

Research Progress of Biochar in Energy Storage

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Abstract. In recent years, the introduction of carbon peaking and carbon neutral policies has placed new demands on clean energy utilization and energy storage devices. The limited reserves of traditional fossil energy sources and the environmental impact of their use have forced mankind to utilize renewable alternative energy sources such as hydro, tidal, biomass. And how biochar is used in the realm of energy storage has become more and more common. Based on the characteristics of biochar materials, this paper analyzes the research progress of how biochar is used in the realm of energy storage. The results show that biochar electrode materials have high charge/discharge energy density, long cycle life and high reversible capacity in supercapacitors. In lithium-sulfur batteries are characterized by easy processing, lower cost, environmental friendliness, and high conductivity. In addition, in response to the current state of research, the article analyzes the shortcomings of biochar applications and proposes solutions for adjusting the pore structure of the biochar material, improving the charge transportation ability and thus increasing the specific surface area, doping some other heteroatoms to introduce excellent functional groups. The article explores the research progress of biochar when it comes to energy storage and contributes to the future development of biochar when it comes to green development and energy storage.

Keywords: Biochar; energy storage area; application; supercapacitor; lithium-sulfur battery.

1. Introduction

In recent years, the introduction of carbon peaking and carbon neutral policies has placed new demands on clean energy utilization and energy storage devices. The limited reserves of traditional fossil energy sources and the environmental impact of their use have forced mankind to utilize renewable alternative energy sources such as, hydro, tidal, geothermal and biomass. Biochar, often referred to as biocoke, is typically a char material produced by pyrolysis, gasification, or hydrothermal carbonization using organic matter as the raw material (such as rice husk, bagasse, or straw). Most of the biomass resources are renewable, low-priced and widely distributed, and many of them are discarded or improperly handled due to their inability to be fully utilized, causing great environmental pollution (e.g., incineration of discarded straw), and thus the development and use of biochar can improve the utilization rate of biofeedstock, and reduce the environmental problems caused by discarded biomass; At the same time, charcoal materials are also important structural and functional materials with great market demand, and the use of biomass to prepare a variety of charcoal materials with excellent performance (e.g., charcoal fibers, synthetic graphite, etc.) not only reduces the cost of these materials, but also achieves the sustainable development of these materials [1].

Graphitized carbon is the key component of the energy storage materials currently available on the market, which have greater capacity, cycle life, and multiple features. The market has set higher standards for energy storage materials, and it is clear that the graphitized carbon materials cannot meet these standards given the rapid development of new energy vehicles. Additionally, graphene, nanotubes, and graphene-like materials are not sustainable due to their high cost and dependence on fossil fuels for their basic materials. Biochar materials are lighter in mass, can be used for a sustained period of time at higher temperatures, and do not affect their own performance in corrosive environments. In addition, the pore structure of biochar materials is richer, contributing to a larger specific surface area, which facilitates the storage of electric charge and improves the electrical conductivity, in addition, the lower cost of biochar is suitable for the field of energy storage.

By analyzing the structure and properties of biochar, this paper finds that biochar has excellent properties such as stable structure, good cycling performance, good electrical conductivity, cheap and environmentally friendly, and has great advantages when it comes to energy storage. This paper proceeds to explore the research progress of biochar materials in supercapacitors and lithium-sulfur batteries when it comes to energy storage, summarizes the problems existing when it comes to energy storage in view of the current situation, and proposes corresponding measures to solve the problems, aiming at promoting the mature application of biochar when it comes to energy storage.

2. Advantages of Biochar in Energy Storage

2.1. Structure

Biomass itself has a variety of natural porous or hierarchical structures, which can promote the penetration of electrolytes and shorten the ion diffusion distance. Moreover, the biocarbon system has a larger surface area and more small pores, which makes it have more energy storage space and more stable service life.

2.2. Characteristic

Most of the biomass itself contains elements such as nitrogen and boron, which can be directly doped as heteroatoms to produce additional active sites. The advantages of biomass-derived carbon materials, such as strong adsorption capacity, good physicochemical stability, and green environmental protection, give biochar a better development prospect for electrochemical storage devices.

2.3. Specificities

Many biomasses are converted from everyday wastes by recycling, a process that is low-cost and environmentally friendly.

3. Biochar in Energy Storage

3.1. Application of Biochar in Supercapacitors

Between conventional capacitors and rechargeable batteries, supercapacitors, or double layer capacitors, are a new form of energy storage device that utilizes reversible redox reactions that can occur on the surface layer of the supercapacitor's electrode material to store energy. What's more, these redox reactions occur rapidly. Compared to conventional capacitors, it has a higher capacity, higher energy, a wide operating range and a long service life; Compared with rechargeable battery, it has high power and does not pollute the environment. Therefore, the performance advantages and disadvantages of supercapacitors can be determined by the performance of its electrode materials.

Biochar has a stable chemical structure and a relatively large specific surface area, so using biochar as the electrode material for supercapacitors can increase the capacitance of supercapacitors and improve the fast charging and discharging ability. The surface structure of the biochar material can form a "double layer" with the electrolyte solution in the supercapacitor, utilizing the reaction that occurs to accomplish the energy storage of the charge. From the data in Table 1, in general, the specific capacitance value of supercapacitors increases with the increase of the specific surface area of the biochar material, and there is a positive relationship between the two. Bilayer supercapacitors mainly utilize the "interfacial bilayer" structure formed by the electrode material and the electrolyte solution to store charge energy. Generally speaking, if the specific surface area of the electrode material is large, the electrode material has more active sites to react with the ions in the electrolyte solution. However, specific capacitance and specific surface area are not strictly proportional to each other, due to the fact that not all pore structures contributing to the specific surface in biochar are

involved in charge transport and storage, and can also be affected by the type of biomass char source, charring method, and later modifications.

Carbon materials prepared from biomass have a variety of pore structures. The macropores, which pore size is less than 2 nm, aid in ion transport and serve as a layer of storage for buffered ions; The mesopore, which pore size is between 2 and 50 nm, decreases the diffusion resistance and shortens the ion's distance of diffusion. This structure of the mesopore allows a large number of ions in the electrolyte to move toward the internal microporous structure; The large number of micropores, which pore size is greater than 50 nm, provides abundant space for the accumulation of electrons. However, if the pore structure of the carbon material is not properly matched, it will directly lead to the blockage of the ion transportation channel and the low performance of high-current charging and discharging.

The electrochemical performance of double-layer biochar-based supercapacitors is significantly impacted by the heteroatom content of biochar (N, B, P, O, etc.). Self-doping and artificial doping are two sources of atom doping. Manual doping is a cumbersome process with high economic and time costs. Therefore, the selection of a biomass capable of self-doping with heteroatoms as a carbon source has received widespread attention. The fundamental purpose of doping heteroatoms is to introduce functional groups that are conducive to improving the electrochemical properties of biochar electrodes, which in turn improves the wettability of biochar and increases the conductivity and specific capacitance. However, due to the complexity of the heteroatom species in biochar, no study has elucidated the mechanism of action in detail, and further research is needed.

Supercapacitors have a very good development prospect when it comes to energy storage. Biochar material has a wide range of sources, well-developed pores and rich functional groups, which makes it a very ideal electrode material. Many large-scale residences of biochar such as the size of the specific surface area, whether the pore structure of biochar is developed or not, and the functional groups introduced by doping of biochar with heteroatoms are the key factors affecting its electrochemical performance and interact with each other. These elements can be optimized and controlled during the biochar preparation process, thereby achieving the goal of enhancing the electrochemical performance. Table 1 is the specific capacitance of different biochars when used as supercapacitor electrodes.

Table 1. Specific capacitance of different biochars when used as supercapacitor electrodes.

Raw material for biomass	Specific surface area/(m ² /g)	Specific capacitance/(F/g)	Reference
bamboo	1472	301	[2]
willow wadding	1533	298	[3]
grapefruit peel	2725	342	[4]
pumpkin	2968	419	[5]
lettuce leaf	3404	421	[6]

3.2. Application of Biochar in Lithium-sulfur Batteries

Governments have recently come to an agreement to support the quicker transition of the energy structure to clean energy in light of the problem of global warming becoming more and more visible. The power and transportation sectors are key sectors for achieving carbon neutrality, and clean energy generation such as wind power and photovoltaics has great potential. The development of China's new energy industry is thriving, and the need to develop new energy technologies has become more urgent. As an intermediate station for new energy generation and utilization, electrochemical energy storage technology plays the role of regulating energy storage and release, and is the key to the development of new energy utilization and related industries.

As the main form of electrochemical energy storage, the commercialization of lithium-ion batteries has greatly contributed to the advancement of human society in the direction of high efficiency and

convenience, and played a significant role in promoting the development of the new energy industry. However, the development of large-scale power storage technology and the rapid popularization of new energy vehicles on the lithium-ion battery in high safety, low cost, high energy density, long life and other aspects of the requirements continue to improve, the current lithium-ion battery energy density has gradually reached its use limit.

Currently, the research on lithium-sulfur batteries is receiving more and more attention in the market. Unlike lithium-ion batteries, lithium-sulfur batteries have shown superior characteristics to lithium-ion batteries in terms of raw material reserves, energy density, production costs, and environmental friendliness, and most of the materials show their application prospects when it comes to energy storage.

Biomass materials come from a wide variety of sources, have different properties, are structurally easy to regulate, and possess an abundance of surface functional groups. It can enhance the electrode's overall structural stability and flexibility when used in lithium-sulfur battery cathode materials; rapid electronic conduction is offered; improvement of the internal active substance's contact area with the liquid electrolyte and the quality of its dispersion; aids in the active substance's ability to endure volume changes; The majority of biomasses already contain heteroatoms, which enhance the general chemisorption properties. Electron transport is made easier by the electrical conductivity of the majority of bio-based carbon material electrode frameworks. As a result, after carbonization, biomaterials have a great deal of potential to serve as electrode frameworks.

At present, in terms of commercialized practical applications in the market, in order for biochar materials to be used as cathode materials for lithium-sulfur batteries, it is also necessary to improve his sulfur loading capacity, which is often an important reference index for cathode materials. The solution to this problem requires the rational design of the physicochemical structure of the biochar material and the design of a reasonable sulfur-carrying scheme, so as to improve the sulfur utilization rate of the cathode material. Biomass materials also have a promising future in other parts of lithium-sulfur batteries, such as diaphragms, electrolytes and collectors.

4. Application of Biochar in the Field of Energy Storage

4.1. Application of Biochar in Supercapacitors

Excellent electrochemical properties are the key for biochar to gain the favor of researchers in the field of energy storage. Among these properties, how the carbon atoms bind to themselves or other substances, and through what form they are arranged, the specific surface area of small pores of the biochar material, the size of the pores, and other internal and external factors all have a certain influence on the electrochemical properties of biochar.

4.1.1 Pore size distribution

For electrochemical energy storage, the structures under different pore sizes in the process assume very different roles, especially for the charge storage capacity. Pore sizes can be broadly classified into three sizes: microporous, macroporous and mesoporous. Due to the large number of small pore sizes and high distribution density under the microporous structure, the unfolded area of all the small pores increases dramatically, and when the pore size matches the size of the electrolyte ions twice the size of the pore size, a positive and negative electric layer can be formed better, so that the storage efficiency of the energy storage material increases, and at the same time, it has a greater impact on the mass specific capacitance.

Large holes, dielectric holes is the main channel for ion transmission, it can increase the ion propagation speed through the large current density, as a way to improve the electrical conductivity of the capacitor, but the pore size is not the larger the better, more than a certain size, it will reduce the energy storage characteristics. Because then the larger the pore size, the stacking density of the material will be decreased, so, from the point of view of a greater degree of charge transfer efficiency

and charge energy storage capacity, mesoporous-microporous hierarchical carbon material structure is the most appropriate.

4.1.2 Electrical conductivity

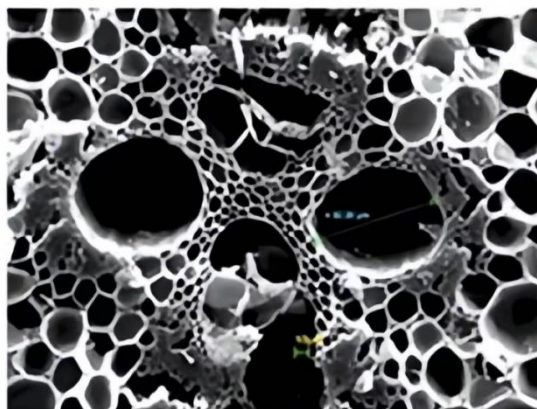
Excellent electrical conductivity is a significant enhancement to electrochemical performance and often makes energy transfer highly efficient. The bonding and arrangement of carbon atoms within the carbon material is the main focus of the research process in terms of the factors affecting electrical conductivity. The processing of biomass also has a significant effect on the electrical conductivity [7]. For common processing processes, such as high temperature carbonization, although it can improve the degree of graphitization of biomass, so that the electrical conductivity is increased, but in the process, the material will be accompanied by carbonization with the collapse of some of the holes, and such a result will affect the electrical conductivity characteristics of biochar.

4.2. Response Measures

From the point of view of biochar energy storage, that is, biomass can be directly carbonized and processed into the electrode material of the double electric layer, or doped with heteroatoms to make it a composite electrode material. It is very critical to regulate the porosity of biochar and carry out the doping of heteroatoms on its electrical conductivity.

4.2.1 Improvement of porosity

In recent years, in order to solve the environmental problems and improve the efficiency of energy storage, various biomass as a new type of energy has been widely studied. Jim et al. [8] used KOH to heat-treat the bamboo biochar to turn it into activated bamboo biochar, which enhances the porosity, and the pore condition is shown in Fig. 1. The ratio of the unfolded area of the small pores of the hollow charcoal to the area of the carbon material exceeds $2,800 \text{ m}^2/\text{g}$, which makes the energy loss of capacitors in charging and discharging significantly reduced and more stable, and the size of the micropores on the surface of the carbon material makes its volumetric specific capacitance more than $470 \text{ F}/\text{cm}^3$; moreover, in the two-electrode system, the capacitance retention is still 91% good even after many cycles when the high current density is certain [9].



Typical Bamboo Biochar SEM image

Fig 1. Schematic representation of macropores, mesopores and micropores of biochar.

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4.2.2 Biochar doped with heteroatoms

Before proceeding with this part of the research elaboration, what the researcher needs to know is that in nature, a large portion of the hetero-elements themselves are naturally present in most biomasses. Wang et al. reported a method of preparing biomass nanosheet electrode materials using maize, whereby the researcher performs a thermal treatment of harvested maize stover in air, and a

hierarchically graded porous carbon with doping of oxygen atoms, i.e., hetero atom Tragically doped. Also because of this porous carbon the supercapacitor exhibits a mass specific capacitance of 407 F/g (1 A/g) in an electrolyte of 1 mol/L H_2SO_4 up to and it has a good capacitance retention of 92.6% when holding a current density of 5 A/g even after cycling more than 10,000 times, which is in line with the market demand [10].

To further improve the electrical conductivity, in situ doping can be accomplished by adding more functional heteroatoms to the biomass surface during the processing of the biochar; This also optimizes the interaction between the electrodes and the electrolyte to enhance energy storage and improve supercapacitor performance.

5. Conclusion

Compared with fossil energy storage materials, biochar materials have many excellent properties, so the advantages of biochar materials when it comes to energy storage are incomparable, and their applications are gradually widespread. Biochar material has a wide range of raw materials, so its preparation cost is low, and it will not cause serious environmental pollution, which is in line with the requirements of sustainable development. In addition, the well-developed pore structure of biochar material provides a large specific surface area, which is convenient for storing charge energy and improving the conductivity of the material, and it is easy to dope other heteroatoms to introduce excellent functional groups, which is easy to process. Currently, biochar electrode materials in supercapacitors are characterized by high charge/discharge energy density, long cycle life, and high reversible capacity. In lithium-sulfur batteries are characterized by easy processing, lower cost, environmental friendliness, and high conductivity. The problem of irreversible capacity of biochar materials when it comes to energy storage and weak charging and discharging ability of high current has been solved accordingly through improving the specific surface area of biochar, compounding of metal oxides, doping of other impurity atoms, and adjustment of pore size of biochar. The article explores the research progress of biochar when it comes to energy storage and contributes to the future development of carbon materials prepared from biomass resources when it comes to green development and energy storage.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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