moreover, lithium-ion batteries (LIBs) have been fully applied to portable electronics and new energy vehicles, but are limited by high costs and resource scarcity^[8]. Potassium-ion batteries (PIBs) operate on the same fundamental principles as LIBs. They consist of three main components: an anode, a cathode, and an electrolyte. During charging, potassium ions move from the cathode to the anode through the electrolyte, and during discharging, the ions move back to the cathode^[9]. This movement of ions creates an electrical current that can be harnessed for power. Furthermore, potassium resources are abundant and easy to exploit. Meanwhile, biomass-derived carbon can achieve excellent specific capacity and cycling stability when used as anodes in PIBs, and is attractive anode material for PIBs due to its abundance, low cost, and environmental friendliness^[10]. Hence, PIBs are favored as a new supplementary energy storage system^[11]. Additionally, a PIB is more energy dense than a sodium-ion battery due to its lower standard electrode potential and closer proximity to lithium ions^[12]. Furthermore, lithium, sodium, and potassium ions change their ionic radii from large to small, whereas Stokes radius changes from large to small^[13]. There are fewer solvated potassium ions, and the potassium ions move faster in electrolytes, which makes the potassium battery hopeful to have better rate performance^[14]. Based on the above advantages, the electrode materials of PIBs have attracted wide attention.

Anodes play one of the most decisive roles in PIBs^[15]. Among the most studied anode materials are carbon-based materials because of their environmentally friendly properties, abundance of raw materials and simplicity of synthesis^[16,17]. There are many kinds of carbonaceous materials, including graphene, soft carbon and hard carbon^[18]. Graphene, due to its two-dimensional structure, offers a high surface area for potassium storage. Both sides of the graphene sheets can store potassium ions, but issues such as stacking and aggregation reduce the available active surface. Despite a theoretical high capacity, issues including low initial Coulombic efficiency and side reactions with the electrolyte hinder its performance. Soft carbon is a form of amorphous carbon that can be partially graphitized at high temperatures. Its flexibility allows for easier structural adjustment, providing better potassium ion transport and storage kinetics. Soft carbon can balance between amorphous and graphitic properties, offering a combination of fast ion transport and low-voltage platforms for PIBs. Hard carbon, an amorphous material, consists of disordered carbon layers with microcrystalline graphitic domains. Its larger interlayer spacing (~ 0.4 nm) allows for better potassium storage and structural stability compared to graphite. It can effectively suppress volume expansion and achieve faster potassium ion transport. Hard carbon, especially when derived from biomass, offers environmentally friendly and cost-effective solutions with promising potassium storage properties^[19].

However, currently, non-biomass-derived carbon, as the raw material for synthesizing carbon-based anode materials, cannot be completely regenerated. The mass production of carbon-based anode materials will inevitably consume a great deal of carbon precursors. Biomass-derived carbon offers a more sustainable and cost-effective alternative to non-biomass-derived carbon. Additionally, the natural heteroatom content (such as nitrogen, sulfur, and oxygen) in biomass materials enhances potassium storage capacity by creating more active sites for ion intercalation and improving conductivity. Compared to non-biomass-derived materials, the utilization of biomass-derived carbon in PIBs contributes to a more sustainable, environmentally friendly and higher-performance battery technology, thereby promoting the commercialization of PIBs^[20]. Therefore, exploring low-cost and renewable carbon precursors for preparing carbon materials as anodes for PIBs with high performance has gradually become a hot research topic^[21].

Biomass-derived carbon is prepared from biomass through carbonization, activation and other methods^[22-24]. Producing these materials involves small-scale and pilot-scale testing stages, which play a crucial part in the development of carbon materials derived from biomass. Featuring a large surface area, rich pore structure, rapid conductivity, and high chemical stability, biomass, as a rich renewable energy, offers abundant sources and low cost, but is constrained by multiple challenges, such as material selection, preparation processes, and reaction mechanisms^[25]. Biomass raw materials include crop straw, municipal refuse and industrial by-products, which are rich in carbohydrate, lignin, cellulose and hemicellulose^[26-28]. There are three types of carbon materials: plant, animal, and microbial. Plant biochar materials include hemp straw, willow leaf, pine nut shell and walnut septum. Animal-based biochar includes chicken bone, and microbial carbon material includes *Ganoderma lucidum* spore^[29-31]. Usually, after direct combustion or conversion into other forms of fuel to generate heat, converting various waste biomass into carbonaceous anode materials can not only reduce pollution and relieve environmental pressure, but also enhance its utilization value^[32-35]. Carbon-based materials synthesized from biomass have gained increasing attention in PIBs. During pilot testing, factors such as process conditions and material handling affect the consistency and reproducibility of performance, highlighting the need for systematic research and technological refinement.

Herein, this review systematically explores critical parameters during the application of carbonaceous anode materials from biomass in PIBs, highlighting the potential in enhancing performance and sustainability. This work discusses the research trends in biomass-derived carbon, such as using plant organs, straw, and animal bones as anodes for PIBs^[36-38]. To improve the electrochemical performance of PIBs, the synthesis schemes of hard carbon with various morphologies and structures by pyrolysis, chemical activation and template methods to build were summarized^[39-42]. The cycling performance and the corresponding potassium storage mechanism of biomass-derived carbon-based materials were deeply analyzed. Schematic illustration of the biomass-derived carbon electrodes for PIBs and corresponding advantages and challenges is shown in Figure 1. The article concludes by reviewing the differences and challenges of biomass carbon anode materials from laboratory to large-scale production, and proposing some prospects for biomass-derived carbon as an anode for PIBs.

SOURCES OF BIOMASS-DERIVED CARBON

Numerous types of biomasses are found in nature. Due to different raw material sources, there can be a significant variety in the performance of biomass materials^[43-45]. Green plants can be seen everywhere on the earth, and their branches, leaves, roots and stems can be chosen as raw materials for anode material in PIBs^[46-48]. Human activities produce millions of tons of agricultural wastes and by-products of all types every year, such as banana peel, coconut coir, corncob, *etc.*, which contain a large amount of organic matter such as lignin, hemicellulose, cellulose, *etc.*^[49-52]. These materials are extensively used and also promote the

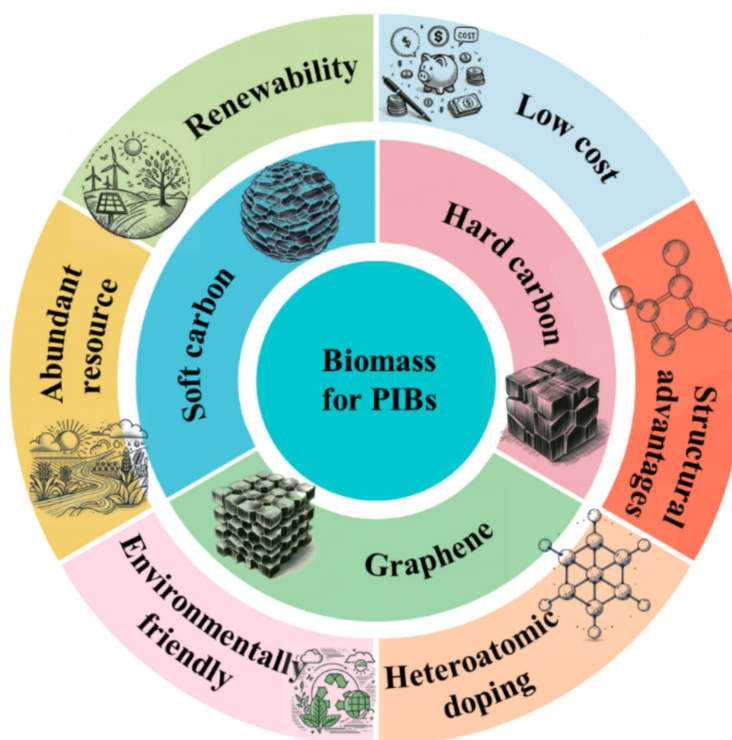


Figure 1. Different carbon materials and corresponding advantages and challenges in PIBs. PIBs: Potassium-ion batteries.

efficient utilization of waste resources^[43,53-55].

Plant organs

Recently, biomass resources have been considered in pilot testing for energy storage materials because of their wide distribution, reproducibility, low cost, and environment-friendly characteristics^[56-58]. At present, biomass used for energy storage includes potatoes and petals, all of which show excellent performance^[50]. In **Figure 2A**, Cao *et al.* synthesized a series of potato biomass porous carbon (termed PBPC-900, PBPC-1000 and PBPC-1100) through a facile two-step carbonization approach at different carbonization temperatures (900 °C, 1,000 °C, and 1,100 °C)^[59]. The SEI film formed on the surface of PBPC-1000 leads to high discharge capacity during the first cycle. PBPC electrodes exhibit excellent electrochemical performance primarily due to their uniformly distributed mesopores which aid in electrolyte diffusion and transport. As shown in **Figure 2B**, Yang *et al.* used *Ganoderma lucidum* spore as biomass raw material, and prepared N/O co-doped cage-type biomass carbon (NOBC)^[60]. According to the different amounts of ammonium molybdate tetrahydrate (0 g, 0.8 g, 1 g, 2 g) added to the mixed solution, the obtained sample named NOBC-2 anode shows ultrahigh cycle life and rate properties. As a result of its unique hollow cage configuration and internal carbon network, NOBC-2 demonstrates outstanding performance. In addition, N/O co-doping has been shown to enhance the adsorption ability of K^+ and improve conductivity.

Wang *et al.* used a simple pyrolysis method to obtain bio-derived carbon materials [**Figure 2C**]^[61]. Nitrogen-doped porous dandelion seeds (DSs) show superior cycling performance. The nitrogen-doped carbon possesses excellent K^+ ion adsorption capacity and better wettability. A further increase in capacity was achieved by adding an activation agent (KOH) during carbonization. Therefore, graded porous doped carbon-derived materials from renewable biomass precursors as PIB anodes show great economic potential. Xu *et al.* prepared hydrolytic cotton-derived oxygen/sulfur co-doped carbon (denoted as H-OS-C) by using

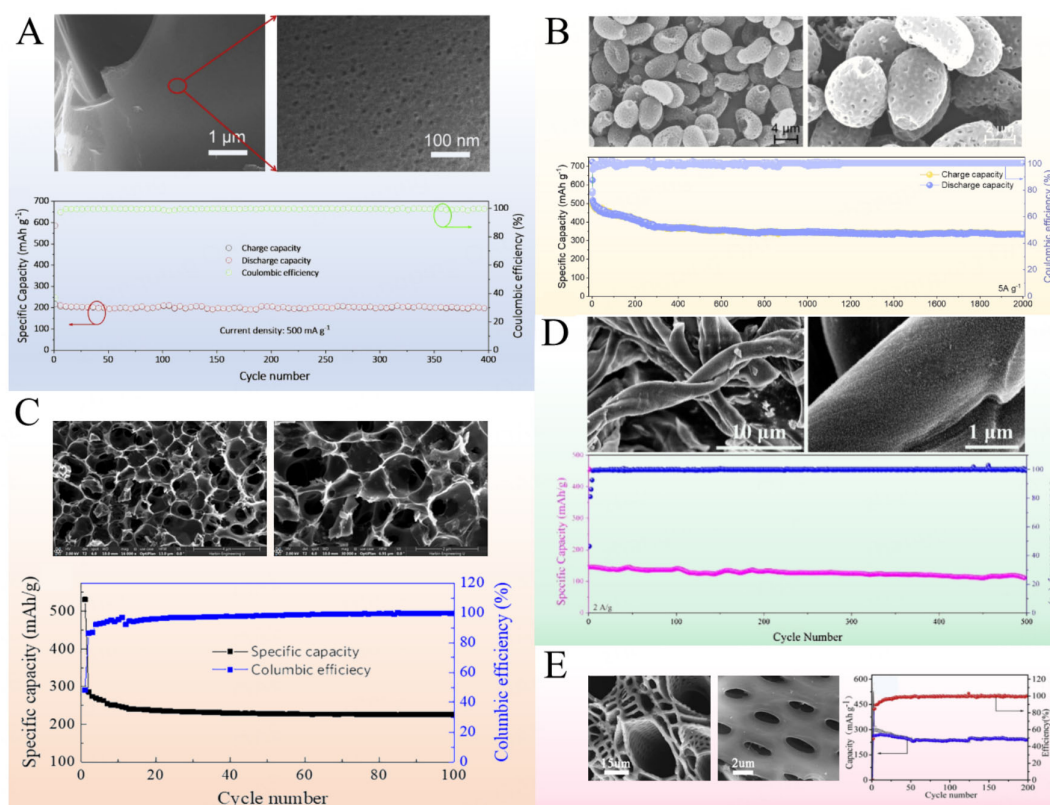


Figure 2. (A) SEM image and cycling stability of PBPC-1000^[59]. Copyright 2018, Elsevier; (B) SEM image and cycling stability of NOBC-2^[60]. Copyright 2021, Elsevier; (C) SEM image and cycling stability of DS^[61]. Copyright 2020, Elsevier; (D) SEM image and cycling stability of H-OS-C^[62]. Copyright 2019, Elsevier; (E) SEM image and cycling stability of NHPC^[63]. Copyright 2019, Elsevier. NOBC: N/O co-doped cage-type biomass carbon; DS: dandelion seeds; H-OS-C: hydrolytic cotton-derived oxygen/sulfur co-doped carbon; SEM: scanning electron microscope; PBPC: potato biomass porous carbon.

the hydrolysis-vulcanization process of cotton [Figure 2D]^[62]. The multiple dopants greatly improve the diffusion rate of K^+ . According to Figure 2E, Gao *et al.* separated N-doped hierarchical porous carbon (NHPC) from walnut septum by pyrolysis^[63]. The target carbon exhibits a hierarchical porous structure with superior electrochemical performance on account of the enhanced ion diffusion kinetics and electronic conductivity resulting from the hierarchical porous structure, large distance between layers, and nitrogen doping of the material. Table 1 concludes the carbon resources, the synthesis method, and the related electrochemical performance of the related plant organs as anode materials for PIBs.

Plant straw

The mass production of biomaterials involves transforming biomaterials into inorganic materials, which have complicated porous structures that range from nanometers to millimeters in size. The surface area of biomaterials is usually very small. Biomass carbon derived from plant straw may be a potential candidate for anode materials. Ou *et al.* synthesized a series of sisal-derived hard carbons (termed HC-1100, HC-1300 and HC-1500) through a two-step hydrothermal reaction and high-temperature carbonization at different carbonization temperatures (1,100 °C, 1,300 °C and 1,500 °C), which has excellent electrochemical properties [Figure 3A]^[64]. Corn husk-derived hard carbon provides a hierarchical porous structure after high-temperature treatment. In contrast to large-surface area anodes, small-surface area biocarbon anodes perform better electrochemically^[65]. Ion diffusion kinetics are enhanced by N/O heteroatoms in biocarbon materials and reasonable interlayer distance. Li *et al.* synthesized a series of rice husk carbon (termed as

Table 1. Plant organs as anode materials for PIBs

Materials	Carbon source	Synthesis methods	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Reversible capacity (mAh g^{-1})	Voltage range (V)	Cycling stability (retained capacity, cycles, current density)
PBPC-1000 ^[59]	Potato	Two-step carbonization	531.67	253 at 100 mA g^{-1}	0.01-2.7	196, 400, 500 mA g^{-1}
NOBC-2 ^[60]	Ganoderma lucidum spore	Hydrothermal reaction and two-step carbonization	0.0217	490.24 at 500 mA g^{-1}	0.01-3.0	334.64, 2,000, $5,000 \text{ mA g}^{-1}$
DS ^[61]	Dandelion seed	One-step high-temperature pyrolysis	1303	243 at 50 mA g^{-1}	0.01-3.0	221, 100, 50 mA g^{-1}
H-OS-C ^[62]	Skimmed cotton	Hydrolyzation-sulfuration process	612	409 at 100 mA g^{-1}	0.01-2.0	120, 500, $2,000 \text{ mA g}^{-1}$
NHPC ^[63]	Walnut septum	One-step carbonization	99.6	305.7 at 50 mA g^{-1}	0.005-3.0	242.5, 200, $1,000 \text{ mA g}^{-1}$

PIBs: Potassium-ion batteries; PBPC: potato biomass porous carbon; NOBC: N/O co-doped cage-type biomass carbon; DSs: dandelion seeds; H-OS-C: hydrolytic cotton-derived oxygen/sulfur co-doped carbon; NHPC: N-doped hierarchical porous carbon.

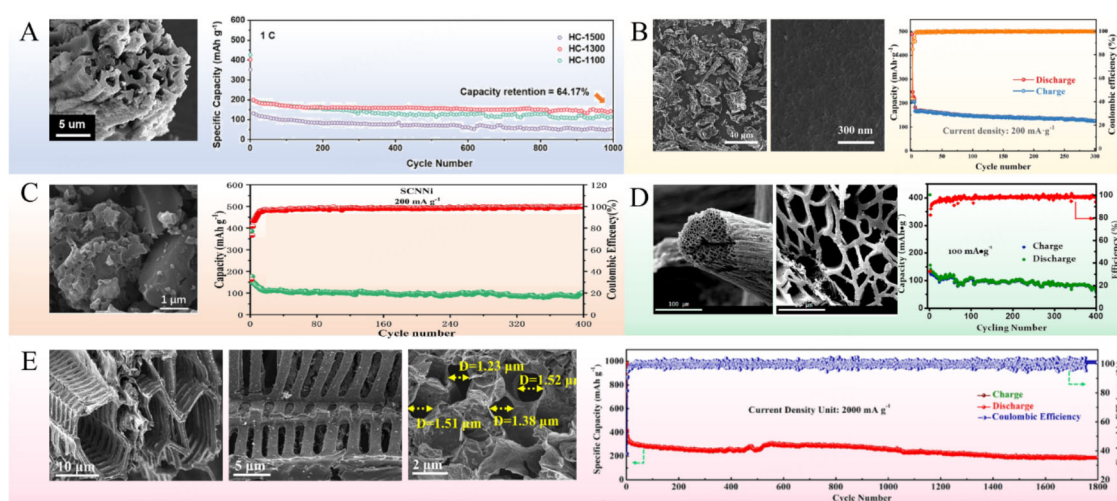


Figure 3. (A) SEM image and cycling stability of HC-1300^[64]. Copyright 2014, American Chemical Society; (B) SEM image and cycling stability of RHC-1100^[66]. Copyright 2020, Elsevier; (C) SEM image and cycling stability of SCNNi^[67]. Copyright 2021, Elsevier; (D) SEM image and cycling stability of LPG^[68]. Copyright 2019, Elsevier; (E) SEM image and cycling stability of NCM^[69]. Copyright 2021, Elsevier. HC: Hard carbons; RHC: rice husk carbon; SCNNi: N-doped three-dimensional (3D) biomass porous activated carbon materials; LPG: loofah-derived pseudo-graphite; NCM: N-doped amorphous carbon/graphite coupled polyhedral microframe; SEM: scanning electron microscope.

RHC-900, RHC-1100, RHC-1300 and RHC-1500) through a facile two-step carbonization approach at different carbonization temperatures (900 °C, 1,100 °C, 1,300 °C and 1,500 °C) [Figure 3B]^[66]. The carbon layer of the sample became increasingly orderly and the graphitization degree increased because of the enhanced temperature.

Deng *et al.* present the N-doped three-dimensional (3D) biomass porous activated carbon materials (termed SCNNi)^[67]. N doping promotes transport of K^+ and electrons [Figure 3C]. Wu *et al.* presented a simple and inexpensive strategy to make loofah-derived pseudo-graphite (LPG) through alkali-based treatment and one-step pyrolysis [Figure 3D]^[68]. As anodes for PIBs, the mesoporous hard carbon materials obtained provide excellent electrochemical performance. The good performance of LPG for PIBs is mainly attributed to its dual storage mechanism, and the wide layered pseudo-graphite unit provides intercalation space for K^+ . Besides, the easily accessible mesoporous structure and defect activation units in the near-surface region facilitate the deposition of K^+ at low voltage. Wang *et al.* successfully synthesized N-doped amorphous

carbon/graphite for PIBs using sycamore leaves as raw material with excellent electrochemical performance [Figure 3E]^[69]. Table 2 concludes the carbon resources, the synthesis method, and the related electrochemical performance of the related plant straw as anode materials for PIBs.

Animal bones

Animal bones are also a renewable biomass resource. As shown in Figure 4A, Chicken bones were subjected to a one-step high-temperature pyrolysis method without the addition of any activator, resulting in the synthesis of a 3D porous carbon scaffold (3D-HPCS) with a graded nanostructure and heteroatom doping^[70]. The 3D-HPCS anode shows good rate and cycle stability during K⁺ insertion/extraction, which is attributed to the increasing interlayer spacing, doping active heteroatoms and complex porous structure, which improves the conductivity and ion diffusion kinetics. The unique forest-like pores come from the pyrolysis of collagen fibrils in the bone and provide abundant pores for effective K⁺ transport and electrolyte penetration. In addition, N/P doping also plays a key role in enhancing the surface-driven electrochemical chemistry of 3D-HPCS. The storage capacity of K⁺ in the synthesized 3D-HPCS material is significantly improved. Zhang *et al.* constructed active sites-enriched hard carbon porous nanobelts (NOCNBs) for increasing K⁺ storage by using mineralized shrimp shells [Figure 4B]^[71]. NOCNBs have a large interlayer distance because of the high level of pyrrolic/pyridinic-N and O dual-doping. The rich active sites in NOCNBs can enhance the adsorption and diffusion of potassium, thus promoting capacitive adsorption and storage. The mechanism of potassium intercalation in hard carbon. Table 3 concludes the carbon resources, the synthesis method, and the related electrochemical performance of the related animal bones as anode materials for PIBs.

SYNTHETIC TECHNOLOGIES

Different molecular structures are present in biomass precursors. Metal or other elements inevitably exist in biomass precursors. The precursor contains a relatively low level of metal, which can be removed by acid treatment following carbonization. Direct carbonization can introduce heteroatoms *in-situ* into the carbon matrix, resulting in heteroatom-doped carbon, and high-temperature carbonization can eliminate them. Different methods have been used to obtain biomass carbon materials with varying structures, including pyrolysis, chemical activation, template method, *etc.*

Biomass pyrolysis refers to the process of transforming biomass into low molecular substances such as charcoal, liquid and gas by thermochemical conversion under the condition of isolating air or passing inert gas. Among the products produced by pyrolysis are fuel oil, wood tar oil, wood gas, and charcoal. Almost all carbon materials we use daily are derived from biomass, including both plant and animal biomass.

The main components of plant biomass are cellulose, hemicellulose, and lignin, which are synthesized through photosynthesis. Traditional high-temperature pyrolysis needs to consume a lot of energy, which is costly and unfriendly to the environment. Accordingly, Wang *et al.* presented the transforming nano-cellulose fibers into highly graphitized carbon [Figure 5A]^[72]. Under conditions of completely isolated oxygen, the dehydration and carbonization (DC) of cellulose nanofibers (CNF) from biomass were carried out continuously with sulfuric acid. The surface of the CNF is then converted to highly graphitized carbon (CNFene). The samples were named DC-CNFene-1 and DC-CNFene-4 according to the reaction time, and the results of Raman spectrum analysis show that the relative strength ratios (I_D/I_G) of DC-CNFene-1 and DC-CNFene-4 are 0.45 and 0.38, indicating the material has a highly regular graphitized structure. The specific capacity exceeds that of most pure carbon, which is close to the capacitance of graphene composites.

Table 2. Plant straw as anode materials for PIBs

Materials	Carbon source	Synthesis methods	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Reversible capacity (mAh g^{-1})	Voltage range (V)	Cycling stability (retained capacity, cycles, current density)
HC-1300 ^[64]	Sisal hemp	Two-step hydrothermal reaction and further high-temperature carbonization	28.65	310.1 at 30 mA g^{-1}	0.001-2.5	140.8, 1,000, 300 mA g^{-1}
RHC-1100 ^[66]	Rice husk	Two-step carbonization	115.4	~200 at 30 mA g^{-1}	0.01-3.0	125.7, 300, 200 mA g^{-1}
SCNNi ^[67]	Bagasse	Carbonization and further activation with NiCl_2	466.621	212.6 at 100 mA g^{-1}	0.01-3.0	100.4, 400, 200 mA g^{-1}
LPG ^[68]	Loofah	One-step carbonization	270	155 at 100 mA g^{-1}	0.01-3.0	~70, 400, 100 mA g^{-1}
NCM ^[69]	Sycamore leaves	Hydrothermal reaction and one-step carbonization	286.6	374.3 at 200 mA g^{-1}	0.01-2.5	189.5, 1,800, 2,000 mA g^{-1}

PIBs: Potassium-ion batteries; HC: hard carbons; RHC: rice husk carbon; SCNNi: N-doped three-dimensional (3D) biomass porous activated carbon materials; LPG: loofah-derived pseudo-graphite; NCM:

Table 3. Animal bones as anode materials for PIBs

Materials	Carbon source	Synthesis methods	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Reversible capacity (mAh g^{-1})	Voltage range (V)	Cycling stability (retained capacity, cycles, current density)
3D-HPCS ^[70]	Chicken bones	One-step pyrolysis	1474.5	314 at 58 mA g^{-1}	0.01-3.0	205, 450, 58 mA g^{-1}
NOCNB ^[71]	Shrimp shells	Self-template assisted pyrolysis	372	468 at 50 mA g^{-1}	0.01-3.0	277, 1,600, 1,000 mA g^{-1}

PIBs: Potassium-ion batteries; 3D-HPCS: three-dimensional porous carbon scaffold; NOCNB: active sites-enriched hard carbon porous nanobelts.

Animal biomass is composed of protein, minerals, or polysaccharides (such as chitosan and chitin) extracted from animal waste. As shown in Figure 5B, Hao *et al.* manufactured N-doped carbon nanofibers (NCFs) as anodes of PIBs by direct pyrolysis of biological waste chitin, and studied the effect of temperature on electrochemical. NCFs with a high aspect ratio and uniform nanofiber structure were successfully fabricated by pyrolysis of chitin^[73].

Chemical activation method is to mix biomass with activators and calcine them at an appropriate temperature in oxygen-free environment. In this process, various types of activators can be used to react with carbon materials, resulting in microporous, mesoporous, and macroporous carbon particles. The purpose of activation process is to increase pore volume, expand pore diameter and increase porosity of activated carbon. The chemical activation method is widely used due to its benefits such as more product, a lower reaction temperature, a larger Brunauer-Emmett-Teller (BET) surface area, and a low cost.

Various chemicals such as H_3PO_4 , K_2CO_3 and KOH have been widely used in chemical activation. These chemical reagents can not only dehydrate and decompose biomass, but also improve the porosity of biomass-derived carbon. Among these activators, KOH is promising with low activation temperature, high product and uniform micropore size distribution. Through KOH treatment, hard carbon owns the micropores and small mesopores with excellent performance in energy storage and conversion. As shown in Figure 6A, Wang *et al.* prepared bio-hard carbon from corn husk (termed CBC), and studied the effect of KOH content on specific surface area and porosity of carbon materials^[65]. The specific surface area of carbon materials increased significantly as the ratio of KOH to corn husk increased. The main reason is that with the rise of KOH content, the amount of K_2CO_3 formed also increases, which reacts with carbon and forms a pore network. Decomposition products containing carbon dioxide can promote the development of

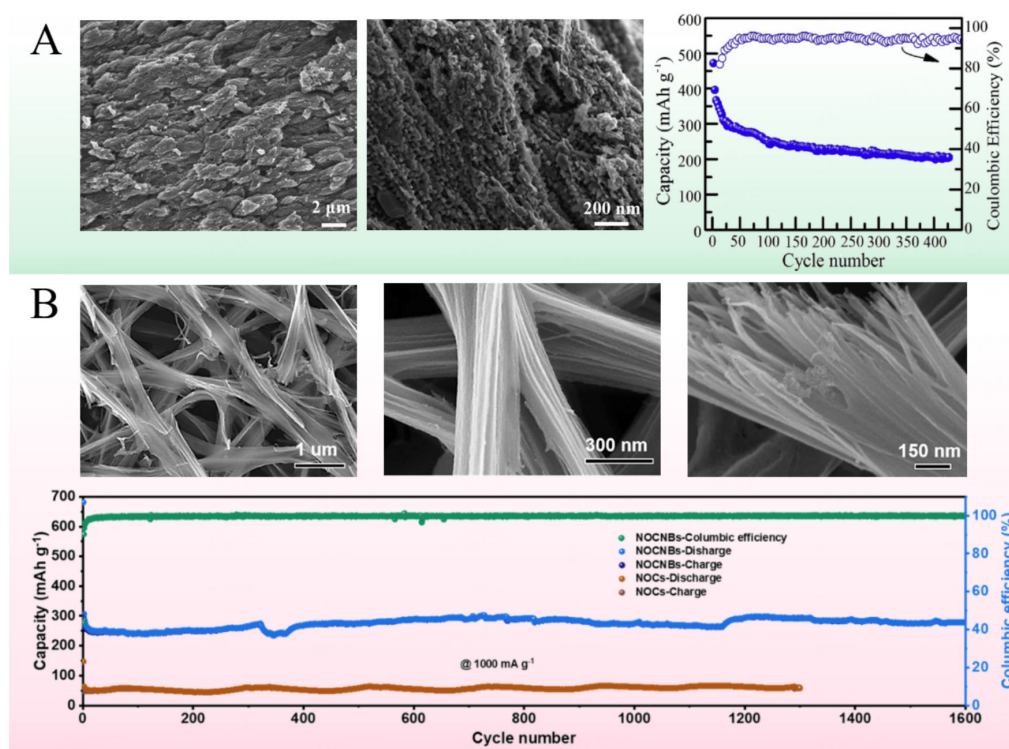


Figure 4. (A) SEM image and cycling stability of 3D-HPCS^[70]. Copyright 2021, Elsevier; (B) SEM image and cycling stability of NOCNBs^[71]. Copyright 2020, Elsevier. 3D-HPCS: Three-dimensional porous carbon scaffold; NOCNBs: active sites-enriched hard carbon porous nanobelts; SEM: scanning electron microscope.

pores, as well as macropore formation. As shown in Figure 6B, Zheng *et al.* synthesized a honeycomb porous hard carbon (CPC) with a sunflower seed shell as a precursor and K_2CO_3 as an activator^[74]. All samples show a typical honeycomb structure. The self-doped nitrogen of porous carbon promotes the adsorption of K^+ and reduces the diffusion barrier of ions between carbon layers. In addition, the chemical activation method can also realize heteroatom doping of biomass-derived materials.

As shown in Figure 6C, Xu *et al.* used H_3PO_4 to activate mushrooms, and obtained a heteroatomic doping mushroom biomass carbon (HDMC)^[75]. Lyophilized mushrooms were treated by acidic hydrothermal reaction, and P-doped precursors were obtained. Porous HDMC provides enough voids to alleviate the volume expansion of the electrode and provides an efficient channel for the rapid transport of electrons and K^+ . The energy-dispersive X-ray spectroscopy (EDS) spectrum shows that precursors are rich in N, S and P heteroatom doping can bring more defects to carbon materials, which promotes the fast transfer of charges and improves the electrochemical activity of biomass hard carbon materials.

The template method involves impregnating templates into biomass precursors and constructing porous structures. The pores will have the same size after carbonization and the removal of templates with strong acids or alkalis. This method has the advantage of enabling ordered porous morphology to be prepared according to different templates, which cannot be achieved by activation. Template methods mainly include hard and soft template methods. Hard template methods are commonly used to prepare carbon-based anodes for biomass-derived PIBs.

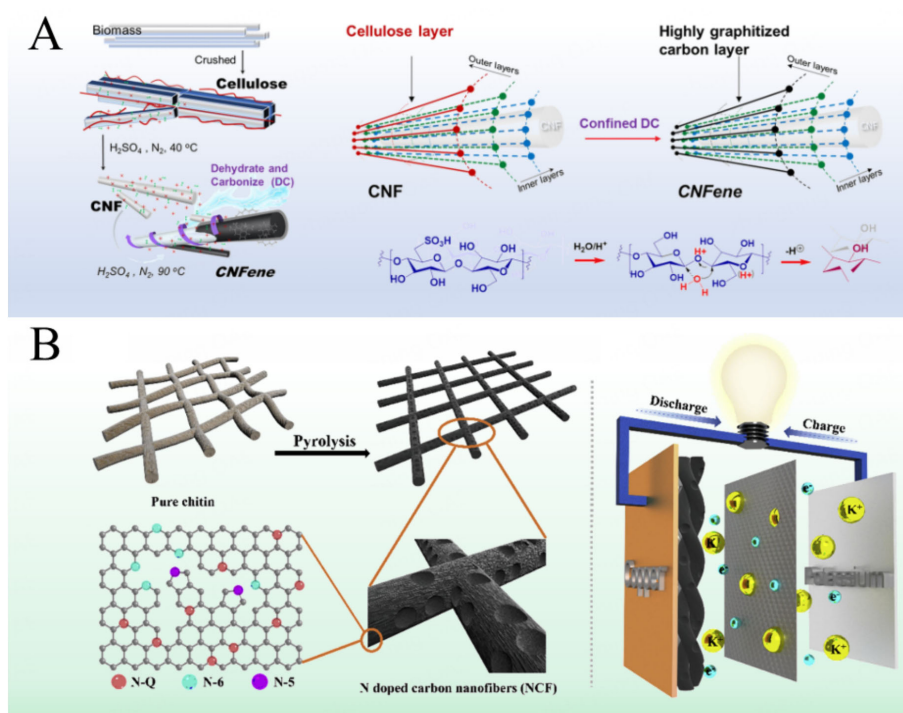


Figure 5. (A) Schematic diagram of the extraction process of CNFs and the mechanism^[72]. Copyright 2021, American Chemical Society; (B) Schematic illustration for the synthesis of the NCFs^[73]. Copyright 2017, Elsevier. CNF: Cellulose nanofibers; NCFs: N-doped carbon nanofibers.

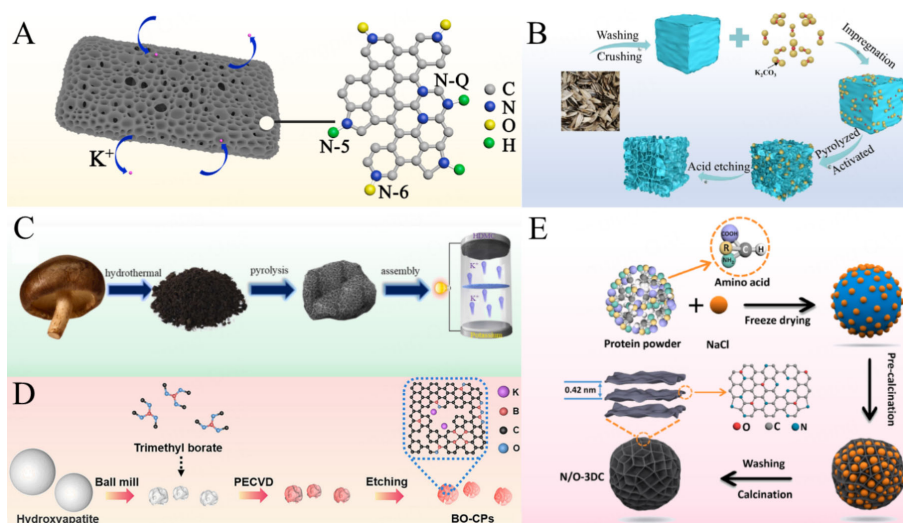


Figure 6. (A) Schematic of the mechanisms of K ion storage in CBC^[65]. Copyright 2019, Elsevier; (B) Schematic diagram for CPC^[74]. Copyright 2022, Elsevier; (C) Schematic illustration of the fabrication process of HDMC samples^[75]. Copyright 2022, Elsevier; (D) Schematic illustration of BO-CPs^[76]. Copyright 2021, Zhengzhou University; (E) Schematic diagram of N/O-3DC^[77]. Copyright 2021, Elsevier. CPC: Honeycomb porous hard carbon; HDMC: heteroatom doping mushroom biomass carbon; BO-CPs: boron/oxygen heteroatom co-doped carbon particles; N/O-3DC: 3D N/O co-doped amorphous biomass-based carbon; CBC: bio-hard carbon.

After carbonization and removal of the template, porous carbon can be obtained by filling monomer templates into biomass precursors by physical or chemical treatment methods. According to Figure 6D, Lian *et al.* fabricated boron/oxygen heteroatom co-doped carbon particles (BO-CPs) by plasma-enhanced

chemical vapor deposition (PECVD) using trimethyl borate as a precursor and hydroxyapatite as a growth template^[76]. After etching the template with a dilute hydrochloric acid solution, BO-CPs show layered morphology. It is evident from the element map of the product that B, O, and C elements are distributed uniformly, which confirms the co-doping of B and O elements in BO-CPs. BO-CPs with dual doping of boron and oxygen exhibit sufficient defects, an enlarged interlayer distance, and a high specific surface area. Porous carbon networks can be improved by B-doping, while potassium ions can be enhanced by O-doping. However, this method requires hydrochloric acid cleaning to remove the template, as the waste acid poses much environmental pollution. As shown in Figure 6E, Sun *et al.* obtained 3D N/O co-doped amorphous biomass-based carbon (N/O-3DC) with large interlayer spacing^[77]. Sodium chloride templates are low-cost, environment-friendly and easily removed. N/O-3DC has a 3D network of interconnected pores and a wall composed of thin carbon nanosheets.

Besides the above methods, hydrothermal carbonization (HTC) and microwave-assisted pyrolysis (MAP) are alternative approaches. Traditionally, HTC involves the simultaneous application of high pressure and high temperature in order to carbonize biomass. A biomass precursor was mixed with water in the proper proportions, sealed, and heat treated at 180–350 °C for a specified period of time. For the preparation of biomass-derived carbon materials (BCM) by HTC, the experimental conditions such as HTC temperature and soaking time have a great influence on the structure of the obtained carbon. Sevilla *et al.* reported the carbon spheres extracted from glucose^[78]. A scanning electron microscope image of glucose water is shown, as well as size histograms, respectively. Structural differences are related to the residence time. A study by Kurniawan *et al.* examined the effects of standing time on the morphology of water hyacinth carbon^[79]. The decomposition of raw materials can be attributed to the formation of carbon microspheres after longer residence times (more than 6 h). At various residence times, the morphological images of water hyacinth and water carbon were obtained. Romero-Anaya *et al.* investigated the morphology of water carbon by using glucose, sucrose and cellulose as precursors^[80]. As a result of a long residence time, carbon spheres with a clear morphology were obtained.

Recent developments have led to the development of MAP as a new technology for converting biomass into BCM. MAP has the following advantages: due to dielectric heating, electromagnetic energy is directly transferred to heat, thus shortening heating time. In addition, water can be removed during the MAP process, so drying pretreatment steps can be reduced. It is possible to control the experimental parameters of MAP, such as the irradiation time and energy density. However, MAP also has limitations on raw materials, and it always requires microwave absorbers. Villota *et al.* prepared porous carbon derived from waste cocoa pod shells by microwave-assisted activation of H_3PO_4 or KOH. In the case of microwave-assisted activation, H_3PO_4 is a better activator than KOH^[81]. The materials activated by KOH have low structural integrity, while the materials activated by H_3PO_4 have higher porosity to the research of Kaewtrakulchai *et al.*^[82]. A significant impact is exerted on the pore characteristics of biomass-derived carbon by the microwave irradiation power and time. Through the combination of MAP and KOH activation, they prepared nanoporous carbon from oil palm male flowers. Moreover, the morphology of the resulting carbon changed considerably, with more pores visible on the 6-min irradiated sample.

STRUCTURE AND MORPHOLOGY OF BIOMASS-DERIVED CARBON

Biomass carbon materials with porous structure have attracted wide attention owing to their unique characteristics (such as high surface area and rich pores), and have great potential to improve specific capacity and magnification performance^[83,84]. Two-dimensional carbon nanosheets have a large specific surface area and shorten the shutting path of ions and electrons, which is beneficial for K^+ storage and transmission. Using almond shell as a carbon source, Pham *et al.* calcined the dried biomass powder in

nitrogen for 2 h at 1,000 °C by cleaning with water and hydrochloric acid to prepare nanosheet hard carbon (termed AC-HC-1000), and studied the relationship between microstructure and electrochemical properties [Figure 7A]^[85]. The surface morphology of synthesized hard carbon confirmed the formation of flake structure with smooth surface. The formation of flake-like nanostructures, which matched the Scanning Electron Microscope (SEM) images of AC-HC-1000. Two carbon layer sheets can be clearly observed, which may provide another surface for potassium ion storage besides the nanoscale graphite layer. Therefore, AS-HC-1100's unique surface characteristics of abundant pores and good surface area can provide a good tissue path for fast transport of electrolyte ions.

Modifying the chemical properties of carbon nanosheets by doping is an effective strategy to improve electrochemical activity and conductivity. The biomass-derived carbon nanosheets were doped with heteroatoms such as N, S and P to increase the interlayer spacing and active sites, thus affecting the specific capacity and rate performance. As shown in Figure 7B, it was demonstrated by Deng *et al.* that biomass-derived hard carbon with nitrogen doping (NHC) based on corn straw was highly graphitized after soaking in urea solution and introducing nitrogen for calcination at high temperatures, and the spacing between the layers was still larger than graphite^[86]. NHC samples are highly efficient and have a low operating potential due to the long-range ordered structure. At the same time, since it contains oxygen-containing functional groups, it can enhance wettability as an electrode material. The excellent electrochemical performance is mainly attributed to the doping of graphite nitrogen.

Researchers have also synthesized carbon fiber from biomass and applied it to PIBs. Biomass-derived carbon nanofibers have huge specific surface area, shorten the diffusion path of ions and electrons, and can effectively electrochemical performance of carbon-based materials. As shown in Figure 7C, Hao *et al.* prepared NCFs by *in-situ* template pyrolysis of chitin^[73]. SEM images reveal the nanofiber structure and amorphous properties of chitin template pyrolysis NCFs. The graphene interlayer spacing decreases from 3.97 Å to 3.76 Å according to the peak center calculation, but is still higher than the graphite interlayer spacing. Ou *et al.* synthesized a series of sisal-derived hard carbon through a two-step hydrothermal process followed by high-temperature carbonization at different carbonization temperatures [Figure 7D]^[64]. Even after high-temperature carbonization, the structure of a 3D porous framework featuring abundant open microchannels is perfectly preserved. The obtained honeycomb-like cross-section can enhance ion storage and transport capabilities. High-resolution transmission electron microscopy (HRTEM) images reveal the overall microstructure which can be divided into three distinct phases: highly disordered, pseudo-graphitic and graphite-like phases.

Wang *et al.* reported N-doped amorphous carbon/graphite coupled polyhedral microframe (NCM) as the negative electrode of PIBs [Figure 7E]^[69]. The advantages of graphite with high conductivity and amorphous carbon with high capacity and high stability are utilized on one electrode, thus obtaining excellent battery performance. Ion dynamics during the cycle may also be enhanced by large interlayer spacings, abundant active centers, and highly accessible surfaces. In addition, the expansion of interlayer spacing caused by N-doping is beneficial to the rapid diffusion of K⁺. In order to determine the stress distribution after K⁺ intercalation, five kinds of hexagonal prism models are established. The hollow hexagonal prism with a hollow porous tube wall is capable of releasing the stress caused by K⁺ intercalation, thereby improving the durability of the electrode.

POTASSIUM STORAGE MECHANISM

Owing to the large size of K⁺, potassium intercalation action needs an increased interlayer spacing, which is benefit for alkali metal ions insertion/extraction of biomass derived hard carbon. Zhu *et al.* prepared

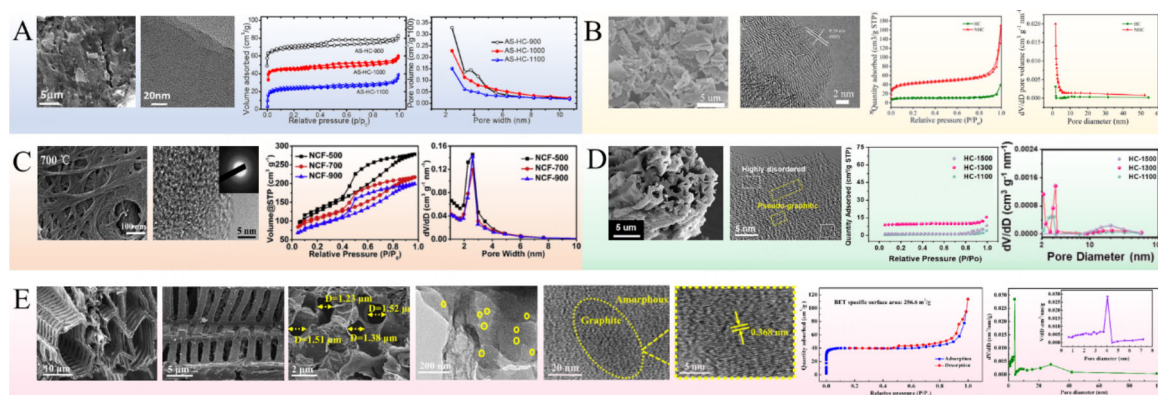


Figure 7. (A) SEM and HRTEM image of AC-HC-1000, and nitrogen adsorption/desorption isotherms of AC-HC samples prepared at three different temperatures with corresponding pore-size distribution curves^[85]. Copyright 2020, American Chemical Society; (B) SEM and HRTEM image of NHC, and N₂ adsorption and desorption isotherms of NHC with corresponding pore distribution^[86]. Copyright 2021, Wiley; (C) SEM and HRTEM image of NCFs, and N₂ adsorption and desorption isotherms of NCFs with corresponding pore distribution^[73]. Copyright 2017, Elsevier; (D) SEM and HRTEM image of HC-1300, and N₂ adsorption and desorption isotherms of HC-1300 with corresponding pore distribution^[64]. Copyright 2024, Wiley. E, SEM, TEM and HRTEM image of NCM, and N₂ adsorption and desorption isotherms of NCM with corresponding pore distribution^[69]. Copyright 2021, Elsevier. HRTEM: High-resolution transmission electron microscopy; AC-HC: nanosheet hard carbon; NCFs: N-doped carbon nanofibers; SEM: scanning electron microscope; TEM: transmission electron microscope; NCM: N-doped amorphous carbon/graphite coupled polyhedral microframe.

carbonized *Magnolia grandiflora* Lima (CMGL) leaf using the MGL leaf as precursors, and its potassium storage mechanism was investigated [Figure 8A]^[87]. *In-situ* X-ray diffraction (XRD) measure shows the changes of interlayer spacing during discharging. Segment I is the high-potential slope region) and II is the low-potential plateau region). With discharge, the peak in segment II slightly splits: part peak moves to a low angle, and a new peak is formed, due to the wide distribution of interlayer spacing in the material. The relatively wide spacing of the graphitic microcrystallites allows for potassium ion insertion, leading to a negative shift in Bragg reflection and a gradual reduction in interlayer spacing. Thus, the high-potential slope region corresponds to the surface adsorption/desorption characteristics of the material, while the low-potential plateau region reflects the insertion/extraction of potassium ions within the interlayers of graphitic microcrystallites. Additionally, *in-situ* Raman spectroscopy (a supplementary tool for XRD) shows the peak position of G band remains unchanged at the beginning of discharge, but shifts after 0.2 V. This is because the insertion of potassium ions increases the electron density on the graphite microcrystalline layer, weakening the interfaced C-C bond, leading to C-C bond lengthen, which is followed by the shift of G-band. Meanwhile, the G-band shift is continuous, with no formation of a double peak, thus following a single-phase intercalation mechanism. Overall, the storage mechanism of K in CMGL is “adsorption-insertion”.

Wang *et al.* introduced the layered porous biomass carbon from corn husks [Figure 8B]^[65]. CBC has a layered network porous structure, provides a 3D ion transport channel and promotes potassium ions to enter CBC, thus realizing high rate performance. CBC embeds K ions in the wide anodic peak between 0.2 V and 0.7 V. Additionally, cyclic voltammetry (CV) curves almost overlapping demonstrate that intercalation and deintercalation processes are highly stable and reversible. Active sites such as defects, functional groups or heteroatoms on the surface of biomass-derived hard carbon enhance the ability of carbon materials to capture potassium ions, and further enrich the reaction during charge and discharge. Chen *et al.* prepared glucose combined with multi-walled carbon nanotubes (GCNT) by hydrothermal method using glucose and multi-walled carbon nanotubes [Figure 8C]^[88]. The pristine GCNT was then annealed with NaH₂PO₂ at 350 °C in an argon atmosphere for 2.5 h. 200 mg NaH₂PO₂ and 300 mg NaH₂PO₂ were added to react with 100 mg of pristine GCNT to obtain 200-GCNT and 300-GCNT. The annealed

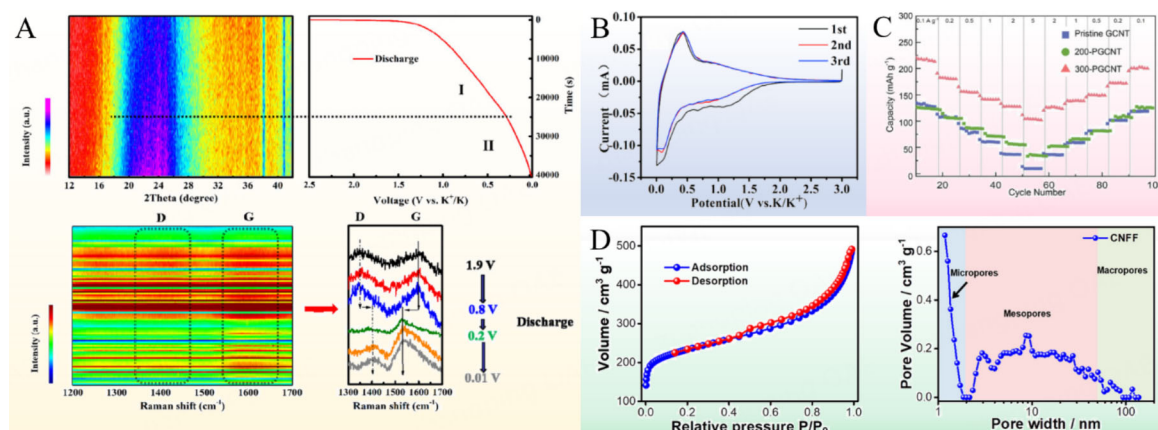


Figure 8. (A) In-situ XRD and in-situ Raman tests of the CMGL electrode during discharging^[87]. Copyright 2021, Wiley; (B) cyclic voltammetry curves of CBC at scanned rate of 0.1 mV s⁻¹ between 0.005 V and 3.0 V^[65]. Copyright 2019, Elsevier; (C) rate performance evaluation of pristine GCNT, 200-PGCNT and 300-PGCNT^[88]. Copyright 2022, Wiley; (D) representative nitrogen adsorption-desorption isotherm curve of CNFF and pore size distribution of the CNFF electrode^[89]. Copyright 2018, American Chemical Society. XRD: X-ray diffraction; CMGL: carbonized Magnolia grandiflora Lima; GCNT: glucose combined with multi-walled carbon nanotubes; CNFF: carbon nanofiber foam; CBC: bio-hard carbon.

carbon nanotubes possess abundant porous structure, which can provide more active sites for K⁺. At high current density, the capacity retention rates of pristine GCNT, 200-PGCNT and 300-PGCNT increase with the P content. It can be concluded that more P atom doping content is beneficial for improving the rate property. Li *et al.* synthesized a compressible and hierarchical porous carbon nanofiber foam (CNFF) using bacterial cellulose [Figure 8D]^[89]. Nitrogen adsorption-desorption isotherm curve and pore size distribution of the CNFF electrode show that the remarkable K⁺ storage capacity is mainly due to the abundant effective sites, meshed network for ions transport, and large interlayer space. Moreover, Nanjundan *et al.* developed an amorphous hard carbon from commercial cellulose and investigated the effect of oxygen functional groups^[90]. The presence of oxygen functional groups is indicated by Raman spectroscopy.

FROM LABORATORY TO INDUSTRIAL PRODUCTION

In alkali metal ion half-battery devices, the Li, Na, and K metals as negative electrodes can achieve an unlimited supply of Li⁺, Na⁺, and K⁺ ions^[91]. However, in practical application, the Li⁺, Na⁺, and K⁺ ions in full batteries is limited due to the N/P ratio and the desire of energy density, which is essentially different from the half-battery system^[92]. Hence, in order to make the transition from the lab to factory, it is important and convincing to explore the performance of eco-friendly hard carbon in the full-cell devices^[93]. The full-cells were assembled and the corresponding electrochemical performances were tested with main traditional materials including layered oxides, polyanionic compounds, and Prussian blue analogs as the cathode and biomass-derived hard carbon as the anode^[94].

Thereinto, using layered P2-K_{0.65}Fe_{0.5}Mn_{0.5}O₂ microspheres as the cathode and hard carbon as the anode, a full battery has been constructed that has long-term cycle stability (capacity retention > 80% after 100 cycles), but far away from mass production and commercialization^[95]. This full cell using low-cost biomass-derived hard carbon and a cathode with a large number of earth elements provides an economical and effective replenishment to LIBs for storing large amounts of energy^[96]. The H-K_{0.7}Mn_{0.7}Mg_{0.3}O₂/hard carbon full cell has a high energy density of 127.9 Wh kg⁻¹ at 100 mA g⁻¹ and maintains an initial capacity of 75% after 100 cycles, demonstrating the potential applications of hard carbon as a high-performance cathode for PIBs despite its low cost^[97]. Besides, when matching the K_{0.5}Mn_{0.8}Fe_{0.1}Ni_{0.1}O₂ with hard carbon, the potassium-ion full battery also exhibits encouraging performance, including a reversible capacity of

113 mAh g⁻¹ and a capacity retention rate of 89% after 150 cycles^[98]. K_{0.5}Mn_{0.85}Co_{0.05}Fe_{0.05}Al_{0.05}O₂ (KMCFAO) and hard carbon were used to assemble the KMCFAO//hard carbon full cell, which exhibits an encouraging energy density of 113.8 Wh Kg⁻¹ at a current density of 100 mA g⁻¹, a capacity retention rate of 72.6% after 500 cycles^[22]. Hard carbon anodes used in PIB full cells can achieve better performance. At low voltage, lithium metal can form alloys with aluminum, while potassium metal cannot. In this regard, PIB full batteries have an advantage over LIBs owing to the lighter and cheaper aluminum foil instead of copper foil as a collector for both the cathodic and anodic electrodes. Thus, the proportion of non-active substances in a full battery of PIBs can be reduced to obtain a higher energy density. In addition, the use of inexpensive aluminum collectors reduces the cost of cathode materials and lowers the overall price of full batteries^[99].

Hence, Figure 9 exhibits the distinction and comparison of hard carbon applications from laboratory to industrial production^[100-104]. First of all, the battery research objectives in the laboratory are mainly focused on exploring new battery materials, technologies and theoretical mechanisms, including optimizing battery performance, realizing long cycles and mining energy storage mechanisms. The main research goals of industrial batteries are: large-scale production, industrial production and expanded production. Industrial battery research includes full battery matching, performance optimization, first coulomb efficiency, energy density and power density. In laboratory battery research, biomass-derived hard carbon is rich in raw materials, has a simple synthesis process, and can be matched with aluminum foil as a collector fluid. In industry, biomass-derived hard carbon has high consistency, high yield and extremely low cost. Therefore, hard carbon, as a potassium ion battery negative electrode, has great industrial advantages. Of course, from the laboratory to industrial production, the development of battery technology is facing the transformation from basic research to technology application, from the scale of the laboratory to industrial production; this process needs to overcome the challenges of technology transfer, large-scale production and application environment changes, but also consider the cost, efficiency and the scope of application.

CONCLUSIONS AND PROSPECTS

Due to the advantages of ultrahigh potassium reserves, low price and environmental-friendliness, the research into PIB systems has become the top priority in the post-LIB era [Figure 10]. Biomass-derived carbon with abundant sources, low price and abundance in organic matter, captured the attention of researchers. We discussed the benefits and drawbacks of various carbon sources for biomass-derived carbon used in PIBs, focusing on the differences in structural properties, preparation techniques, and performance characteristics. Plant-based carbons, such as those derived from potatoes or DSs, offer high specific surface areas and mesoporous structures, enhancing potassium ion diffusion and electrochemical stability. However, they may face challenges in large-scale production due to variable material quality. Straw-based carbons, such as rice husk-derived carbon, feature a hierarchical structure and favorable graphitization but require optimized synthesis temperatures for consistency. Animal-based carbons, such as those derived from chicken bones, demonstrate high surface areas and heteroatom doping, which improve conductivity and potassium storage. Additionally, carbons doped with nitrogen and other heteroatoms tend to perform better due to improved active sites for ion intercalation and higher conductivity, enhancing overall anode performance. Based on this comparison, plant-based biomass (particularly from agricultural residues such as sisal hemp) and animal bones are the most promising for PIB anodes. Sisal-derived carbon offers an ideal combination of high porosity, structural stability, and ease of processing, making it suitable for scalable and cost-effective production. Animal bone-derived carbons also show excellent performance due to their inherent heteroatom content and surface area, though they may require more complex processing. Future work should focus on refining synthesis techniques to ensure consistency across batches and optimize these biomass types for large-scale, high-performance PIB applications.

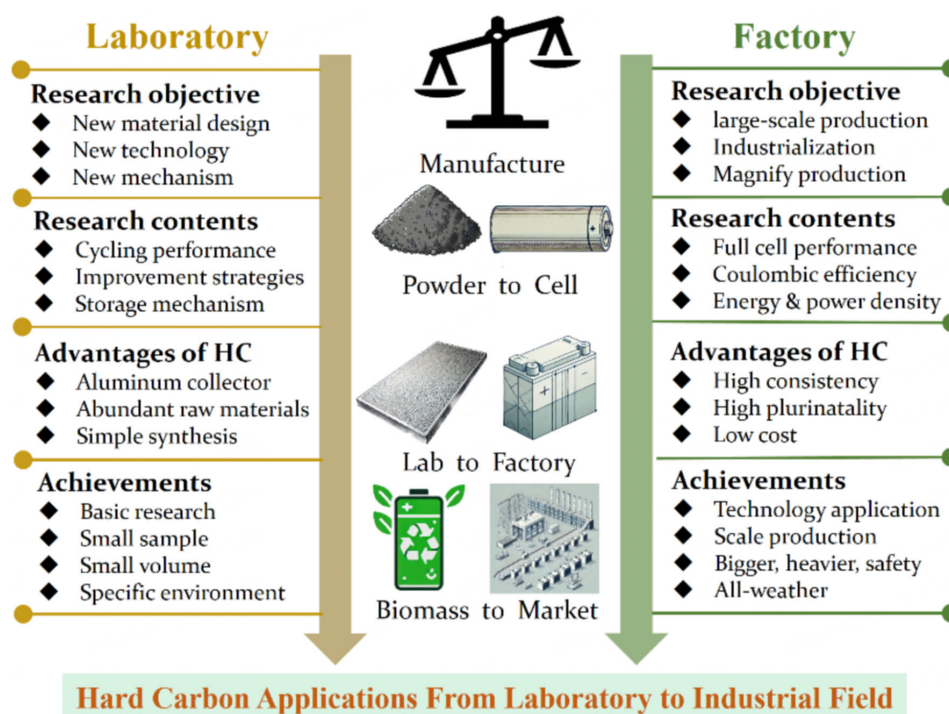


Figure 9. The distinction and comparison of hard carbon applications from laboratory to industrial production.

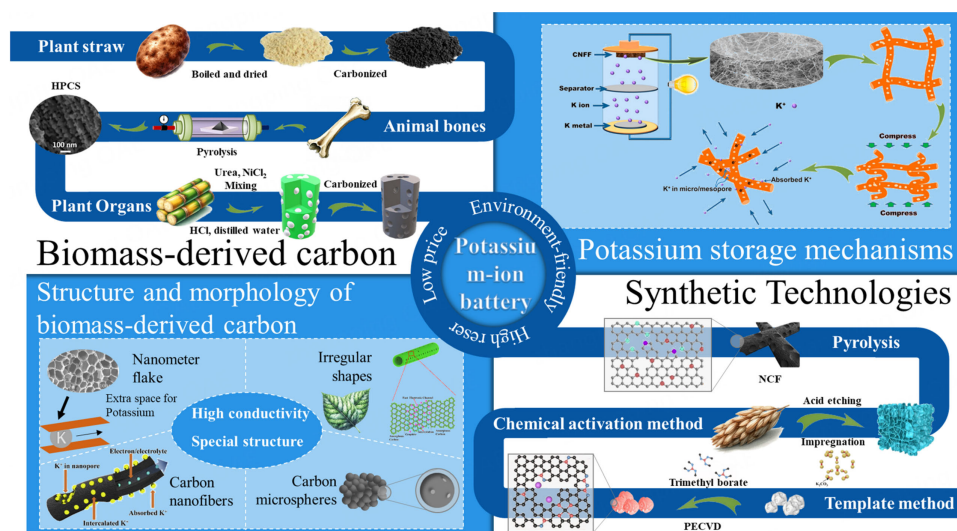


Figure 10. Biomass-derived materials: from raw materials to engineered products: synthesis technologies, diverse structures, and reaction mechanisms [59,67,69,70,73,74,76,80,86,89]

Different carbon synthesis methods significantly influence the structure and electrochemical performance of biomass-derived hard carbon, particularly for use as anodes in PIBs. Each method offers distinct benefits, largely shaping the porosity, surface area, heteroatom doping, and structural integrity of the carbon material, which in turn influence potassium ion storage, capacity, and cycling stability. High-temperature pyrolysis can improve graphitization, enhancing conductivity and requiring substantial energy input. Chemical activation forms micropores and mesopores, enhancing specific surface area and porosity.

Templating can achieve a high level of structural precision, though it often involves complex steps and potentially harmful chemicals for template removal. HTC also allows for controlled doping with oxygen and nitrogen, enhancing conductivity and wettability, although the process is slower than pyrolysis. MAP allows fine control over pore structure and dopant integration but requires microwave-compatible absorbers, limiting some raw material choices. Overall, the choice of synthesis method allows for tuning the carbon structure, porosity, and electrochemical properties of biomass-derived hard carbon. Pyrolysis and chemical activation are especially beneficial for creating high-capacity materials with extensive active sites, while templating and HTC offer enhanced structural stability. MAP presents a promising alternative for faster, energy-efficient synthesis with high electrochemical performance, positioning it as an attractive choice for scalable applications in PIBs.

By employing potassium storage mechanisms including the adsorption-intercalation-filling and active site potassium storage, biomass-derived hard carbon with various structures can achieve reversible potassium deintercalation during charging and discharging. Additionally, the good conductivity of biomass-derived carbon and its structure, which buffers K^+ deintercalation to control volume change, provide excellent capacity, rate performance and cycle stability for PIBs.

The future of biomass-derived carbon for PIB anodes is promising, driven by advancements in sustainable energy storage technology. Biomass sources, such as plant residues and animal-derived materials, are abundant, renewable, and cost-effective, making them well-suited for scalable, eco-friendly carbon production. Innovations in synthesis techniques (such as chemical activation, templating, and MAP) enable precise control over pore structures and heteroatom doping, which enhance potassium ion diffusion, capacity, and cycling stability. Future research may focus on optimizing these processes to improve material consistency and reproducibility at an industrial scale. Additionally, computational modeling, such as density functional theory, will deepen understanding of potassium ion storage mechanisms, further advancing the design of biomass-derived carbon anodes.

To achieve a cost-effective, stable, and high-capacity biomass-derived carbon for PIBs on a large scale, further optimization and improvement of current materials are essential. Research can proceed along three main pathways: first, using recycled animal bones with natural internal doping of heteroatoms as precursors, while minimizing the use of chemical activation, minimizing carbonization temperature and time, and avoiding secondary carbonization. This approach aims to create cost-effective, heteroatom-doped carbons that reduce energy loss, simplify synthesis, and facilitate scale-up. MAP is another promising method, as it allows direct electromagnetic heating of animal bone precursors, offering precise control over pore structure and dopant integration, which enhances energy efficiency and shortens reaction times. However, suitable microwave absorbers still need development. Finally, using plant straw with a highly consistent 3D pore structure as a carbon source, combined with pyrolysis and chemical activation, can create materials with abundant active sites and heteroatom doping, increasing specific capacity. Techniques such as templating and HTC can further improve the structural stability of porous or pseudo-graphitic carbon, resulting in anode materials with high capacity, fast charge/discharge rates, and long cycle life.

Meanwhile, developing low-cost biomass carbon treatment methods and establishing controlled synthesis techniques of biochar materials are of great significance for the development of PIBs. High-quality products can be prepared in large quantities, such as carbon nanofibers, carbon nanotubes, hard carbon, *etc.*, thus facilitating the commercial production process of carbon materials as anode materials. To achieve the goal of carbon peaking and carbon neutrality, PIBs will play an important role in smart grid and large-scale energy storage technology.

DECLARATIONS

Authors' contributions

Led the review design, conducted an extensive literature search, synthesized key findings, and performed data analysis: Liu, Z.; Zhang, G.

Providing essential input on the conceptual framework and organization: Chen, J.

Supported literature collection and organization: He, K.; Fang, Z.

Contributed to data synthesis and editing: Zhang, H.; Gong, Z.

Facilitated resource coordination and literature access: Ding, S.

Data visualization and figure preparation: Fang, Z.; Wang, T.

Oversaw the review process, guiding the analysis to ensure comprehensive coverage of key topics: Liu, Q.

Availability of data and materials

All data supporting the findings of this review are available within the manuscript or referenced sources. Additional datasets or materials used in this study are available from the corresponding author upon reasonable request.

Financial support and sponsorship

The work was financially supported by the National Natural Science Foundation of China (No. 52204308), the Natural Science Foundation of Liaoning Province (2023-MSBA-101), the Fundamental Research Funds for the Central Universities (Grant No. N2025018 and Grant No. N2025009). Additionally, the Pingshan District Innovation Platform Project of Shenzhen Hi-tech Zone Development Special Plan in 2022 (No. 29853M-KCJ-2023-002-02) is gratefully acknowledged.

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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