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Electrochemical Performance of Bamboo Porous C@SiO$_2$ Anode Composites

Jiahao Wang[1], *Haojie Li*[2], *Leiting Han*[2], *Wei Zhang*[2], *Jiajie Cai*[2],
Mingqiang Zhong[1] *and Zhengping Zhao*[2,*]

[1]College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, P.R. China
[2]Zhijiang College, Zhejiang University of Technology, Hangzhou 310014, P.R. China
[*]E-mail: sjzhaolei@163.com

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With the continuous development and utilization of energy, people have to look for new energy because of the scarcity and non-renewable nature of traditional energy. Seeking for new energy has become an important task at present. Bamboo carbon, as a kind of renewable resources with cheap, high specific surface area and adsorption performance, began to be concerned by the majority of researchers. Lithium battery as a new energy source has been the main research direction of many researchers. silicon dioxide is a mineral with a low discharge potential and a high theoretical specific capacity (1965 mAh/g). And its low price, environmental protection, as an anode material has great significance. Bamboo carbon was reamed with hydrochloric acid to increase its specific surface area. Then bamboo carbon and silicon dioxide to prepare carbon-silicon composites by hydrothermal method, making batteries to explore its lithium storage performance. After the hydrothermal reaction between the bamboo carbon reamed with hydrochloric acid and nano silicon dioxide, the silicon dioxide is loaded onto the bamboo carbon and calcined in a tubular furnace at high temperature to form the carbon@silicon composites. Using the composites as the anode of lithium battery can increase the stability of the battery. It can also improve its cycle performance, which is great significance to the improvement of the negative electrode. By exploring the influence of the two materials as battery anode on the charge-discharge capacity, electrical conductivity and coulomb efficiency of lithium battery, it is could help us more clearly understand the influence of lithium battery anode on lithium battery. Lithium battery has better energy conversion ability, and the development of lithium battery is of great significance to the development of human society.

Keywords: Bamboo carbon, Silicon dioxide, Anode, Electrochemical Properties

1. INTRODUCTION

Before the 20th century, fossil fuels such as coal, oil and gas have always been the main source of energy for human activities. With the consumption of coal, oil and other natural mineral raw material, lead to the rising prices of energy. People began to look at a relatively low price of biomass carbon materials, including bamboo carbon is a kind of very important biomass carbon raw materials. China is rich in bamboo carbon resources, and especially in Zhejiang province. Bamboo resources were widely distributed and be a large number. Bamboo carbon is not only friendly to the environment, and it has strong adsorption ability and contain a variety of impurity element, has good conductive ability. Bamboo biomass carbon materials have high specific surface area and large pore size structure [1]. Carbon is by far the most correct and the efficient improvement negative grade silicon compound matrix, in many of the alternative negative materials, silicon carbon composites, whether from production, properties, costs and many other aspects have significant advantages.

The development history of lithium-ion batteries can be roughly divided into the following stages. In 1887, the British made the original battery. Compared with liquid battery, the battery electrolyte for paste, is not easy to leak, beneficial to carry, and therefore has been widely used. In 1890, rechargeable iron nickel battery was installed by Thomas a. Edison. Iron nickel 1910 rechargeable batteries commercial production. 1976 Whittingham developed layered TiS_2 cathode and lithium metal anode for lithium-ion batteries, reached the lithium battery charge and discharge for the first time [2,3]. In the early 1980s, the university of Illinois institute of technology has discovered that the lithium-ion can be embedded in the performance of the graphite. By 1983, manganese pointed crystal Goodenough will confirm to save the cost of the cathode material [4-6]. In the early 1990s, lithium-ion battery production became large-scale and tends to industrialization. In 1990, SONY of Japan first produced smoothly $LixC_6$, calcined petroleum coke as cathode, cobalt acid lithium anode of lithium-ion batteries, and mentioned for the first time the new concept of lithium battery, achieve the commercialization of the ‘rocking-chair batteries’ use [7]. From the commercialization of lithium-ion batteries in the past to the present, with the advantages of high energy density, cycle durability, high charge and discharge voltage, no memory and durable storage, it has set off a storm in the entire battery market. Later, the lithium battery is widely used all kinds of electronic devices quickly, even medical instrument, aerospace, military field areas such as new energy vehicles.

At present, most of the lithium-ion batteries in the market use carbon materials such as graphite and metal oxide as the cathode materials of the batteries. Graphite has excellent cycling stability, and the lithium-ion batteries formed by it also have high specific capacity and specific power, but their disadvantages are also obvious [8]. First of all, the capacity limit of the battery is not ideal enough, and the capacity limit cannot meet the requirements of high specific capacity or be applied to devices that need to work for a long time. Secondly, the deposition potential of lithium metal is close to the embedded lithium potential of lithium-ion battery, and lithium metal is likely to produce dendrites on the surface of electrode material, which will precipitate out, causing a short circuit inside the battery and causing potential safety hazards. Third, due to the limitation of graphite or metal oxide performance, the battery with this negative material has poor response to the rapid charging and discharging process. It is difficult to realize the fast charging and high-rate discharge. At present, the performance of lithium-ion batteries is far from meeting the requirements of electric vehicles for large capacity and high-power batteries. Electrode material is one of the key and core technologies of lithium-ion battery technology and an effective means to improve the performance of lithium-ion battery. The advantages and disadvantages of electrode materials will directly affect the specific power, specific capacity, cycle times and other electrochemical properties of lithium-ion batteries [9]. Therefore, the research and development of high-performance lithium-ion battery electrode materials has become a top priority.

Bamboo is the main product of bamboo pyrolytic carbon, ordinary bamboo carbon materials the specific surface area of 360 m^2/g, so the bamboo carbon is a porous material with good adsorption performance. Bamboo carbon composition is simple, it is mainly composed of carbon, what weight 75% until 95% of bamboo carbon. Molecular structure is hexagonal, bamboo charcoal with porous structure, is similar to the structure of carbon nanotubes and its molecular density porous, hard. The bamboo carbon as an adsorbent, the surface structure characteristics are specific surface area, pore size distribution, etc. Bamboo carbon adsorption performance mainly depends on its internal porosity ratio and the structure, surface chemical properties. Can be modified to strengthen through the bamboo carbon adsorption performance of bamboo carbon material, for the modification of bamboo carbon, the main physical modification, chemical modification and heat treatment method [10]. Bamboo charcoal has strong adsorption and can be roughly divided into two categories: physical adsorption and chemical adsorption. Physical adsorption of bamboo carbon is mainly caused by van der Waals force, in the whole process of bamboo carbon composition does not produce any change. Compared with the physical adsorption and chemical adsorption are mainly due to some chemical reactions take place in the adsorbate and adsorbent, some of the group branches order, forms a new component. Chemical adsorption because of its monolayer adsorption, adsorption capacity is big. Adsorption of molecules can't move. Physical adsorption will cause multi-layer adsorption, but the adsorption force is small. So chemisorption is more powerful than physical adsorption [11].

Nano silicon dioxide theoretical specific capacity up to 1965 $mAhg^{-1}$, and the discharge voltage is low, have a great development value. Silicon dioxide is one of the most abundant minerals on earth, cheap, sources. If as the cathode material, successfully used to industrial production, the future. Since the initial SiO_2 lithium process can form nano-Si and inert Li_4SiO_4 or Li_2O materials, it is very helpful to maintain the integrity of the electrode. Practice, SiO_2 nano structure as lithium battery cathode material, facing poor conductivity and its inherent in the sectors of repeated charging and discharging size change is big, the effect of causing the low utilization rate of active material, low structural stability and low range features. Is not necessarily all of SiO_2 nanocomposites full of high specific capacity [12,13].

Today, such as coal, oil, natural gas consumption of non-renewable resources was high flow rate, energy is gradually shortages. The burning of fossil fuels also caused environmental problems, the deterioration of ecological environment and energy shortages have become more vulnerable to the earth. In order to make the survival of mankind, had to seek green and renewable, clean new energy to replace traditional fossil fuel [14-16]. In order to achieve high efficiency energy storage density and high efficiency of energy conversion efficiency, focus on the development of human beings gradually to design high performance electrochemical energy storage battery [17,18]. Electrochemical energy storage technology, much attention has been paid to the development of high performance in order to achieve high energy storage density and high energy conversion efficiency [19-21].

Bamboo carbon has better adsorption ability and stability, and silicon dioxide has high specific capacity, based on the design of the lithium battery has the green environmental protection, the advantages of lower cost, is of great significance to the development of lithium battery.

In this article, through the bamboo carbon after the hydrothermal reaction between hinge with hydrochloric acid and nano silica, silica is loaded into the bamboo carbon and the high temperature tube furnace carbon calcination in silicon composite materials. Using composite material for lithium battery anode can increase the stability of the battery. Through exploring influence on the performance of the two materials as anode electrochemical.

2. EXPERIMENTAL SECTION

2.1 Materials

Ethanol, hydrochloric acid, tetraethyl orthosilicate (TEOS), 3-Aminopropyl-Triethoxysilane (APES), $KHCO_3$, $NH_3 \cdot H_2O$, N-methyl-2-pyrrolidone (NMP), polyvinylidene fluoride (PVDF), acetylene black, lithium-ion battery, lithium, copper foil. All materials are from Sinopharm Chemical Reagent Co., Ltd..

2.2 Bamboo carbon materials

A certain amount of bamboo charcoal powder was weighed and added into a beaker containing a certain amount of concentrated hydrochloric acid for ultrasonic vibration. After the ultrasound, the solution was placed for 1h and then poured into the centrifugal tube for centrifugation. Wash with deionized water 2-3 times. The black solid obtained by centrifugation is placed in a vacuum drying oven, and the product is ground and sealed for use after drying.

2.3 Preparation of the bamboo porous C@Si composites

Take two beakers, A and B, and fill a beaker with anhydrous ethanol, ammonia water and deionized water. B. Add TEOS, anhydrous ethanol and bamboo carbon in beaker and stir for 10min at constant temperature.

Table 1. The component list of bamboo C@Si composite

CODE	Bamboo porous C (wt.%)	SiO_2 (wt.%)
sample-0	100	0
sample-5	95	5
sample-15	85	15
sample-30	70	30
sample-45	65	45

Pour the solution in two beakers into a hydrothermal reaction kettle, drop silane coupling agent (triethoxylsilane), and react for 6h in an oven at 180 °C. The reaction products were centrifuged and the solid was dried for 12 h in a vacuum drying oven at 60 ℃. The powder was put into the porcelain boat and sintered to 600 ℃ in a tubular furnace. After cooling, the powder was ground into black powder and sealed after grinding in a grinding bowl.

The silicon content of bamboo carbon composites is shown in the table 1 below.

2.4 Preparation of lithium-ion batteries

With electronic balance is carbonized bamboo carbon composites 0.16 g, 0.02 g, acetylene black PVDF 0.02 g (8:1:1). Fully grind in the agate research Hugh (after dry grinding), adding suitable amount of N-methylpyrrolidone (NMP), and then fully and then fully and uniformly grind (wet method). Take a clean piece of copper foil, fixed on the glass, use coating machine to grinding samples evenly coated on the copper foil (uniform) when coating. And then into the vacuum drying oven 60 ℃ dry 12 h. Will dry good copper foil with a clean A4 paper clips, with 8 mpa in tablet press medium pressure 1 min, then remove with slicing machine cut into small round 16 mm in diameter, with intact and tweezers to pick out the incision of coated uniformly small wafer with good electronic balance in the glove box. Set aside. In the glove box assembly battery: carefully put the anode material in the anode shell is center. Clip battery diaphragm, diaphragm again add electrolyte (2-3 drops) (diaphragm must be placed on center, the batteries are diaphragm material center of the circle and the anode material circle overlap). In drop has been added electrolyte battery diaphragm, put on lithium, mount gasket and shrapnel, cover the battery cover, curling of using hydraulic pressure molding. Battery in the fume hood after 24 hours, can begin to measure the charge and discharge performance.

2.5 Characterization

Transmission electron microscopy (TEM) is using transmission electron imaging technology, the material properties of electron microscope method. Absorption and scattering contrast material can be used to study the internal microscopic structure (including density, crystallinity, etc.) and material composition. Can get material internal microstructure, the bamboo carbon/oxygen silicon dioxide have successfully loaded, and how to load. In the test, X-ray diffraction happens through the sample, the intensity of the beam is different in every direction. According to the images provided by the XRD, can analyze the material internal crystal structure. Laser Raman spectrum is used to test the material of graphitization degree, degree of graphitization material can be made of abscissa is about 1300 cm abscissa D peak height and the ratio of the peak height is about 1600 G of cmL, the greater the ratio, the material of the lower the degree of graphitization, the opposite is smaller. Test pore size distribution, pore size distribution is divided into the pore and micro hole, the hole and the hole, the final proportion of, need is a hole in the microporous also need, big hole a bit less, specific surface area and adsorption capacity is measured, the bigger the better. Under the program control temperature measuring the relationship between the quality of the sample under test and the temperature change a thermal analysis technique, used to study the thermal stability of materials and components. Charge and discharge characteristic test is to study the electrochemical performance of the most basic research methods. Including the constant current charge and discharge test and ratio test. Can get the material charge and discharge specific capacity, voltage platform and the information such as coulomb efficiency. This paper, by using high performance battery testing system for testing, in the first three loop drawing into a line chart. Cyclic voltammetry is a commonly used electrochemical methods. The method of controlling the electrode potential at different rates uses a triangular waveform to scan once or repeatedly over time. The potential range is to enable the electrode to alternately undergo reduction and oxidation reactions, and record the current to form a potential curve. In this article, through electrochemical workstation to 5 h scanning of battery, get data used to draw the line chart.

3. RESULTS AND DISCUSSION

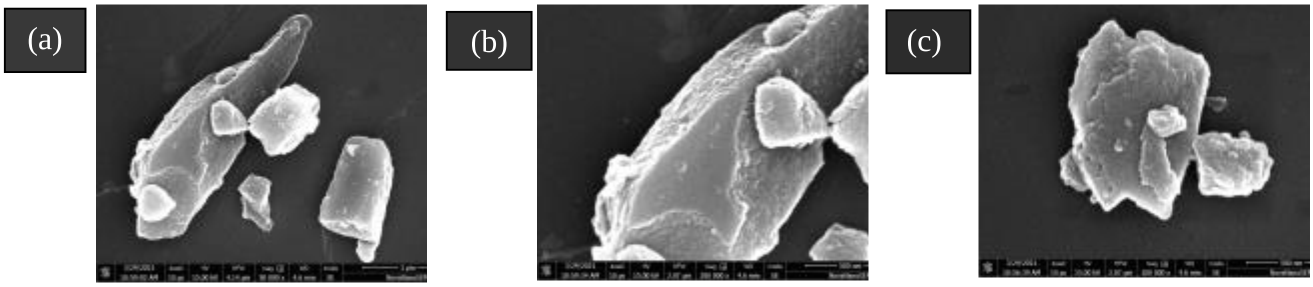

Figure 1. SEM of bamboo charcoal after pore reaming with concentrated hydrochloric acid

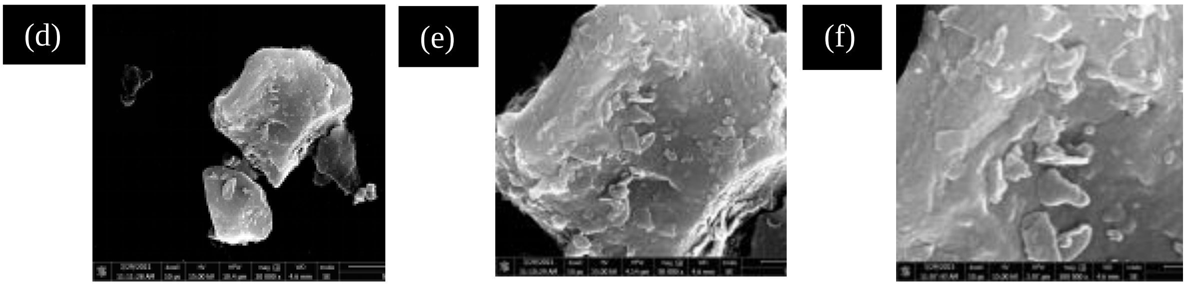

Figure 2. Micromorphology of bamboo carbon composites loaded with 5 wt.% SiO_2

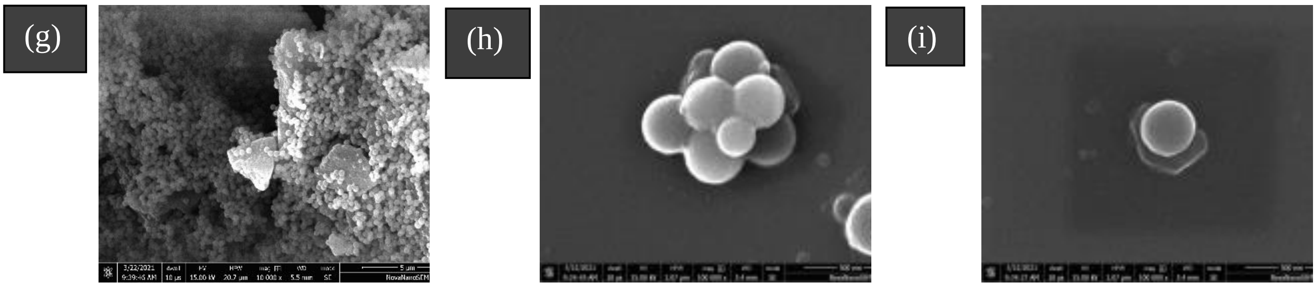

Figure 3. Micromorphology of bamboo carbon composites loaded with 15 wt.% SiO_2

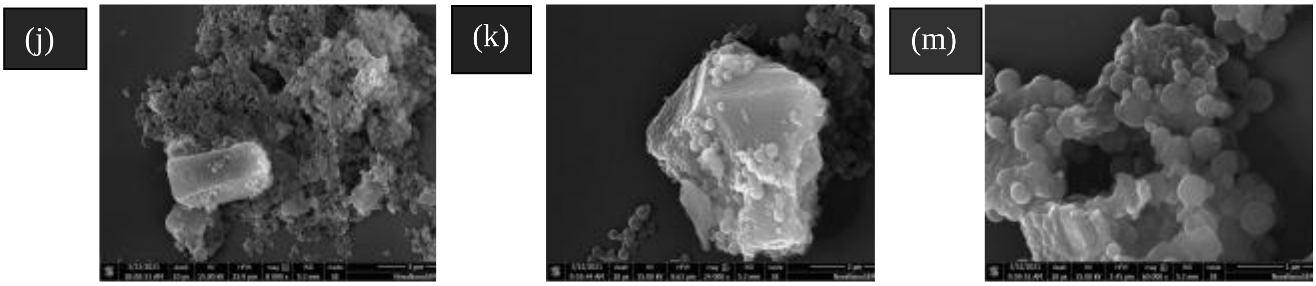

Figure 4. Micromorphology of bamboo carbon composites loaded with 30 wt.% SiO_2

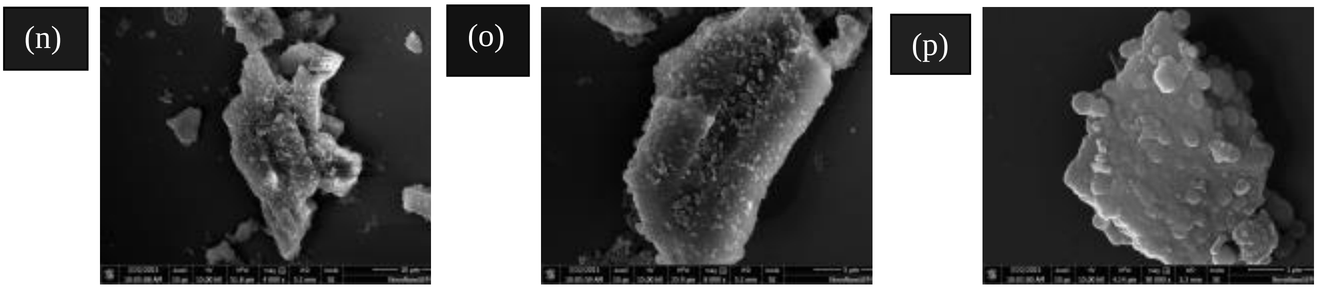

Figure 5. Micromorphology of bamboo carbon composites loaded with 45 wt.% SiO_2

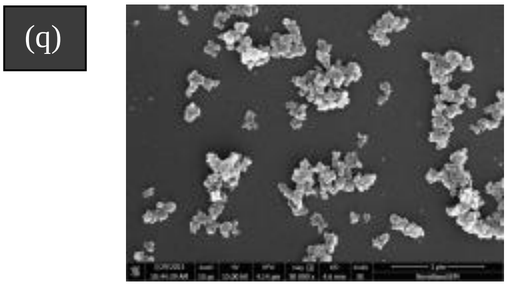

Figure 6. SEM of bamboo charcoal after pore reaming with $KHCO_3$

Above SEM micromorphologies are bamboo charcoal after pore reaming with hydrochloride and $KHCO_3$ and different loading capacity of SiO_2. It can be clearly seen from Figure 1(a), (b) and (c) that the bamboo carbon particles reamed with hydrochloric acid are micron-sized blocks with fine holes on the surface. It can be seen from Figure 1(q) that the bamboo carbon in the pore expansion of $KHCO_3$ is dispersed and granular. With the increase of silica loading, the silica loading on the surface of bamboo charcoal also increased. It can be clearly seen from Figure 1(g), (h) and (I) that the surface of bamboo carbon material is loaded with a layer of spherical silica. With the increase of load ratio, the number of silica load layers keeps increasing and it also can be seen from Figure 1 (n), (o) and (p) that the agglomeration phenomenon is significant. In the process of hydrothermal polymerization, it is easy to agglomerate nanoparticles due to hydrogen bonding on silicon surface. Therefore, it is feasible to prepare bamboo C@SiO_2 composite by hydrothermal method, but it is still urgent to solve the agglomeration phenomenon between SiO_2 nanoparticles.

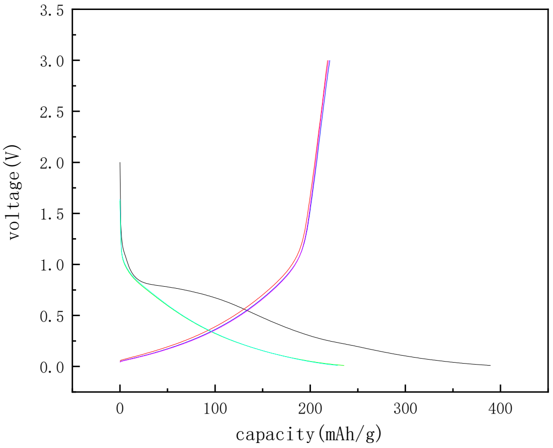

Figure 7. Charge-discharge curves of bamboo charcoal after hole enlargement sample-0

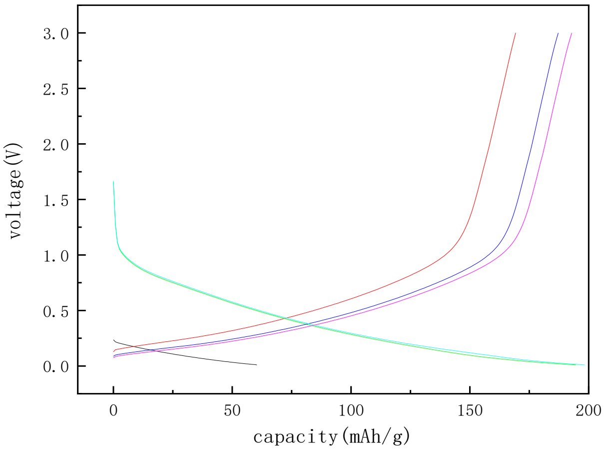

Figure 8. Charge-discharge curves of bamboo C@SiO$_2$ composites sample-15

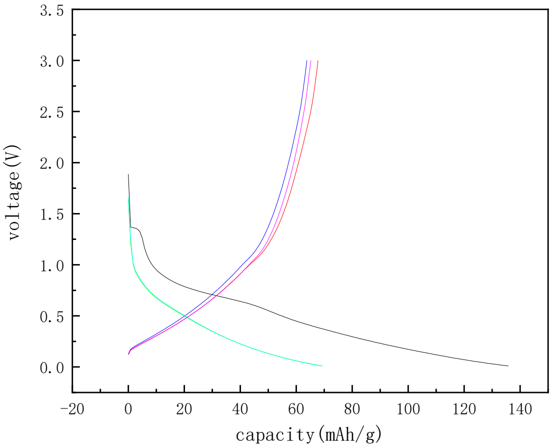

Figure 9. Charge-discharge curves of bamboo C@SiO$_2$ composites sample-30

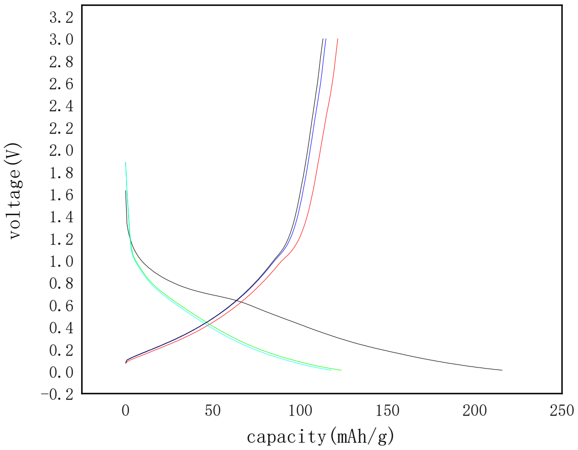

Figure 10. Charge-discharge curves of bamboo C@SiO_2 composites sample-45

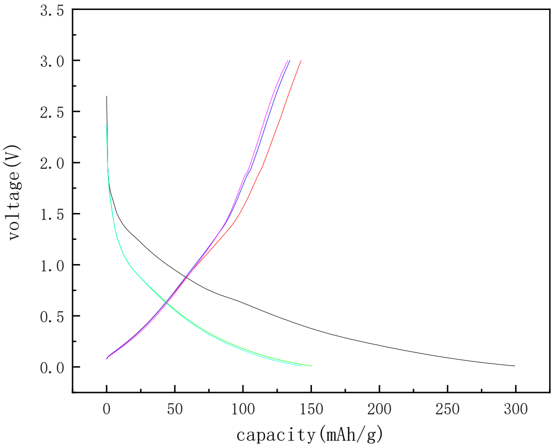

Figure 11. Charge-discharge curves of bamboo charcoal after hole enlargement by $KHCO_3$

The charge-discharge curves of bamboo C@Si anode composites with different SiO_2 loading are shown above figures. Figure 7-11 shows that the initial discharge curve of the lithium battery loaded with SiO_2 generates an obvious working voltage platform at 0.4V, which is inferred to be due to the formation of Li_2O and Li_4SiO_4, resulting in the formation of SEI film on the surface of SiO_2. Discharge is a reduction reaction, which must consume a large amount of Li^+, and the reaction is irreversible [22]. Therefore, the initial discharge irreversible storage is large and the Coulomb efficiency is low. The lithium battery with sio2 mass fraction of 15% produces a very obvious low voltage platform at the first discharge, which is preliminarily judged to be the problem of cathode material preparation. The bamboo carbon with $KHCO_3$ pore expansion did not produce a very obvious working voltage platform at about 0.4V, while the bamboo carbon with HCl pore expansion produced a working voltage platform at about 0.4V, which shows the influence of silicon dioxide on battery voltage. Figure 7-11 shows that the specific capacity of the battery is inversely proportional to the silicon dioxide content. The higher the silicon dioxide content, the lower the specific capacity. The reason for this phenomenon may be that the poor conductivity of silica reduces the conductivity of the anode material. At the same time, silicon dioxide reacts with lithium ions to produce relatively stable silicon-lithium compounds, which consume large amounts of lithium ions and reduce specific capacity.

The specific capacity of carbon composites were compared in table 2.

Table 2. The specific capacity of some common cathode materials

Cathode materials	Overpotential (V)
This work	0.406
Lignin carbon[4]	0.442
VA-NCNT[23]	0.302
NOMGAs[24]	0.317
C-PDDA[25]	0.358
Traditional petroleum carbon	0.514

It can be seen from Table 1 that the traditional carbon material has a high over-potential, while the other carbon matrix composites have a relatively low over-potential. Transition metals and their oxides can provide low chemical sites and significantly reduce the overpotential of composites, which provides a new idea for the improvement of hydrogen evolution electrode. The porosity of carbon materials is also one of the hot topics for further research and development in the future.

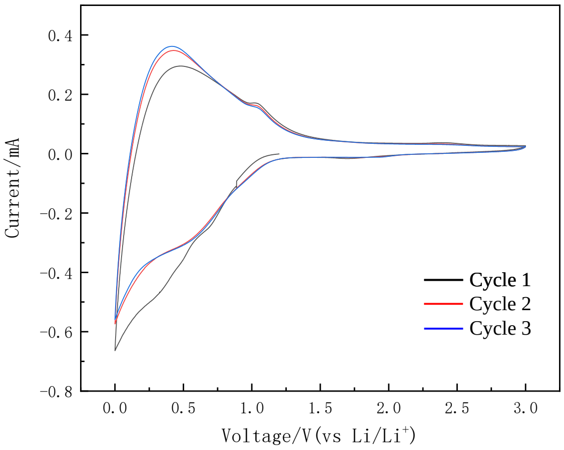

Figure 12. Charge-discharge curves of bamboo charcoal after hole enlargement sample-15

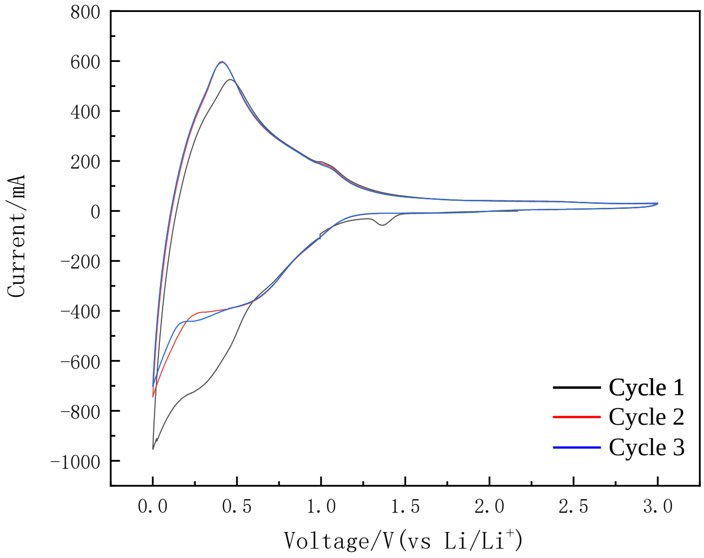

Figure 13. Charge-discharge curves of bamboo C@SiO$_2$ composites sample-30

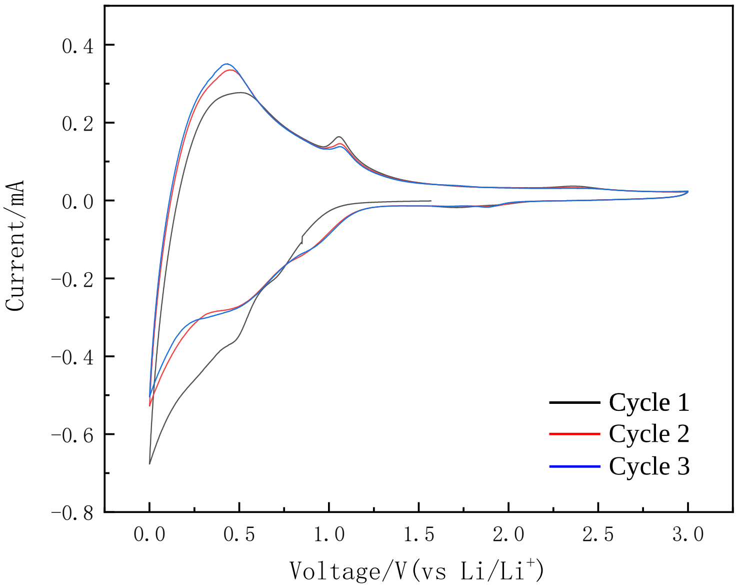

Figure 14. Charge-discharge curves of bamboo C@SiO$_2$ composites sample-45

Figure 12-14 is the CV curve of bamboo C@SiO$_2$ batteries with different loading loads. It can be seen that the three carbon composite anode materials all present sharp reduction peaks at 0 V, corresponding to the alloying process of Si and Li$^+$. The three materials all produce a small reduction peak at about 0.5V, and the reduction peak of SiO$_2$ is offset at 0.7V. In addition, the quadratic and cubic CV curves of 30 wt.% bamboo C@SiO$_2$ composites sampl-30 have excellent overlap and are closed loops. It indicates that the stable SEI film is formed in one cycle and shows high stability and reversibility in the subsequent cycle. However, sample-15 and sample-45 shows breakpoints in the second and third

CV curves without forming a closed loop. This indicates that no stable SEI film is formed in the first cycle, and its stability and reversibility are not as excellent as sample-30 in the subsequent cycle. In the cycle diagram of voltage and current, it is not diffficult to see that its stability from large to small is sample-30, sample-15 and sample-45.

4. CONCLUSION

The demand for new energy battery has been more and more urgent, but for the good performance of the new energy battery research and development is still large space. Based on the green environmental protection, low prices of bamboo carbon materials as bamboo carbon source preparation of porous carbon materials, and silicon dioxide composite, lithium battery research conclusion its electrochemical performance mainly summarized as follows:

SEM results show that the bamboo C@SiO_2 through the hydrothermal method can better load, fully increase the bamboo the specific surface area of carbon materials itself, but need to consider the reunion. Bamboo C@SiO_2 composites have good cycle stability and reversibility, but does not improve the battery charge and discharge specific capacity. C@SiO_2 composites also have significant differences on lithium battery charge and discharge performance, but due to the nature of the silicon dioxide itself, battery capacity problem didn't get very good solve. C@SiO_2 composites all present sharp reduction peaks at 0 V, corresponding to the alloying process of Si and Li^+. The three materials all produce a small reduction peak at about 0.4V, and the reduction peak of SiO_2 is offset at 0.7V. Sample-30 have the best overlap and are closed loops.

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