

Preparation of biochar materials and their research progress in supercapacitors

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ABSTRACT

With the depletion of fossil fuels causing a series of energy and environmental problems, accelerating the development of green and clean energy is urgent. Supercapacitors are favored by researchers due to their excellent performance such as high specific energy and good stability. Biochar is obtained from biomass materials after pre-carbonization and activation treatment, with developed pore size, high active specific surface area, and abundant resources. It has good application prospects as a supercapacitor material. This article provides a brief introduction to biomass charcoal materials and introduces the preparation methods of biomass charcoal and its research progress in the field of supercapacitors. Finally, it looks forward to the development trend of biomass charcoal materials, providing a reference for further improving the research application of biomass charcoal materials in the field of supercapacitors in the future.

KEYWORDS

Biochar; Supercapacitors; Porous materials

1. INTRODUCTION

Energy is essential in daily life. In the future, sufficient and sustainable energy production will be a major issue. Currently, over 80% of the energy used in society is provided by fossil fuels, such as oil, coal, and natural gas, which are all nonrenewable [1]. Therefore, before fossil fuels are depleted, energy must be provided by sustainable sources. The Chinese government has proposed that green production and lifestyle should be widely formed by 2035, carbon emissions should be stable after reaching the peak, the ecological environment should be fundamentally improved, and the goal of building a beautiful China should be basically achieved [2]. Therefore, the unused biomass and waste generated in the energy production process can be effectively used as carbon materials for energy storage/conversion devices such as synthetic batteries, supercapacitors, solar cells, and fuel cells. On the one hand, it avoids the waste of biochar resources and solves the environmental pollution it causes, which is conducive to achieving China's long-term plan of carbon peak and carbon neutrality. Biochar, also known as biochar, refers to a highly aromatic, carbon rich porous solid particle material generated by high-temperature pyrolysis of carbon rich biomass under anaerobic or anaerobic conditions [3]. This article first introduces biomass charcoal materials, and then introduces the preparation methods of biomass charcoal and its research progress in the field of supercapacitors, providing reference for further improving the research and application of biomass charcoal materials in the field of supercapacitors in the future.

2. INTRODUCTION TO BIOMASS CHARCOAL MATERIALS

Biomass refers to materials or by-products extracted from plants, which can serve as potential sources of energy. Biomass is composed of carbohydrates, lignin, starch, proteins, and lipids, which vary depending on geographical conditions and sources. Biomass resources are abundant, including energy crops, crops, and their residues, wood and wood waste, urban waste and animal waste, aquatic plants, and algae. However, these biomaterials can be divided into four categories, namely plant-based, fruit and vegetable-based, microbial-based, and animal-based biomass, as shown in Figure 1 [2]. By understanding the chemical and elemental composition of different types of biomass, it is possible to accurately predict the composition and structure of corresponding biomass-derived carbon. The carbon-rich in biomass forms a network structure, and the doping of organic compounds enhances electronic conductivity and reaction activity. After removal, inorganic minerals in biomass can act as pore-forming agents, forming nanopores, including micropores and mesopores, which are conducive to the rapid infiltration of electrolytes and the rapid conduction of electrolyte ions and electrons [3]. There are various types of raw materials for preparing biochar, with different raw materials and preparation methods, and the composition elements of biochar are also different. In addition, different preparation methods of biochar have a significant impact on the performance of biochar. Therefore, the following will introduce several different preparation methods of biochar and the application progress of biochar in supercapacitors.

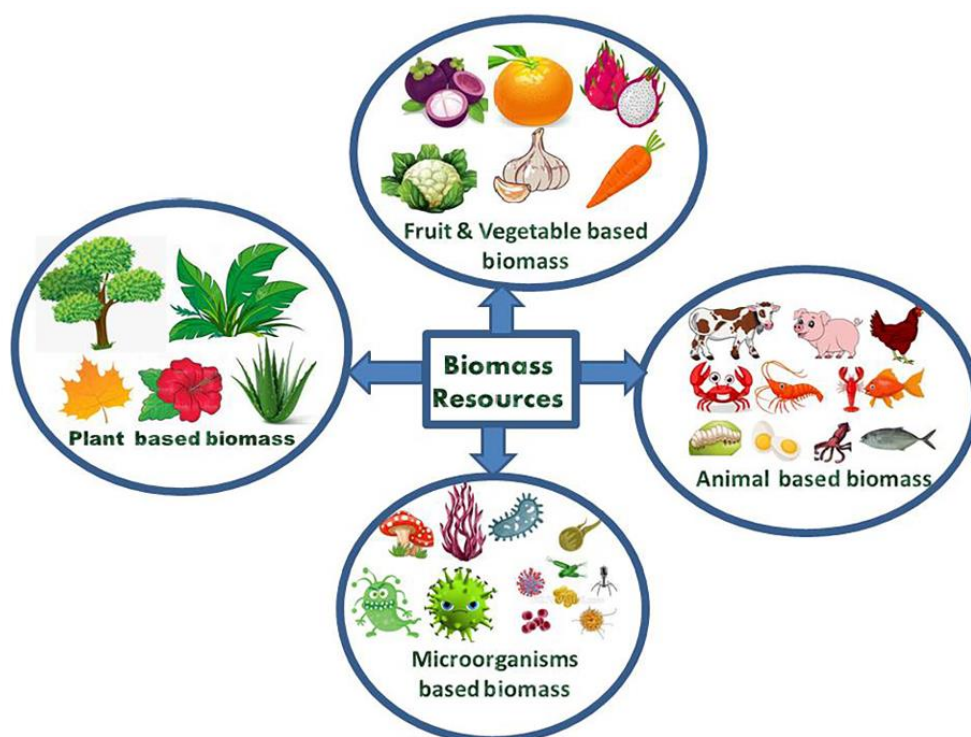


Figure 1. Classification of different types of biomass charcoal sources [2]

3. PREPARATION METHOD OF BIOMASS CHARCOAL

The preparation of biochar mainly involves two processes: carbonization and activation, which can be carried out in steps or simultaneously. The pretreatment of biomass can lower the activation temperature, shorten the activation time, or increase the yield of activated carbon. Pre treatment mainly includes deashing, pre oxidation, or impregnation [4]. According to different heating methods, the preparation of biomass charcoal can be divided into the thermal decomposition method, microwave carbonization method, and hydrothermal carbonization method.

3.1. Pyrolysis

Pyrolysis refers to the method of obtaining biomass charcoal materials by placing biomass raw materials at a higher temperature and maintaining a certain temperature under anaerobic or anaerobic conditions to undergo a cracking reaction. At present, the thermal decomposition method is considered the most commonly used method for preparing biomass charcoal. According to the heating rate during the preparation process and the duration of maintaining temperature, it can be divided into three technologies: rapid pyrolysis, medium pyrolysis, and slow pyrolysis.

The biomass char produced by slow pyrolysis is mainly composed of a graphite layer. Under high-temperature conditions, the surface alkyl oxygen and alkyl carbon will be further converted into aromatic carbon. Although the process of preparing biochar using a slow thermal decomposition method is slow, the yield of biochar is high. Among them, carbonization temperature is one of the key factors affecting the physical and chemical properties of biomass charcoal, thereby affecting its application ability.

Wang et al. [5] prepared calcite/biochar composite materials using coconut shell and calcite as raw materials and co-thermal decomposition at 500°C, 600°C, and 700°C, respectively. The effect of pyrolysis temperature on the adsorption of Pb (II) by calcite/biochar composite materials was investigated. By comparing the adsorption capacity, it was found that the biomass charcoal prepared had the best adsorption effect when the pyrolysis temperature was 700°C.

Chen et al. [6] used berry seeds as raw materials and evenly dispersed 20g of berry seeds in 1L of water. After stirring, 0, 10, 20, and 30g of CaCl₂ solutions were added respectively. After freeze-drying, the obtained multi-layer precursor was heated at 600°C for 1 hour in a mixture of 95% argon and 5% hydrogen gas. After soaking and drying with 1M acetic acid, CACF-0, CACF-1, CACF-2, and CACF-3 pectin-derived carbon were prepared. The research results indicate that the CACF-2//CACF-2 PIHC device provides a high energy density of 178.4 Wh kg⁻¹ under 1115 W kg⁻¹ conditions. Even at a high power density of 10500 W kg⁻¹, the obtained PIHC can still maintain an energy density of 115 Wh kg⁻¹, and under 5 A g⁻¹ conditions, a capacity retention rate of 75.2% can be achieved after 10000 cycles. The schematic diagram of the synthesis process of CACF samples is shown in Figure 2 [6].

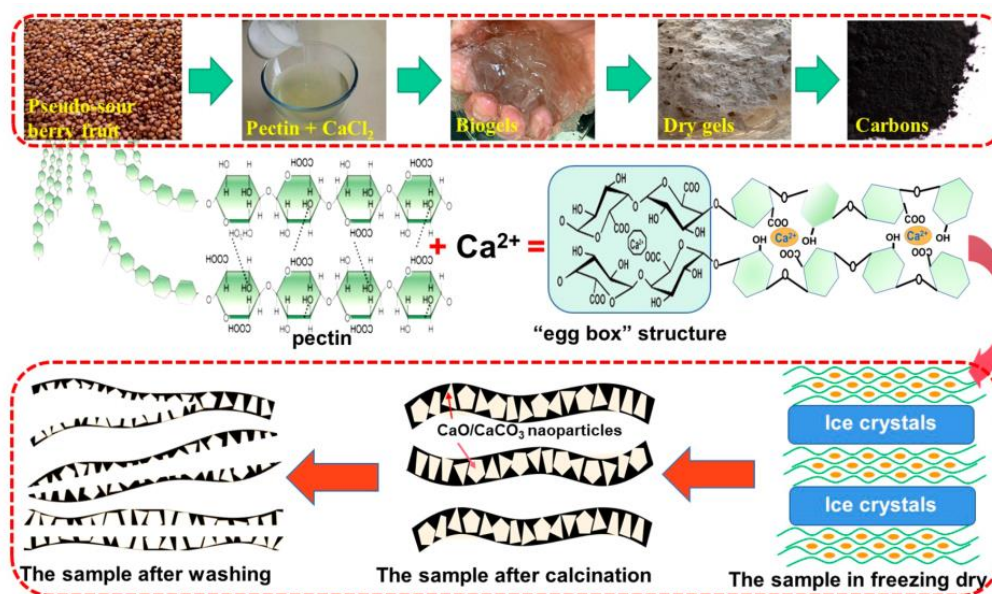


Figure 2. The schematic diagram for the synthesis process of the CACF samples [6]

3.2. Hydrothermal Carbonization Method

Due to the high moisture content of most biomass raw materials, both thermal decomposition and microwave carbonization methods require drying to reduce energy consumption during the preparation process, and the hydrothermal carbonization method precisely solves this problem.

The hydrothermal carbonization method is the process of carbonizing biomass by heating the biomass, catalyst, and water in a hydrothermal reactor at a certain temperature and pressure. Hydrothermal carbonization can accelerate the physical and chemical interactions between solvents and biomass, promote the reaction between ions and acids/bases, decompose the carbohydrate structure in biomass, and ultimately form biomass charcoal materials and precipitate [7].

Liu Shouxin et al. [8] used commercial activated carbon and glucose as raw materials and adopted a hydrothermal carbonization method. The commercial activated carbon was mixed with 30ml of 0.1-1.0mol/L glucose solution and reacted at 180°C for 5 hours in a high-pressure reactor to produce biomass charcoal material with a specific surface area of 441.0m²/g. The saturated adsorption capacity of the material for Cr (VI) was 0.48mmol/g, which was four times higher than the adsorption capacity of the modified activated carbon.

In addition to using hydrothermal carbonization alone to prepare biomass charcoal, hydrothermal carbonization can also be used in conjunction with other preparation methods. Wang et al. [9] used sunflower stems as raw materials, dried them at 105°C, ground them into fine powder, and screened them through an 8000-mesh sieve to obtain an average particle size less than 2μm sunflower stem powder was rapidly heated to 230°C using a high-pressure reactor using a hydrothermal carbonization method to prepare activated carbon material (HC). Then, AC was prepared by pyrolysis in an N₂ atmosphere at a mass ratio of 2:1, 800°C between KOH and HC, and the activated carbon material PC was obtained by pyrolysis at 800°C. The morphology and electrochemical properties of HC, AC, and PC were compared. The research results indicate that the prepared AC has a specific surface area of 1505m² g⁻¹ and a special mesoporous layer stacking random network structure. It was tested using a three-electrode and symmetric electrode system, and exhibited excellent capacitance of 365 and 259 F g⁻¹, respectively. In addition, in the three-electrode system, the excellent capacitance retention and good stability values obtained after 15000 cycles at 20 A g⁻¹ were close to 81% and 95%, respectively, and the electrochemical performance was better than HC and PC. The schematic diagram of preparing carbon materials from sunflowers is shown in Figure 3 [9].

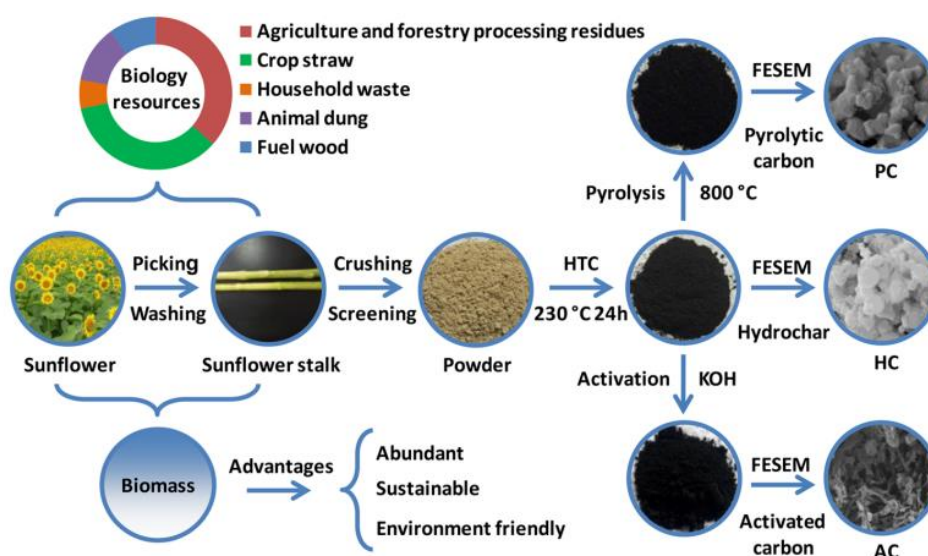


Figure 3. Schematic illustration of preparing carbon materials derived from sunflower stalk [9]

3.3. Microwave Carbonization Method

Microwave carbonization method refers to the high-temperature pyrolysis technology that combines thermal decomposition technology and microwave pyrolysis technology by heating biomass raw materials to a certain temperature in the absence of oxygen, resulting in a solid biomass charcoal material.

Compared with traditional pyrolysis methods, microwave carbonization method uses microwave radiation to cause high-frequency reciprocating motion and collision of atoms and molecules inside the heated biomass raw materials, rapidly generating a large amount of frictional heat energy, thereby rapidly heating the inside and outside of the biomass raw materials, greatly reducing reaction time.

Zhang Libo et al. [7] prepared high surface area activated carbon using carbonized tobacco stalks as raw materials, KOH as activator, and microwave heating potassium hydroxide activation method. At the same time, the effects of microwave heating time and alkali carbon ratio on the yield and adsorption capacity of activated carbon were investigated. The results showed that when the alkali carbon ratio was 4:1, microwave power was 700W, and heating time was 30 minutes, the biomass charcoal produced had a higher specific surface area. Lu et al. [10] used lignin (CF) as the raw material, and uniformly mixed CF with 6mol L⁻¹ KOH. After 48 hours, the solution was adsorbed onto a carbon felt and placed in a crucible. After microwave heating, the electrode material (L-CF) was obtained. After research, it has been shown that the capacitance in 6mol L⁻¹ KOH electrolyte reaches 394.8F g⁻¹ at 1 A g⁻¹, and D2 has strong cycling stability. After 100000 cycles (10A g⁻¹), the retention rate is 83.69%. Then, the capacitor was prepared with high energy density (15.062Wh kg⁻¹) and high power density (750W kg⁻¹). When cycled 15000 times at 3 A g⁻¹, the retention rate of the capacitor was 74.45% of the initial value, demonstrating good cycling stability performance. The L-CF preparation process diagram and the cyclic stability diagram at 10A g⁻¹ are shown in Figure 4 [10].

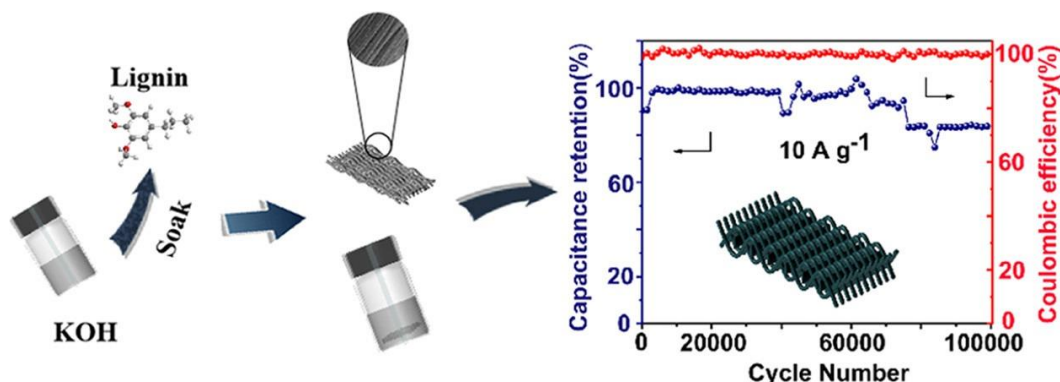


Figure 4. L-CF preparation flow chart and cyclic stability diagram at 10A g⁻¹[10]

4. RESEARCH PROGRESS OF BIOCHAR MATERIALS IN SUPERCAPACITORS

4.1. The Energy Storage Mechanism of Supercapacitors

Among various energy storage systems, the most important one is electrochemical energy storage systems, including lithium-ion batteries, supercapacitors, and fuel cells [11]. In recent years, with the development of technology in the fields of electronic information and energy, supercapacitors have attracted the interest of researchers due to their advantages such as large specific capacity, fast charging and discharging speed, and longer cycle life. Supercapacitors, also known as electrochemical capacitors, are a new type of efficient and green energy storage device that lies between traditional capacitors and rechargeable batteries. They have many advantages such as larger capacity than ordinary electrostatic capacitors, higher power than secondary batteries, faster charging

and discharging speed, long cycle life, wide operating temperature range, no pollution to the environment, no memory effect, maintenance-free, and high safety. They have received widespread attention in the field of energy storage [12]. According to the energy storage mechanism, supercapacitors can be divided into two categories: double-layer supercapacitors (EDLC) and pseudocapacitive supercapacitors, among which pseudocapacitive supercapacitors are further divided into under potential deposition, oxidation-reduction, and embedded supercapacitors. The schematic diagram of charge storage mechanisms for different types of capacitors is shown in Figure 5 [13].

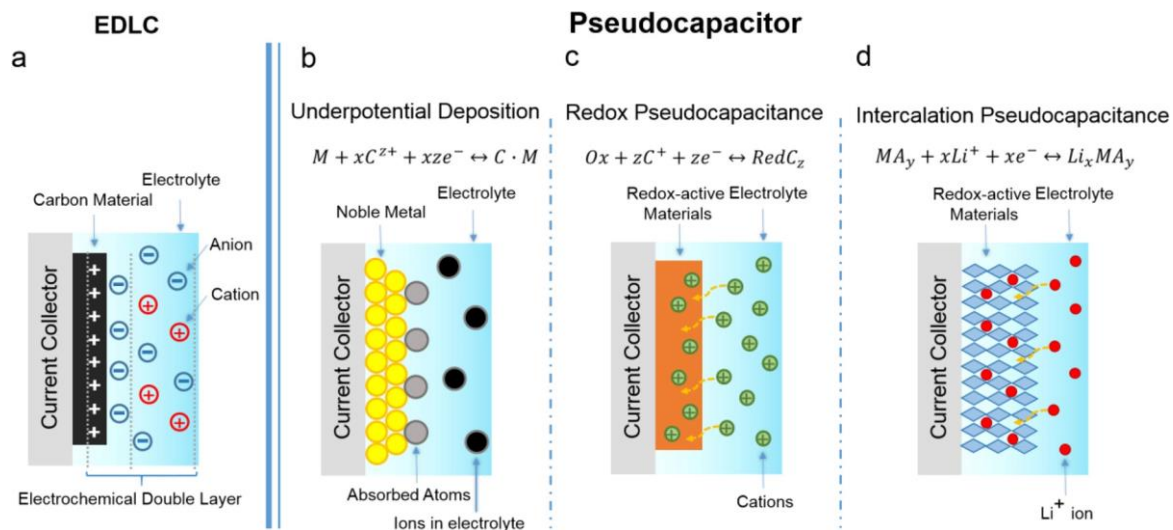


Figure 5. Schematic diagram of charge storage mechanism for different types of capacitors [13]

Supercapacitors are usually composed of electrodes, electrolytes, current collectors, separators, and corresponding auxiliary devices, among which the electrode material plays a core role, determining the main performance parameters of the capacitor [11], and also affecting the electrochemical performance of the supercapacitor. At present, there are three main types of electrode materials: carbon-based materials, metal oxide and hydroxide materials, and conductive polymer materials. To achieve the long-term plan of "carbon peak and carbon neutrality", carbon-based materials using biomass charcoal as a precursor have the advantages of low cost, easy availability, nontoxicity, green environmental protection, good conductivity, and stable chemical properties, making them the first choice of electrode materials for supercapacitors.

4.2. Biomass Carbon Electrode Materials

The porous structure of biomass charcoal materials increases its specific surface area, and biomass charcoal also exhibits high specific capacity, high energy storage, and high conductivity in electrochemical performance. Biomass charcoal materials have the following characteristics: short diffusion path of electrolyte ions; Adjustable porosity and surface area promote rapid charge transfer and transfer [14]; The microstructure, morphological composition, and crystallinity of materials can be controlled. The porous structure of lignin-based carbon materials can not only improve the efficiency of transporting electrolyte ions but also improve the permeability of the electrolyte. Therefore, lignin-based porous carbon materials should have higher capacitance [15].

Cheng et al. [16] used commercially available absorbent cotton as raw material and conducted thermal treatment in an N_2 atmosphere at $800^{\circ}C$ using the pyrolysis method. Then, KOH was used as an activator to activate the heat-treated biochar material with a mass ratio of 4-7:1 between KOH and biochar. They successfully prepared biochar-activated material (aCF) and studied the performance of biochar-activated materials with different mass ratios as electrode materials for supercapacitors. The research results indicate that the aCF product maintains the high elasticity characteristics of the starting cotton, while the presence of a large number of micropores gives it a high surface area and good conductivity. The aCF-6 electrode can provide high specific capacitance, high-speed

performance, and excellent cycling stability. At a current density of 1 A g^{-1} , the capacitance can reach 283 F g^{-1} . When the current density increases to 100 A g^{-1} , the capacitance can still reach 224 F g^{-1} , demonstrating excellent capacitance retention. The manufacturing steps of the aCF electrode and the schematic diagram of electrode ion/electron transfer behavior are shown in Figure 6 [17].



Figure 6. Schematic Illustrating the Fabrication Steps and Ion/Electron Transport Behavior in aCF Electrode [17]

4.3. Biomass Carbon Composite Electrode Material

In supercapacitors, biochar material is an excellent electrode material. Biomass materials generally have inherent uniform and precise biological structures as templates, and the prepared biochar electrode materials are conducive to forming a determined and controllable geometric shape. Meanwhile, the basic elements of biomass are carbon, nitrogen, oxygen, and sulfur, with a unique natural ordered hierarchical structure, as well as the rich surface characteristics of biomass-derived carbon materials, which are compatible with electrochemical reaction processes such as ion transfer and diffusion [18]. However, a single biomass charcoal material still cannot avoid the drawbacks of low energy density, small specific capacity, and poor hydrophilicity. Therefore, binary system composite electrodes such as biochar/metal compounds or biochar/conductive polymers have become a research hotspot.

Lu et al. [19] used terrestrial silver white fallen leaves and fresh mature aquatic kelp as carbon precursors and obtained primary carbon materials through high-temperature calcination. After that, the carbon electrode materials were further modified by activating pore formation and composite MnO_2 with pseudocapacitive characteristics to improve the electrochemical performance of biomass carbon-based electrode materials. Zhang et al. [20] used willow catkins as raw materials and controlled the morphology of the materials to composite high conductivity biomass charcoal materials with nickel-based compound materials. The conductivity, specific capacity, and cycling stability were improved. The modified nickel-based compound materials were used in water-based hybrid supercapacitors to broaden the working voltage and further enhance energy density. Rui et al. [21] used vacuum impregnation to load graphene onto the surface and pores of biochar and found that graphene not only increased the conductivity of biochar but also increased the specific surface area. The results showed that the specific capacitance of the biochar/graphene composite electrode was 159.74 F g^{-1} at a current density of 0.5 A g^{-1} , which was more than four times higher than that of the pure biochar electrode without loaded graphene. After 5000 cycles of charging and discharging, the performance showed no degradation and exhibited good stability.

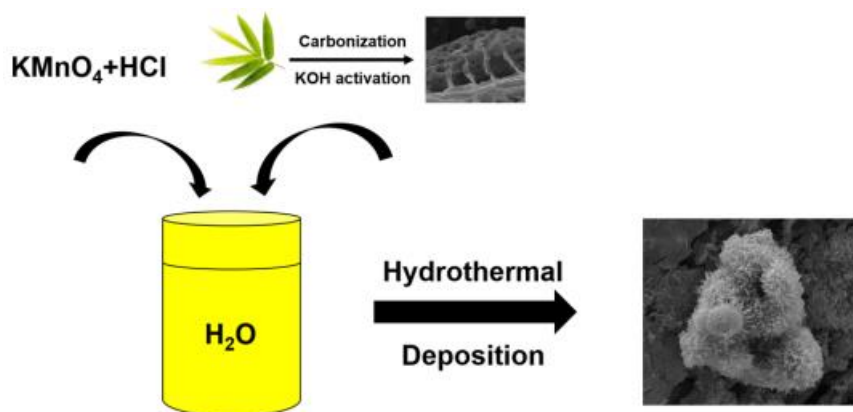


Figure 7. Synthesis of $\text{MnO}_2@\text{BL-x-y}$ [22]

Yu et al. used bamboo leaves (BL) as raw materials and activated BL and KOH in a mass ratio of 1:1, 1:2, and 1:3, respectively. They heated them to 700°C to prepare BL-x ($x=1, 2, 3$). At the same time, BL was mixed with melamine and 1.5g of KOH at 700°C to prepare nitrogen-doped porous carbon material NBL-700. Then, 50mg of BL-x, 0.395 g of KMnO_4 , and 1.25mL of concentrated HCl were uniformly mixed in a high-pressure reactor and kept at 140°C for 6, 8, 10, and 12 hours to prepare $\text{MnO}_2@\text{BL-x-y}$ ($x=1, 2$, and 3; $y=6, 8, 10$, and 12 hours) and compare the electrochemical performance. $\text{MnO}_2@\text{BL-x-y}$ the synthesis diagram is shown in Figure 7. The ratio of BL to KOH was 1:3, and the hydrothermal time was 6 hours, resulting in a maximum specific capacitance of 76 F g^{-1} (at 0.5 A g^{-1}). Supercapacitors in asymmetric systems, $\text{MnO}_2@\text{BL-3-6h} // \text{NBL-700}$ exhibit a large potential range of 0-1.6V and high energy density. At 0.5 A g^{-1} , the energy density of the porous carbon material is 11.47 Wh kg^{-1} , and it maintains 85.3% of the original specific capacitance after 5000 cycles (as shown in Figure 8 [22]).

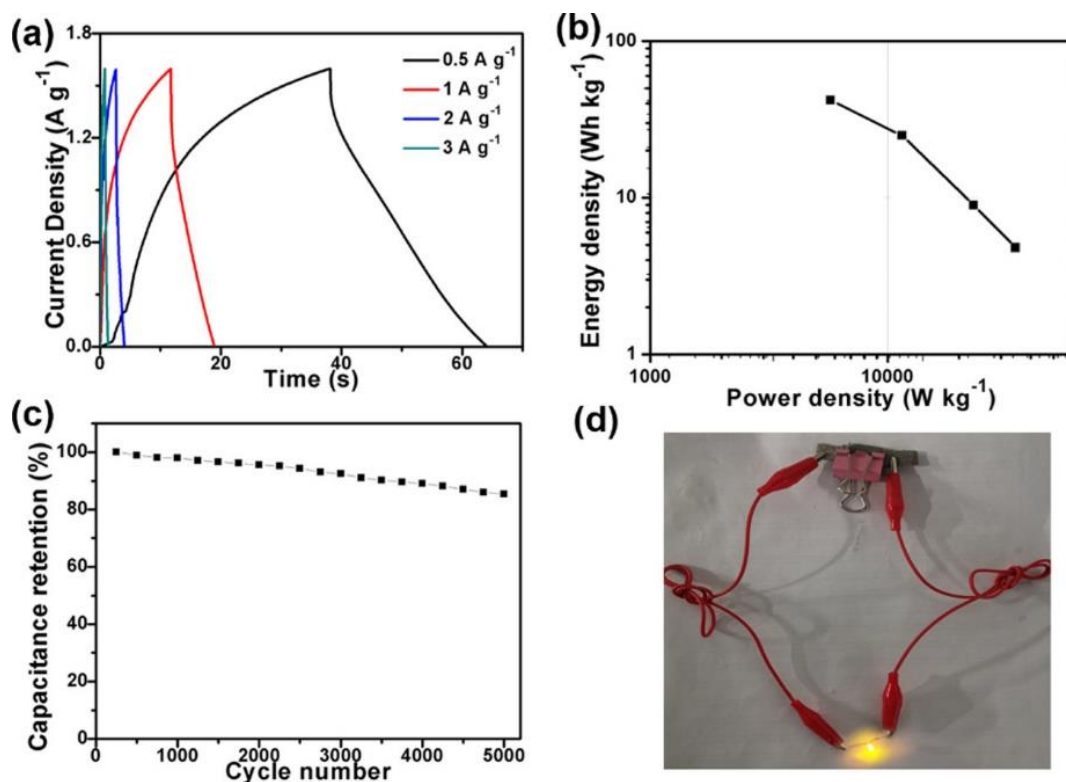


Figure 8. $\text{MnO}_2@\text{BL-3-6h} // \text{NBL-700}$ Electrochemical performance of NBL-700 in an asymmetric dual-electrode system: (a) GCD curves at different current densities, (b) Ragone plots, (c) cycling stability at a current density of 0.5 A g^{-1} , (d) using $\text{MnO}_2@\text{BL-3-6h} // \text{NBL-700}$ solid capacitor [22]

Wang et al. [23] used wild black fungus (AAJ, iron content 0.026wt%) and urea as the nitrogen source to decompose the mixture of AAJ and urea using pyrolysis method at temperatures of 900 °C, 950 °C, and 1000 °C to obtain Fe-ISA/NC900, Fe-ISA/NC, and Fe-ISA/NC1000, as shown in Figure 9. The research results indicate that the absorption of urea and subsequent simultaneous decomposition with AAJ increase the content of N doping and active sites. The prepared Fe-ISA/NC exhibits excellent ORR activity and good stability, providing a new idea for the doping of atoms in biochar and its application in supercapacitors.

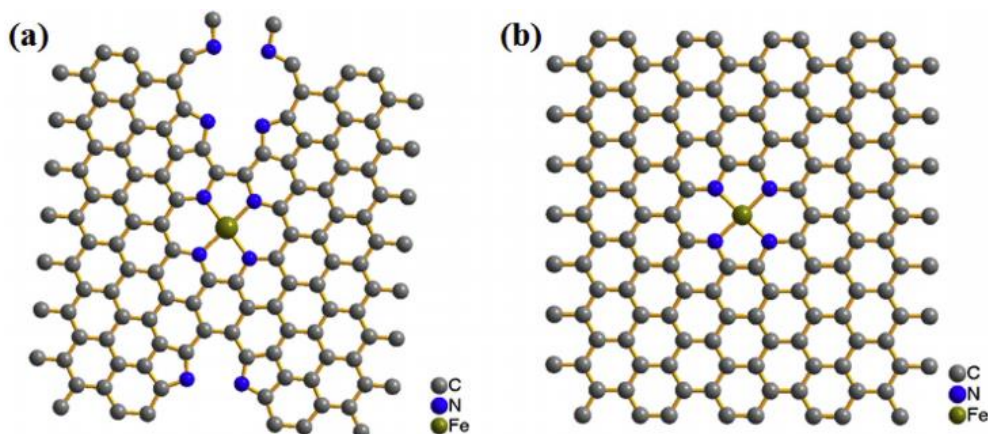


Figure 9. (a) Schematic model of Fe-N₄ moiety anchored on carbon with pyrrolic-N doping (Fe-N₄/NC). (b) Schematic model of Fe-N₄ moiety anchored on carbon without pyrrolic-N doping (Fe-N₄/C) [23]

Zhao [24] and others successfully prepared LEPC4/PANI4 aerogel with pectin (LEPC, esterification degree: 33%) with low methoxy concentration and conductive polymer aniline (AN) as raw materials. Through research, LEPC4/PANI4 aerogel shows a self-supporting 3D nanoporous network structure, with high specific surface area and graded pores, which makes it have high mechanical strength and considerable conductivity, and the specific capacitance can reach 184F g⁻¹ at 0.5A g⁻¹. After 1000 cycles of cyclic voltammetry testing, the capacitance retention rate of PANI is 57%, which shows good cycle stability. The formation of LEPC/PANI aerogel and the schematic diagram of its cross-linking structure are shown in Figure 10 [24].



Figure 10. Schematic illustration of LEPC/PANI aerogel formation and its cross-linking structure[24]

The above experiments all indicate that the electrochemical performance of biomass charcoal-based composite materials is superior to that of single-component electrode materials. This synergistic

effect compensates for the shortcomings of any single material, and as an electrode material for supercapacitors, it has better conductivity, specific capacity, and energy storage performance.

5. CONCLUSION AND PROSPECT

Due to its unique properties such as low cost, easy availability, non-toxic, environmentally friendly, and biocompatibility, biochar materials have potential application prospects in the field of supercapacitors and are the most widely studied electrode active material for supercapacitors. Research has shown that biomass porous carbon has many unparalleled advantages, such as large specific surface area, wide pore size distribution, and good electrochemical performance. Most biomass porous carbon also has a graded pore structure and stable chemical properties, thus exhibiting good cycling and rate performance. It is a natural resource rich in carbon and can be used as a low-cost, non-toxic, and renewable precursor for the production of functional carbon materials. However, biochar itself contains abundant heteroatoms (such as N, O, S, etc.), which can enhance its electrochemical performance. Catalytic doping of biomass porous carbon can also further enhance its performance.

Biomass resources are abundant and have the characteristics of green and sustainable development. The focus of future biomass charcoal preparation is to develop green, environmentally friendly, mild reaction conditions, energy-saving and efficient conversion methods. By improving the carbonization activation process, catalyst types and content, better physical and electrochemical properties of biomass charcoal microporous structure can be obtained, and it can play a broader application in the field of supercapacitors. However, defects such as poor dispersibility, poor refillability, and multi-layer brittleness can hinder the complete realization of the physical, chemical, and high specific surface area properties of biomass carbon materials. Therefore, when used as electrode materials for supercapacitors, their energy density is often not high. Therefore, future research should combine porous biochar materials with pseudocapacitive materials and apply them to supercapacitors to further improve the electrochemical performance of biochar.

ACKNOWLEDGEMENTS

College student innovation and entrepreneurship Project of North China University of Science and Technology (T2022047); Project of Hebei Provincial Basic Research Business Fee Research Project for Provincial Universities (No. JST2022005); Project of Science and Technology Plan of Tangshan City (21130229C).

REFERENCES

- [1] Kong Sifang, Yao Xingcheng, Zhang Jianguo, et al. Review of Characteristics of Biochar and Research Progress of Its Application [J]. *Journal of Ecology and Environment*. 2015. 24(04):716-723.
- [2] Manasa P, Sambasivam S, Ran F. Recent Progress on Biomass Waste Derived Activated Carbon Electrode Materials for Supercapacitors Applications-a Review [J]. *Journal of Energy Storage*. 2022. 54.
- [3] Kaur P, Verma G, Sekhon SS. Biomass Derived Hierarchical Porous Carbon Materials as Oxygen Reduction Reaction Electrocatalysts in Fuel Cells [J]. *Progress in Materials Science*. 2019. 102:1-71.
- [4] Zhao Liyuan, Lu Jianming, Li Qingli, et al. Present Situation and Progress in Preparation of Activated Carbon[J]. *Science Technology and Engineering*. 2008. (11):2914-2919.
- [5] Wang Shenwan, Zhong Shuang, Zheng Lili, et al. Preparation of calcite/biochar composite by co-pyrolysis and its adsorption properties and mechanism for Pb(II) [J]. *Journal of Composite Materials*. 2021. 38(12):4282-4293.
- [6] Chen M, Liu W, Du YX, et al. "Plains-Hills": A New Model to Design Biomass-Derived Carbon Electrode Materials for High-Performance Potassium Ion Hybrid Supercapacitors [J]. *ACS Sustainable Chemistry & Engineering*. 2021. 9(10):3931-3941.

- [7] Hu B, Wang K, Wu LH, et al. Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass [J]. *Advanced Materials*. 2010. 22(7):813-828.
- [8] Liu Shouxin, Sun Jian. Carbon Sphere/Activated Composite Materials Prepared by Solvothermal Method [J]. *Journal of Inorganic Materials*. 2009. 24(06):1132-1136.
- [9] Wang XD, Yun SN, Fang W, et al. Layer-Stacking Activated Carbon Derived from Sunflower Stalk as Electrode Materials for High-Performance Supercapacitors [J]. *ACS Sustainable Chemistry & Engineering*. 2018. 6(9):11397-11407.
- [10] Lu Z, Zhao HD, Luo JJ, et al. Self-Supporting Lignin-Based Carbon Material Flexible Supercapacitor Prepared by the Microwave Method [J]. *Energy & Fuels*. 2022. 36(15):8480-8487.
- [11] Li Xueqin, Chang Lin, Zhao Shenlong, et al. Research on Carbon-Based Electrode Materials for Supercapacitors [J]. *Journal of Physical Chemistry*. 2017. 33(01):130-148.
- [12] Miller JR, Simon P. Materials Science - Electrochemical Capacitors for Energy Management [J]. *Science*. 2008. 321(5889):651-652.
- [13] Shao YL, El-Kady MF, Sun JY, et al. Design and Mechanisms of Asymmetric Supercapacitors [J]. *Chemical Reviews*. 2018. 118(18):9233-9280.
- [14] Zhao Yuqi. Preparation of lignin-based biochar materials and its application in electrode materials for supercapacitors [D]. Changzhou university. 2021.
- [15] Li X, Wei BQ. Supercapacitors Based on Nanostructured Carbon [J]. *Nano Energy*. 2013. 2(2):159-173.
- [16] Cheng P, Li T, Yu H, et al. Biomass-Derived Carbon Fiber Aerogel as a Binder-Free Electrode for High-Rate Supercapacitors [J]. *The Journal of Physical Chemistry C*. 2016. 120(4):2079-2086.
- [17] Cheng P, Li T, Yu H, et al. Biomass-Derived Carbon Fiber Aerogel as a Binder-Free Electrode for High-Rate Supercapacitors [J]. *Journal of Physical Chemistry C*. 2016. 120(4):2079-2086.
- [18] Gao Man. Study on the Preparation and Performance of Pinecone-based Carbon Supercapacitor Materials [D]. China University of Geosciences. 2021.
- [19] Lu Yuting. Preparation of biomass carbon-based MnO₂ composites and study on their electrochemical properties [D]. Dalian Ocean University. 2022.
- [20] Zhang Xuetao. Preparation of Nickel-based Compounds and Research on the Performance of Supercapacitors [D]. Qilu University of Technology. 2021.
- [21] Rui Baozhen, Shi Ying, Xie Jianjun, et al. Preparation of biochar/graphene composite electrode via vacuum impregnation and study on its charge-discharge property [J]. *Modern chemical industry*. 2019. 39(12):145-149.
- [22] Yu J, Li M, Wang X, et al. Promising High-Performance Supercapacitor Electrode Materials from MnO₂ Nanosheets@Bamboo Leaf Carbon [J]. *ACS Omega*. 2020. 5(26):16299-16306.
- [23] Wang X, Du J, Zhang Q, et al. In Situ Synthesis of Sustainable Highly Efficient Single Iron Atoms Anchored on Nitrogen Doped Carbon Derived from Renewable Biomass [J]. *Carbon*. 2020. 157:614-621.
- [24] Zhao HB, Yuan L, Fu ZB, et al. Biomass-Based Mechanically Strong and Electrically Conductive Polymer Aerogels and Their Application for Supercapacitors [J]. *ACS Appl Mater Interfaces*. 2016. 8(15):9917-9924.