

Research Progress on the Application of Biomass-Based Porous Carbon Materials in Lithium Battery Electrode

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Abstract. With the growth of the world population, limited non-renewable energy sources, oil and coal mine are becoming increasingly exhausted. The long-term consumption of fossil energy not only causes an energy crisis, but also makes ecological and environmental problems more significant. Therefore, lithium batteries, as an energy storage tool, have been studied by a number of researchers due to their advantages such as high specific energy, little environmental pollution and long cycle life. For secondary batteries, the performance of electrode materials affects the development of batteries. Biomass-derived porous carbon materials have the advantages of cheap, easy-to-obtain from raw materials, large specific surface area, many pore structures, strong electrical conductivity, adjustable pore structure, and have been widely concerned in recent years and used as electrode materials for energy storage lithium batteries application. In the process of charging and discharging lithium batteries, porous carbon materials can provide more space for lithium ions to be embedded and removed from the electrode, improving the capacity and thus the efficiency of the battery. In this paper, the main preparation technology of biomass-derived carbon materials and the improvement technology of heteroatom doping are reviewed. The application effects of different activation methods on the porous carbon materials prepared by plant materials in the negative electrode of lithium battery are compared, and the performance of the materials in practical application is evaluated in the paper, which provides reference materials for the beginners of using biomass structure to prepare porous carbon materials.

Keywords: Biomass porous carbon, lithium battery, activation, heteroatom doping.

1. Introduction

Compared with traditional secondary batteries, lithium-ion batteries (LIBs) have the advantages of light weight, high capacity, long life and environmental friendliness and no memory effect. Lithium-ion batteries consist of: positive and negative electrode, diaphragm, electrolyte, and external packaging [1]. The conversion between electrical and chemical energy and the phase cycling of electrical energy storage and release processes of lithium batteries are realized by the reversible embedding and disembedding of lithium ions through electrode materials. The principle of lithium battery is: When charging, Li ions transfer from the cathode to the anode, first coming out of the positive electrode material, moving through the diaphragm in the electrolyte and then concentrating at the anode, where they are embedded in the negative electrode material. When discharging, Li ions move from the anode to the cathode. When the Li ions come out of the graphite layer, they diffuse to the cathode, and are embedded in the cathode materials [2]. The ideal anode material usually requires a low redox potential to ensure a high output voltage, a large number of lithium ions that can be embedded and removed quickly, a low volume change in the material, and a low cost and environmental friendliness [3, 4].

Biochar is a solid product with high carbon content obtained by pyrolysis of biomass materials under fully or partially anoxic conditions, which has high carbon content and aromatic structure, large total area per unit mass of material, i.e., large specific surface area (SSA), and high porosity with macropores, mesopores and micropores. The size of SSA and the distribution of pore size structure

directly affect the electrochemical performance of carbon electrode materials. Proper pore size distribution can help reduce the resistance of ions during diffusion in pores, while having a large specific surface area, thus increasing the charge and discharge rate [5].

The pyrolysis process of biomass conversion into biomass carbon mainly goes through the water loss stage, cellulose and hemicellulose pyrolysis stage, lignin pyrolysis stage, and carbonization stage [6]. Physical activation and chemical activation are the commonly applied approaches for activation of biomass carbon materials. For physical activation, CO₂, water vapor, air and other oxidizing gases can serve as physical activators to activate carbonized biomass-derived carbon materials (BDC). Initially closed pores of BDC can be opened by physical activation, and the expanded pores can be even larger, thus resulting in a more developed pore structure. This method is not complicated, no need for multiple cleanings, and causes little environmental pollution. However, these drawbacks still limit the widespread because of high activation temperature and long activation time required during this process and the small SSA of the activated products. In chemical activation, the biochar is first mixed with chemical activators (for example: H₃PO₄, KOH, K₂CO₃ and ZnCl₂) in proportion and soaked, then carbonized and activated at high temperature at the same time. Different chemical activators are required to prepare activated carbon with different effects. The activated carbons prepared by different chemical activators have different effects. Such activated carbon is rich in micro- and mesopores. The disadvantages of chemical activation are also more obvious: the chemical residues need to be cleaned several times, the equipment will be corroded to some extent, and some environmental pollution will be caused. For physical-chemical activation coupling is to first impregnate the raw material with a chemical activator to increase the activity, and through the channels formed by the chemical activation, the active gas is transported to the interior, and then the gas is physically activated by passing it through at high temperature. physical-chemical activation coupling can control the pore structure of the obtained activated carbon to a certain extent, but the process is complicated and costly [7].

Biomass carbon materials are characterized by its excellent electrical properties, outstanding physical and chemical stability as well as large specification surface area than metal oxides, metal nitrides, and conductive polymers, and also have properties such as low cost and easy access to environment friendly [8].

2. Activation

Carbon electrode materials are influenced by two important factors, pore size distribution and SSA, regarding their electrochemical performance. It is necessary to have a suitable pore size distribution while having a large SSA. A proper pore size distribution is conducive to reducing the diffusion resistance of ions in the pore structure, thereby improving charge and discharge rate.

In the process of preparing biomass organic porous carbon materials, activation refers to the reaction between biomass raw materials or precursors and activators. With the progress of the reaction, new pores are continuously generated on the materials' surfaces, and the original pores will be further expanded, resulting in a more complex pore structure of the material [9].

Activation is one of the most significant processes in preparing biomass carbon materials. As a result of this process, biomass carbon materials develop pore structure, and their specific surface area increases, allowing them to store more charge and improving their electrochemical performance [10].

The activation method is mainly divided into physical activation method and chemical activation method. At present, researchers use different preparation methods, different activators and dosages, and various carbonization temperatures to prepare biomass raw materials into carbon materials. Carbon materials with different morphologies have great differences in pore structure, SSA and electrochemical performance.

2.1. Physical activation

The physical activation method refers to the method of obtaining porous carbon materials by introducing gases such as H₂O, CO₂, and O₂ during the high-temperature heating process of biomass raw materials [Sevilla et. al, 2014] [11]. The physical activation method includes two steps of carbonization and activation. First, the carbon-rich raw material is heated under the protection of an inert gas, and then the pore structure is lifted by water vapor, CO₂, air, flue gas and other gases at about 900 ° C. The activation process is in an oxidizing gaseous medium. The activation is divided into three stages [Yajun Wu,2018] [12]. At the first stage, the activated gas removes the adsorbate that blocks the carbon pores of the precursor; at the second stage, the pores that have been opened are further activated to increase the pore size; at the third stage, the reactive properties of the carbon precursor Higher partial selective oxidation forms new pore structures. The physical activation process of CO₂ and water vapor is mainly the reduction of CO₂ to CO, and the formation of CO and H₂ at high temperature of water vapor. During the carbonization of biomass raw materials, the researchers use water vapor and CO₂ to control the pore structure and increase its specific surface area [13].

2.2. Chemical activation

Chemical activation method is more effective than physical activation. In this method, raw biomass materials are reacted with chemical activators at high temperatures in order to produce porous carbons. In the chemical activation process, the main activators are KOH, ZnCl₂ and H₃PO₄, which have dehydration and erosion effects on biomass materials [Liangjia, 2014] [14]. The activation process is carried out at a specific temperature and produces impurities. In general, by comparing with the physical activation, the pore size distribution and SSA can be better controlled and obtained by chemical activation. As the number of functional groups on the surface of the material increases, the wettability of the electrolyte will be improved and the diffusion resistance between electrode and electrolyte will also be reduced. The additional pseudo capacitance that occurs due to rapid Faraday reactions between surface functional groups and electrolytes allows carbon materials to perform more electrochemically.

3. Heteroatom doping

The following are the principal consequences of heteroatom doping on porous carbon materials. The hydrophilicity and wettability of porous carbon materials are enhanced by the addition of heteroatoms. What is more, it affects the surface electronic structure of porous carbon materials, then improving materials electrical conductivity and electrochemical properties. Heteroatoms can also interact with metal active components to improve the dispersion and catalytic performance of metal active components. Heteroatom doping is can effectively improve the physical and chemical properties of carbon materials. Heteroatom doped carbon materials are used as Lithium battery electrode, which can improve the performance of batteries to a certain extent. The electronegativity of heteroatoms and carbon atoms is different. The incorporation of heteroatoms breaks the electrical neutrality of carbon materials, then produces many charged sites, which will provide many active sites for the storage of Li ions. As a result, the capacity of carbon materials is increased, which provides possibilities for their application in electrochemistry. In addition, the incorporation of heteroatoms will cause many defects in carbon materials, which will promote the disorder of carbon materials. The most common heteroatoms in heteroatom-doped carbon materials include N, P, S, B, etc. Among them, nitrogen doping is currently the most effective and popular heteroatom doping. The nitrogen species in nitrogen-doped carbon materials are mainly divided into four types, namely graphite nitrogen, pyridine nitrogen, pyrrole nitrogen and pyridine nitrogen oxide.

Parts of the biomass is rich in heteroatoms (N, S, O, etc.), which can realize the in-situ doping of heteroatoms. By using biomass resources, it can also improve the electrochemical performance of Li-ion batteries and protect environment. Biomass as a carbon source of carbon materials, which can

be used as the anode in Lithium battery electrode and it is one of the current research hotspots. Some biomass can also be doped by adding other heteroatoms. Ou et al. successfully synthesized N-doped porous carbon derived from ox horns (OHC), which BET surface area is $1300 \text{ m}^2\text{g}^{-1}$ [15]. In this experiment, the dried ox horn was dipped in KOH solution. Then carbonized and activated at the same time to obtain rich nitrogen content and porous carbon structure. The OHC was used as the anode in lithium battery electrode and exhibited superior electrochemical performances with a high reversible capacity of 1181 mAhg^{-1} at a current density of 100 mAg^{-1} and a superior rate capability of 304 mAhg^{-1} at 5 Ag^{-1} .

Compared with doping a single heteroatom in a carbon material, doping multiple heteroatoms will produce greater charge density to a certain extent, thereby improving the performance of the battery.

Multiple heteroatoms can also increase defects and speed up electron conduction, which will produce many charged sites. Using biomass containing a variety of elements as the anode in lithium-ion battery, it is easy to incorporate multiple heteroatoms in the carbon network. Yu et al. (2016) successfully prepared hierarchical porous carbons from biomass algae *Enteromorpha* (abbreviated as EDCs), which BET surface area is $2037 \text{ m}^2\text{g}^{-1}$ [16]. In this experiment, the *Enteromorpha* was dipped in KOH solution. Then EDCs were obtained. The EDCs were carbonized and activated at the same time to produce graded porous carbon materials with N and O. It was used as the anode of LIBs. It showed a specific capacity of $1347\text{--}1709 \text{ mAhg}^{-1}$ and an initial coulombic efficiency of 61–64%. Xiong et al. (2018) successfully synthesized biomass carbon materials containing N and S, which derived from discarded cotton balls [17]. The method was to dip cotton in $\text{Mg}(\text{NO}_3)_2$ solution, and then carbonized and activated at the same time to obtain cotton carbon (abbreviated as CC). In order to obtain N and S co-doped biomass materials (abbreviated as NSCC), CC was dipped in thiourea solution. The NSCC was used as the anode in lithium battery electrode, which exhibited high reversible capacity of 1101.1 mAhg^{-1} after 150 cycles at a current density of 0.2 Ag^{-1} . What is more, it maintained a specific capacity of 531.2 mAhg^{-1} after 5000 cycles at a current density of 10 Ag^{-1} and had a specific capacity of 689 mAhg^{-1} at a current density of 5 Ag^{-1} .

Egg yolk, wheat straw, peanut shell and other biomass can all be widely used in Lithium battery electrode. In summary, the selection and preparation method of biomass raw materials are of great significance for the development of anode materials with high-performance [18–20].

4. Discussions

The pore structure and SSA of biochar materials are important factors affecting their electrochemical performance. The larger SSA can offer active sites for the electrochemical reaction inside the battery, increase the contact area with the electrolyte to provide more Li ion transport pathways and increase the transport speed Li ions [21]. The pore structure mainly affects the capacitance performance of biomass materials. Biochar has a distribution of pores of various sizes, including macropores, mesopores and micropores, the three size can be distinguished by the pore diameter, which are 50 nm, $2 \sim 50 \text{ nm}$ less than 2 nm respectively [22].

Pores of different sizes play different roles in the electron transport in the battery. Due to their small size, micropores can show certain selectivity for adsorbing electrolyte ions, and a large number of micropores can provide abundant accumulation space for electrons. Since the mesoporous is larger than the electrolyte ions, the diffusion distance of ions is shortened and the diffusion resistance is reduced. To a certain extent, the diffusion rate of electrolyte ions in the pore structure can be improved, so that ions can easily penetrate the internal micropores. Macropores can act as a storage layer for buffering ions and facilitate ion transmission. Therefore, porous carbon materials must have a suitable pore size distribution while having a large specific surface area. Through physical activation and chemical activation, it can help to adjust the pore structure of porous carbon materials, increase the SSA and affect the performance efficiency of lithium batteries.

In order to compare the optimization degree of two activation methods on the structure and properties of biomass based carbon materials, Table 1 shows the SSA of plant-based porous carbon

materials after activation, and the charge and discharge capacity of the battery when used as a lithium battery electrode. Since the organic electrolyte system exists inside the lithium-ion battery, its internal resistance is relatively large. When a large current is discharged, the two poles and the diaphragm of the battery will be damaged, and at the same time, the impedance of the electrolyte will be increased, resulting in an increase in the internal resistance of the battery and shortening the battery life. Therefore, the discharge current density of Li-ion batteries cannot be too large, usually less than 0.5 C [23]. Therefore, the current density of the following data is concentrated between 0 and 0.5C. ($1C=372mA\cdot g^{-1}$)

Table 1. Properties of electrodes under different activation methods

Material	Activation method	BET surface area (m^2g^{-1})	Current density	First charge capacity ($mA\cdot hg^{-1}$)	First discharge capacity ($mA\cdot hg^{-1}$)	Reversible Capacity (100 circles) ($mA\cdot hg^{-1}$)	Reversible capacity (500circles) ($mA\cdot hg^{-1}$)
corn stalk [23]	Chemical activation	1266.83	0.2C	—	1614.1	504	—
ginkgo leaf	Chemical activation	1940	$0.1Ag^{-1}$ $\approx 0.269C$	776	1516	—	—
			$2Ag^{-1}$ $\approx 5.376C$				299
jute fibre	Chemical activation	1028.62	0.2C	—	2732.3	742.8	—
coffee grounds	Physical activation	503	$0.1Ag^{-1}$ $\approx 0.269C$	—	—	200	—
hemp stem	Physical activation	605	$0.3Ag^{-1}$ $\approx 0.806C$	217	630	190	—
Pine cone shell	Physical activation	380	$0.01Ag^{-1}$ $\approx 0.0269C$	321	660	—	—

As shown in Table 1, the raw materials chosen are plants, which is the quantification of the contract. Although different species of plants may cause data errors due to different fiber distribution, the errors are relatively small compared with cross-species comparison. The three plant raw materials preparing porous biochar anode materials by chemical activation were corn stalks, ginkgo leaves and jute respectively. The three plant raw materials for the preparation of porous biochar electrode materials by physical activation are coffee grounds, hemp stalks and pine nut shells respectively.

The specific surface areas of six different biomass raw materials after activation were ranked, and the top three biochar porous carbon materials were all prepared by chemical activation. Among them, Jiang Zepeng [24] used ginkgo leaf as a raw material to prepare a porous carbon material with an SSA of $1940m^2g^{-1}$ at $600^{\circ}C$ by using as an activator. Compared with chemical activation, the SSAs of the three plant-based porous carbon materials prepared by physical activation are much lower. Therefore, to a certain extent, chemical activation is significantly better than physical activation in optimizing the preparation of porous carbon materials from plant-based raw materials.

Using the aforementioned ginkgo leaf as the raw material, KOH as the activator, the porous carbon material electrode prepared by planting and the pine cone shell as the raw material, CO_2 as the activator prepared porous carbon material electrode for comparison. When the current density of the former is 100 times higher than that of the latter, the charging and discharging capacitance of the former is still far higher than that of the latter, which are $776mA\cdot hg^{-1}$, $1516mA\cdot hg^{-1}$ and $321mA\cdot hg^{-1}$, $660mA\cdot hg^{-1}$, respectively. The porous carbon material prepared with jute as raw material and $ZnCl_2$ as activator also prepared by Liu Xin is compared with the porous carbon material (physical activation) mentioned above with pine nut shell as raw material [25]. The current density of the former is 7.43 times than that of the latter, the discharge capacitance is still much higher than the latter. This proves

that the biomass-based porous carbon materials vegetated with chemical activators are also superior to physical activation in the optimization of charge-discharge capacity.

The reversible capacity of the battery reflects the recoverability of the battery, and a larger reversible capacity indicates higher battery efficiency and battery life. The reversible capacity of the battery decreases with the increase of cycle number and current density. Comparing the aforementioned ginkgo leaf-based porous carbon material (chemical activation) with the hemp stem-based porous carbon material (physical activation), the results show that the current density of the former is 6.67 times that of the latter, and the cycle period of the latter is 5 times that of the latter, its reversible capacity is still much higher than the latter [26].

Comparing ginkgo leaf-based porous carbon material (chemical activation) with the coffee grounds-based porous carbon material (physical activation) [27], the current density of the former is 20 times that of the latter, and the number of cycles is 5 times that of the latter, and its reversible capacity is still much higher than that of the latter. This proves that the carbon materials prepared by the chemical activation method are superior to the physical activation in optimizing the reversible capacity.

It follows that chemical activation is superior to physical activation in optimization of specific surface area, charge-discharge band content, and reversible capacity. It is worth mentioning that although the performance of porous carbon materials has been improved after activation, the specific capacity is still low when it used as electrode materials for electrochemical energy storage devices. The performance of the material when used as an electrode can help improve the active sites for lithium ion storage through heteroatom doping, further improve its specific capacitance, and maximize the working efficiency of lithium batteries (Table 2).

Compared with discard cotton balls before and after doping, the specific surface area, first charge and discharge capacity, cycle performance and rate performance were improved. To a certain extent, it shows that heteroatom doping can improve the performance of lithium-ion batteries. Comparing single-atom-doped ox horns and multi-atom-doped cotton balls and biomass algae, it is proved that polyatomic doping can further promote the active site of electrochemical reaction.

Table 2. Properties of electrodes under chemical activation methods

material	activation methods	Heteroatom doping	BET surface area m^2g^{-1}	first charge capacity	first discharge capacity	0.1A g^{-1} reversible capacity (100 circle)	0.2A g^{-1} reversible capacity (150 circle)	2A g^{-1} reversible capacity (150 circle)	10 Ag ⁻¹ reversible capacity (500circle)	5Ag ⁻¹ specific capacity
CC	Chemical activation	—	1235.35	—	3275.1	—	637.1	—	283	370
NSCC	Chemical activation	N S	1326.20	—	4179.1	—	1101.1	—	532.1	689
OHC	Chemical activation	N	1300	1290	2166	1178	—	—	—	304
EDC	Chemical activation	N O	2073	1709	—	—	—	299	—	—

5. Conclusions

This research has introduced the effects of physical and chemical activation and heteroatom doping on the electrochemical properties of biomass carbon materials, and then compares the change in SSA and electrical properties of biomass carbon materials before and after physical and chemical

activation, which include current density, charging specific capacitance, discharging specific capacitance, and reversible capacity. The results show that the performance of biomass carbon materials by physical activation is still not satisfactory in terms of capacitance of current. Biomass carbon materials activated by chemical activation have higher charge/discharge specific capacitance and reversible capacity also larger specific surface area. Although physical and chemical activation optimize the performance of carbon materials as electrodes, the overall electrical capacity is still low and can be further optimized by heteroatom doping. Among them, nitrogen-doped carbon materials are very promising electrode materials for lithium batteries. For no atomic doping and single atomic doping two or more different heteroatom doping can further promote the electrochemical reaction active sites and thus improve the electrochemical performance of the material. Different activation methods and the doping of heteroatoms can have an impact on the surface properties and pore structure of the prepared carbon materials, and it is also necessary to select the most suitable biomass materials for different scenarios and explore a more reasonable and efficient combination of activation methods to improve their electrochemical performance.

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