Preparation of biochar microspheres from leaves of several plants by hydrothermal method

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Abstract: In the paper, by means of orthogonal experiment, hydrothermal carbonization method, with the principle of preparation of carbon microspheres from glucose by hydrothermal method as reference and charring three different plants (ginkgo leaf, maple leaf and pine needle), we seek the possibility to carbonize plants into porous carbon with specific morphology and then to use the biochar for negative electrode of lithium ion battery. In process of the research, it was found that biochar microspheres (0.5um-5um) existed in several plant carbon obtained by hydrothermal carbonization, and some special elements (Mg, K, Ca, etc) were doped. Therefore, different materials were studied separately, the reaction temperature and reaction time were changed, and ultrasonic oscillation processing was used to find the best conditions for the preparation of biochar microspheres with specific doped elements, uniform particle size distribution and high yield.

1. Introduction
Biochar microspheres are one kind of carbon microspheres that have good thermal stability, chemical stability, high specific surface area and bulk density[1,2]. It is widely used in the preparation of electrode materials for batteries. The traditional graphite-carbon theory has a low specific capacity, while the new anode materials with high theoretical capacity, such as tin base[3,4], silicon base[5] and metal oxide[6-8] are prone to generate volume expansion during the cycle leading to the instability of battery. Therefore, the specific capacity of carbon matrix can be significantly improved by doping modification on the premise of ensuring the stability of the cycle.

The preparation methods of carbon microspheres include hydrothermal carbonization[9], emulsion method[10], template method[11], etc. Hydrothermal carbonization is a common method to prepare carbon microspheres with low cost, high quality and simple process conditions. Monosaccharides, disaccharides and polysaccharides are common carbon sources for the preparation of carbon microspheres by hydrothermal carbonization[12-14].

Deciduous leaves are a kind of biomass with great utilization value, especially in areas with low temperature, where there is a large amount of biomass waste every year[15], and in low-temperature environment, microorganisms are often difficult to be decomposed quickly, resulting in the accumulation of deciduous leaves, which to a certain extent leads to the waste of natural resources. If not handled properly, deciduous leaves will also cause pollution to the surrounding environment.

In this paper, three plants are selected for study: ginkgo leaf, maple leaf and pine needle. Hydrothermal carbonization method is used to explore the preparation conditions of high yield biochar microspheres with uniform particle size by controlling variable experimental conditions.
2. Experiment section

2.1 Plant treatment and hydrothermal carbonization method
The raw materials used in the experiment were ginkgo leaf, maple leaf and pine needle. Biochar microspheres specific preparation process is as follows: first, washed raw material with deionized water and put them in a drying oven at 50°C for 12 hours. Then weighed three kinds of dried plants of 10g each and placed them in three hydrothermal reactors of 100ml in volume, and took 20ml of water each and put it in the reactor, seals and then placed in the oven[16]. Controlled reaction temperature at 180°C-300°C for 6-24h, then cooled naturally. The products were cooled to room temperature, then cleaned with deionized water and ethanol, respectively, and finally dried in a 90°C oven for 5h.

We took reaction time and temperature as experimental factors and the each factor set up three gradient levels, respectively, to test by controlling variable method. The size uniformity and yield of the prepared biochar microspheres were used as evaluation indexes to explore preparation conditions of biochar microspheres, studied the effects of reaction time and temperature on hydrothermal carbonization of different plants. The gradient levels set by each factor are given in table1.

2.2 SEM and EDS characterization
Scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS) of Phenom proX working at 10-15 kV was used to observe the microstructure, particle size distribution and composition of biochar microspheres under various reaction conditions.

Table 1. Selected orthogonal experiment factors

| Horizontal gradient | Plant      | Reaction time/h | Reaction T/℃ |
|---------------------|------------|-----------------|--------------|
| 1                   | Ginkgo leaf| 6               | 180          |
| 2                   | Maple leaf | 12              | 240          |
| 3                   | Pine needle| 24              | 300          |

3. Results and discussion

3.1 Biochar morphology of hydrothermal carbonization without ultrasonic treatment
First of all, under the condition of 180°C, we studied the influence of different reaction time on preparation of different plants microscopic morphology characteristics and the degree of average particle size. During the experiment, the non-linear relationship between the generation of biochar microspheres and the reaction time was observed. The number of biochar microspheres showed an increasing trend at the reaction time of 6-12h, but there was no significant change in the number of biochar microspheres prepared after the reaction time of 12h. Then, ginkgo leaves, maple leaves and pine needles were used as reactants, and the fixed reaction time was 12h. By changing the factors of reaction temperature, we found out the optimal reaction conditions (table 2) for the plants to obtain high yield and high-quality biochar microspheres with the help of SEM analysis.

Table 2. Orthogonal experiment scheme for the fixed reaction time of 12h

| Sample number | Floristics    | Reaction temperature/℃ |
|---------------|---------------|-------------------------|
| 1#            | Ginkgo leaves | 180                     |
| 2#            | Ginkgo leaves | 240                     |
| 3#            | Ginkgo leaves | 300                     |
| 4#            | Maple leaves  | 180                     |
| 5#            | Maple leaves  | 240                     |
| 6#            | Maple leaves  | 300                     |
| 7#            | Pine needles  | 180                     |
| 8#            | Pine needles  | 240                     |
| 9#            | Pine needles  | 300                     |
When ginkgo leaves are subjected to water heat treatment at 180°C for 12 hours, the ginkgo leaf ball (figure 1a, biochar microspheres formed by carbonization of Ginkgo biloba, similarly hereinafter) is most abundant, the reunion phenomenon appears, and most of the biochar microspheres distribute in the suspension. As the raw material, the product quantity after the reaction of pine needles is lower than that of ginkgo leaves, but its biochar (figure 1b) has a graded porous structure, which is conducive to the production of batteries[17]. By comparing the SEM images of the surface of the carbonized pine needles with the optical micrograph (figure 1d) before carbonization, it was found that the biochar microspheres may be generated from the saw-tooth gap on the surface of the pine needles. Figure 1c is biochar from the maple leaves of hydrothermal treatment at 300°C for 12 hours, there are more maple leaf balls (carbonized maple leaves form ball-shaped biochar microspheres, similarly hereinafter), but there is serious phenomenon of reunion and poor dispersibility. In spite of this, the graded porous structure formed by maple leaves after heating still has certain research potential and value.

3.2 Biochar microspheres prepared by hydrothermal carbonization and ultrasonic shock treatment.
Without ultrasonic oscillation treatment, the biochar microspheres have agglomeration phenomenon and poor dispersion. Therefore, biochar product in figure 1a with serious agglomeration were treated via ultrasonic oscillation, reduced the impacts of the reunion phenomenon during hydrothermal carbonization. The results are shown in figure 2. The agglomeration problem of biochar microspheres is solved to a certain extent and the dispersion is improved.
3.3 The composition of biochar microspheres with different materials.

Figures 3 are EDS energy spectrum of biochar microspheres from maple leaves. In case of biochar microspheres prepared from ginkgo leaves and pine needles are mainly composed of carbon, oxygen and nitrogen (not shown here). However, the biochar microspheres from maple leaves look very complex in composition, besides carbon and oxygen, they also contain silicon, magnesium, potassium and calcium (figure 3) measured under different scanning spots, which suggests that maple leaf with rich chlorophyll and anthocyanin pigments contains many inorganic mineral elements.

4. Conclusions

In general, after a series experiments and analyses, we obtain the following 3 interesting conclusions. First, reaction temperature is the main factor affecting the yield of biochar microspheres and the quality of biochar microspheres. Second, the dispersion of biochar microspheres can be greatly affected by ultrasonic oscillation treatment. The last, the composition of maple leaf biochar ball contain many inorganic elements that may improve its properties as a functional material. Of course, the difference is also very large in using different plants as precursors to obtain biochar microspheres. In this study, maple leaves are the best precursors among the three selected plants.
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