Balsa-Wood-Derived Binder–Free Freestanding Carbon Foam as High-Performance Potassium Anode

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The binder-free freestanding electrode is assumed as a proven and effective method of increasing the energy density of potassium-ion batteries (PIBs) because of the addition of binder and conductor. However, an expensive and complex synthesis process hampers its development. Herein, a binder-free freestanding biomass hard carbon (BHC) foam with balsa wood as the precursor is put forward. The prepared BHC foam maintains a highly hierarchical structure, in which the channels are interconnected and the pipe walls form an extremely stable 3D structure. This 3D porous network is synthesized in one step by a simple, environmentally friendly method, which ensures efficient ion and electrolyte transfer without structure change during the electrochemical cycle. When used as PIB anodes, the binder-free freestanding carbon foam delivers a high reversible capacity of 252.7 mAh g⁻¹ at 100 mA g⁻¹ with a high initial coulombic efficiency of 63.7%, excellent long cycle stability (95.1% capacity retention after 500 cycles, and the average decay rate per cycle is 0.012% over 2500 cycles), and superior rate capability (the capacity of 165 mAh g⁻¹ reserved at 2000 mA g⁻¹). This strategy provides a simple and fast way to fabricate a stable and high-performance anode for PIBs.

1. Introduction

A potassium-ion battery (PIB) is a promising technology in energy storage systems with the advantages of abundant reserves, similar working mechanism to lithium ion batteries and competitive cost.⁷¹–⁷⁴ Carbon materials are the cornerstone of the commercialization of PIBs, which attracted lots of attention. A wide variety of carbon materials, such as hard carbon,¹⁰,¹¹–¹⁸ soft carbon,¹³,¹⁹–²¹ carbon nanofibers,²² and reduced graphene oxide,²³ have been investigated as the promising anodes for PIBs in terms of the superior thermal stability,²⁴ extensive resource,²⁵ and excellent potassium storage capacity.²₆ However, complex synthesis methods, high cost, and poor conductivity are the main obstacles, which seriously restrict the development of carbon material.²⁷–³⁰ Besides, the traditional carbon electrodes are usually coated on the metal collector with conductive agent and binder, which will result in a great decrease in battery's energy density.³¹ In addition, due to the limitation of the contact area between the active substance and the electrolyte, electrolyte infiltration is not effective. In the process of circulation, large volume expansion will also lead to electrode pulverization and falling off.²³ Therefore, it is of great significance to develop a novel 3D freestanding electrode for PIBs.²¹,³¹–³³

Biomass-derived carbon materials, such as egg-shell membrane,¹⁴ rice straw,¹⁵ and auricularia³⁶ are well sourced, renewable, and environmental friendly, have attracted more and more attention.²³–³⁹ In higher plants, sieve tube is often used to transport various organic substances. The sieve tube molecules are longitudinally connected and distributed in the skin of angiosperms. At the same time, there are many pores on the end wall of the connection between sieve elements, which are called sieve pores,⁴⁰ and this provides the conditions for the multistage interconnected pore structure after carbonization. Plant cell walls are rich in lignin, cellulose, and hemicellulose. On this basis, the flexibility of wood after carbonization is noticed. Balsa wood, the lightest wood in nature, is used as a carbon source and fixes a 3D multistage porous structure through the natural structure of wood. In terms of material transport, liquid flow, and gas diffusion, plants have evolved multistage structures with stable chemical and physical properties.⁴¹

In this work, we used the lightest wood (balsa wood) in nature to prepare a biomass hard carbon (BHC) as a freestanding electrode through a simple and environmental friendly carbonization process.³⁸ The BHC material shows a good mechanical compressibility due to the multichannel 3D structure of natural wood. The uniformly distributed large pores accelerate the transport of electrolyte and improve the kinetic effectively. At a certain carbonization temperature, it exhibits a charge/discharge curve similar to that of soft carbon, and more capacity can be released in the low-voltage region. Based on a unique structure, the BHC anode shows a capacity of 252.7 mAh g⁻¹ with high initial coulombic efficiency (ICE = 63.7%) at the current density of 100 mA g⁻¹. In the meantime, almost no capacity degradation can be observed; noted that the capacity retention rate is
95.1% in 500 cycles, and the average decay rate per cycle is 0.012% over 2500 cycles in repeated charge–discharge test over 1 year. In addition, after five consecutive currents vary from 100 to 2000 mA g⁻¹, a capacity of 159 mAh g⁻¹ can be delivered at 2000 mA g⁻¹, which achieves a high-level rate performance.

2. Results and Discussion

A simple, green synthetic method is used to prepare the porous carbon nanostructure. In Figure 1a, pre-oxidation was carried out to destroy the binding layer of lignin and hemicellulose, which made the carbon chain of organic polymer form the 3D cross-linking structure and the bulk phase material, and to avoid the melting process in the subsequent carbonization process. Thus, the 3D structure of BHC itself can be preserved. At the same time, oxygen-containing functional groups are introduced. The oxygen-rich functional group may enhance the wettability of the surface. Then, the samples are carbonized in Ar atmosphere at high temperature, Figure 1a shows the macromorphology of balsa wood during carbonization at 800 °C, and the raw material has no obvious volume change. The production yield is about 36.1%. In Figure 1b, pipes and holes are interconnected in the 3D space, and this interconnection structure is more conducive to the electrolyte infiltration and shortens the ion transport path. To confirm the tubular structure inside BHC, the cross section of the material is observed. The morphology was characterized by scanning electron microscope (SEM). Figure 1c shows that the large pores formed after the pipe are cut, and the holes formed by cutting the pipe are evenly distributed, with the diameters ranging from 15 to 60 μm. It should be noted that nano-holes are arranged in the inner wall of the channel to form an interconnected structure (Figure S1a,b, Supporting Information), which was originally the channels for wood to transport biomass to various parts of the plant. This structure provides more paths for the electrolyte to infiltrate into the material, thus shortening the distance of ion diffusion. When we ground BHC samples, the interconnect holes (diameter is around 0.8 μm) could be seen more clearly on the micrometer side of the channels (Figure 1d). At the same time, we observed the longitudinal section of the BHC (Figure 1e) and found that the tube is wrapped by a thin and flat surface, which provided more adsorption sites for ions. When the BHC surface is magnified (Figure S1c, Supporting Information), fine and uniform cracks can be seen. The electrolyte can be attached to its surface evenly and flatly, which also provides more defect sites for K⁺ storage. The nanoscale sheet-like structure is found by the transmission electron microscopy (TEM) image (Figure S1d, Supporting Information), which is because in the initial pre-oxidation process, cellulose, lignin, and hemicellulose separated, resulting in the rupture of the cell wall. The broken cell walls are pressed against each other and stacked to form a unique layering mechanism, and multiple arched layers were connected together. This layer structure can show a certain degree of mechanical compressibility after carbonization. To explore the internal surrounding structure of BHC, a high-resolution TEM image is used to demonstrate that the BHC

![Figure 1. The synthetic route and morphology characterizations of BHC. a) Schematic of the material synthesis for BHC. b) Schematic of the structure for BHC. c–e) SEM images of BHC-800.](image-url)
presents turbine laminar, as shown in Figure 2a–c. With the increase in secondary carbonization temperature, carbon atoms rearranged, which made the microstructure of BHC has a tendency to an orderly process. At 700 °C, the graphite microcrystals were almost completely amorphous. With the increase in temperature, the short-range ordered structure gradually appeared. In addition, the samples with a carbonization temperature of 700, 800, and 900 °C are measured by X-ray diffraction (XRD) and Raman spectroscopy, and the microstructure of BHC was further determined (Figure 2d–f). The samples have two typical broad diffraction peaks belonging to carbon at ≈23° and 44°, which is attributed to the (002) and (101) diffractions, respectively, and the intensity of (101) diffraction peak increases with the increase in temperature, probably indicating that the samples gradually become ordered but still remained amorphous.[17] Raman spectra are also used to analyze the structure of BHC. Two peaks corresponding to the D and G bands appear at 1349 and 1584 cm⁻¹, which indicated the disordered and ordered structures of the material, respectively, and the ratio of D peak to G peak intensity can represent the graphitization degree of carbon. Among them, BHC-700 showed the lowest I_D/I_G value (I_D/I_G = 0.826), whereas BHC-800 and BHC-900 showed similar I_D/I_G values (0.944 and 0.942, respectively). This indicates that the edge of BHC increases greatly when the temperature increases from 700 to 800 °C.

Nitrogen adsorption/desorption tests were performed using the Brunner–Emmett–Teller (BET) model, to explore the proportion of micropores (<2 nm) and mesopores (2–50 nm). The adsorption/desorption isotherms (Figure 3a) exhibit a hybrid feature of type-I and type-II, which can be a supporting evidence of the hierarchical porous structure.[42] BHC-800 shows the largest specific surface area (69.3 cm² g⁻¹), higher than BHC-700 (15.6 cm² g⁻¹) and BHC-900 (26.6 cm² g⁻¹). Proper surface area can provide better interface contact among the liquid electrolyte and the active material. It could also reduce the formation of solid electrolyte interphase (SEI) and improve the ICE (ICE = 63.7%), and provides a large attachment space for the intercalation and adsorption of ions in the meantime. The pore size distributions (Figure 3b) for the BHC materials are investigated by the Barrett–Joyner–Halenda (BJH) method. All three materials possess the major size of around 3 nm. In the meantime, BHC-800 possesses more micropores (the major size around 0.28 nm). The existence of micropores provides more active sites for ion intercalation. An X-ray photoelectron spectroscopy (XPS) full spectrum curve (Figure S2, Supporting Information) shows the peaks corresponding to C1s (284.2 eV) and O1s (532.2 eV). The peak intensity of C1s peak is much higher than that of O1s peak, and almost no other impurity peaks were shown. The atomic ratio of C and O is 98.05% and 1.75%, respectively. With the increase in temperature to 1200 °C, the intensity of C peak decreased. Besides, the fitting of C1s peak in BHC-800 (Figure 3c) showed four potential components, which were O–C=O (290.9 eV), C=O (287.89 eV), C–O (286.3 eV), and C=C (284.65 eV). The fitting of O1s peak (Figure 3d) also showed C=O (532.5 eV) and C=O/H/C=O/C (532.02 eV) peaks.[5,23,32,37] C–OH group could increase the wetting effect of the electrolyte and further promote the storage of K⁺.

We scraped the surface of the block BHC, and the length and width of the electrode are about 4 mm and 3 mm, respectively (Figure S3, Supporting Information). When BHC is used as...
anode of PIBs, we found that it has excellent cycle stability. It is worth noting that the test was on the basis of a traditional electrolyte system by dissolving 0.8 M potassium hexafluorophosphate (KPF₆) in a one-to-one mixture of ethylene carbonate (EC) and diethylene carbonate (DEC). Figure 4a shows the cyclic voltammetry (CV) curves of the BHC-800 for the initial three cycles between 0.01 and 3 V at the scan rate of 0.5 mV s⁻¹. In the first CV scan, due to the complex phase transition and side reaction caused by the intercalation of K⁺, a cathode peak appeared in a wide area, and two obvious reduction peaks appeared at 0.01 and 0.71 V. K⁺ insertion in the graphitic carbon layer results in the peak located at 0.01 V. A strong reduction peak of 0.71 V appeared at the first scan and disappeared in the subsequent cycle, due to the decomposition of the electrolyte and the formation of an SEI covering the carbon surface. It can be observed that the area difference between the first curve and the subsequent curves was not large, which means that the low initial capacity loss leads to high ICE. We evaluated the electrochemical performance of BHC by a half-cell testing at a current density of 100 mA g⁻¹, as shown in Figure 4b. BHC-800 showed a reversible capacity of 252.7 mAh g⁻¹ and exhibited two slopes in the course of charge/discharge, similar to soft carbon. This allows it to release more capacity (about 73.1%) in the low voltage region (<1.5 V). All of BHC-700, BHC-800, and BHC-900 represent the high ICE of 60.8%, 63.7%, and 61.3%, respectively. The discharge capacities of the BHC-800 freestanding electrodes in the 1st, 2nd, 10th, 50th, and 100th are 396.9, 270.5, 258.0, 256.5, and 254.8 mAh g⁻¹, respectively. From the second cycle, the discharge/charge platform of the four curves has not changed, and the capacity basically has no attenuation, indicating the excellent cycle performance of BHC-800. In Figure S4, Supporting Information, to select the electrolyte with the best performance, we used two additional electrolytes for testing; one is 4 M potassium bis(fluorosulfonyl)imide (KFSI) in ethyl methyl carbonate (EMC), and the other is 3 M KFSI in dimethoxyethane (DME). When using both electrolytes, the capacity is not satisfactory (163.3 mAh g⁻¹ in 4 M KFSI in EMC and 93.63 mAh g⁻¹, respectively). On the other hand, ICE is the highest when we use KPF₆ electrolyte (23.3% in 4 M KFSI in EMC and 22.5% in 3 M KFSI in DME). In summary, we choose KPF₆ electrolyte. To prove its stability, a long cycle test is carried out at a current density of 100 mA g⁻¹. Significantly, as shown in Figure 4d, BHC-800 can provide an ultrahigh capacity retention of 95.1% after 500 cycles with a remaining capacity of 241.5 mAh g⁻¹. In Figure 4f, we also tracked the performance of BHC in subsequent cycles, and it still provides a reversible capacity of 178.9 mAh g⁻¹ over 2500 cycles in more than one year (13 months). The high stability of this kind of long pager is mainly due to the natural advantages of biomass precursors. The stable 3D structure of multicell interconnection accelerates the electrolyte permeation and reduces the strain through multistage porous skeleton (mainly macropores) during the cycle. In Figure 4c,e, ICE and capacity retention of PIBs, which used the same electrolyte, are compared, respectively. BHC has
the higher ICE and capacity retention compared with previously published work. [24, 31, 37, 43-49]

High rate property is the key index to evaluate the power characteristics of PIBs. When the current densities consecutively increase from 100 to 200, 500, 1000, and 2000 mA g⁻¹, the BHC-800 film has a reversible capacity of 244, 227, 201, 186, and 165 mAh g⁻¹ (Figure 4g). However, the battery would remain a charge capacity at the level of 238 mAh g⁻¹ when

Figure 4. The electrochemical performance of BHC anode for PIBs. a) CV curves at a scan rate of 0.5 mV s⁻¹. b) The 1st, 2nd, 10th, 50th, and 100th charge/discharge curves at 100 mA g⁻¹. c) ICE plot of PIBs, which is compared with the energy storage devices reported at 100 mA g⁻¹. d) Charge/discharge capacity and coulombic efficiency of BHC-800 at 100 mA g⁻¹. e) Capacity retention plot of PIBs, which is compared with the energy storage devices reported. f) Comparison of the cycling performance of the BHC freestanding electrodes at a current density 200 mA g⁻¹ for 500 cycles. g) Comparison of rate performance at various current densities from 100 to 2000 mA g⁻¹. h) The cycling performance of the BHC freestanding electrodes at a current density 100 mA g⁻¹ from 500 to 2500 cycles.
the current density backs to 100 mA g\(^{-1}\). Compared with BHC-700 (provide 189, 172, 152, 135, and 116 mAh g\(^{-1}\) at the current rates of 100, 200, 500, 1000, and 2000 mA g\(^{-1}\)) and BHC-900 (provide 199, 177, 158, 141, and 120 mAh g\(^{-1}\) at the current rates of 100, 200, 500, 1000, and 2000 mA g\(^{-1}\)), BHC-800 shows the best rate performance. The charge/discharge curves at different current densities show that a little polarization occurs at high current due to the disordered structure of amorphous carbon, which makes the conductivity slightly poor (Figure S6, Supporting Information). In addition, we compared the cycle performances of the three samples. Figure 4f shows 500 cycles at 200 mA g\(^{-1}\); BHC-800 possessed the largest reversible capacity of 233.1 mAh g\(^{-1}\) in initial cycle, and the discharge/charge capacities of BHC-700 and BHC-900 were 187/307 mAh g\(^{-1}\) and 174/285 mAh g\(^{-1}\). All three materials exhibit excellent long cycle stability (the capacity retention of BHC-700, BHC-800, and BHC-900 is 86.6%, 90.1%, and 92.2% after 500 cycles, respectively). This excellent cycling stability is due to the 3D stable interconnection structure, which provides abundant buffer space for potassium ions to alleviate the volume change during repeated cycles. The charge/discharge curves of BHC-700 and BHC-900 (Figure S5, Supporting Information) show different voltage platforms from BHC-800, illustrating that deintercalation behavior of K\(^+\) differs in samples. As the carbonization temperature increases, the voltage plateau period tends to be flat, demonstrating that the deintercalation behavior of ions is more obvious and indicating a higher degree of graphitization, which is in good agreement with the TEM results.

To prove the stability of the 3D carbon structure, SEM is used to observe the cyclic BHC-800 freestanding electrode (Figure 5a–d). After 50 cycles, its pristine surface morphology of the anode remained intact throughout the test. The pore structure and microchannel are also well preserved, which means that no emissions remain on the channel wall, and ensure the smooth flow of the electrolyte and ions. The large pores with a diameter of 4 μm were still observed. Therefore, it can be determined that the stability of this structure is the basis of long-term cycle, illustrating that deintercalation behavior of K\(^+\) differs in samples. As the
carbonization temperature increases, the voltage plateau period tends to be flat, demonstrating that the intercalation behavior of ions is more obvious and indicating a higher degree of graphitization, which is in good agreement with the TEM results (Figure 5e). It is clear that K⁺ stored on the BHC surface uniformly, which indicate that the laminar structure of the channel provides abundant adsorption/embedding sites for K⁺.

As CV techniques are the important method in the investigation of the kinetics of K ion insertion in BHC-800, data shown in Figure 6a show different scan rates ranging from 0.4 to 1 mV s⁻¹ of the BHC-800's CV curves. Moreover, the similar shapes present at different stages of scanning rate in the CV curves. The CV curves presented similar shapes at different scanning rates. There is a redox peak in the low potential region, which are ascribed to the surface-induced double layer capacitance process as well as diffusion-controlled intercalation process. The capacitive effect is depend on/driven by the correlation of the measured current (i) and the scan rate (ν), with the purpose of exploring the ratio of both processes. With respect to \( i = aν^b \), a and b are considered as positive variables, whereas the value of b equals to difference between the slope of the plot of log (i) versus log (v). Provided that b = 0.5, which means there is a diffusion behaviour, while for the capacitive response where b should be almost 1. According to Figure 6b, when the b values are 0.50 and 0.76, respectively, the BHC-800 freestanding electrode can both show battery and capacitor properties.

The charge storage contribution rate present in the pseudocapacitance can be calculated by the following display:\[ \frac{i(V)}{\nu^{1/2}} = k₁ν^{1/2} + k₂ \]

In the formula, ν represents the specific scan rate, whereas V stands for the specific voltage. \( k₁ \) and \( k₂ \) are used as the adjustable parameters to determine the relationship of \( iv^{-1/2} \) versus \( ν^{1/2} \) plot, and \( k₁ν \) and \( k₂ν^{1/2} \) represent the contribution of capacitive behavior and diffusion control behavior in charge storage. The nonlinear relationship between V and \( k₁ν \) is calculated by the value of \( k₁ \) at 120 voltage points. Thus, the percentage of the capacitance contribution to the curve integral under a specific scanning rate can be calculated. Through the abovementioned calculation process, Figure 6c shows that the pseudocapacitive contribution reaches 29.2% at 0.4 mV s⁻¹. Contribution rate of pseudocapacitance and corresponding scan rates are shown in Figure 6d. Obviously, along with the increasing scanning rate, the contribution rate of pseudocapacitance will also grow, which demonstrates the significance of pseudocapacitive behavior in the high rate property of K ion storage.

Figure 6. The electrochemical kinetic properties of BHC-800 in K⁺ half-cells. a) CV curves at different scan rates. b) The corresponding curves log(i) versus log(ν) for all corresponding peaks. c) CV curve and the pseudocapacitive contribution (shaded area) at 0.5 mV s⁻¹. d) The pseudocapacitive contribution in percentage at various scan rates.
3. Conclusion

In summary, we developed freestanding BHC foam as anode material for PIBs. Balsa wood was used as a precursor to completely fix its special multistage structure. The prepared carbon foam skeleton provided a 3D conductive network, which enhances the electron transfer. In the meantime, the porous structure fixed by the sieve tube structure of higher plants can accelerate the infiltration of electrolyte and provide buffer for the change of ion volume. The results showed that the structure of BHC electrode changed little before and after the cycle. As a result, BHC freestanding electrode exhibits high specific capacity (252.7 mAh g\(^{-1}\)) at the current density of 100 mA g\(^{-1}\)), high rate performance (a capacity of 165 mAh g\(^{-1}\) can be delivered at 2000 mA g\(^{-1}\)), outstanding cycling stability (capacity retention rate is about 95.1% in 500 cycles, and the average decay rate per cycle is 0.012% within 2500 cycles), and high ICE (ICE is about 63.7%). In addition, CV with different scanning rates confirms the role of pseudocapacitor behavior in high rate property of K storage. We provide a simple and highly stable anode material for PIBs and a new method for the structural design of hard carbon.

4. Experimental Section

Synthesis of BHC Samples: Balsa wood was purchased from aviation model material. First, cutting the wood into pieces and putting it into a petri dish, and then washing it repeatedly with deionized water. Next, putting the washed balsa wood into 70 °C incubator and drying it thoroughly before the cleaned wood was put into a muffle furnace for pre-oxidation (heated in 220 °C for 0.5 h, and heating rate is 5 °C min\(^{-1}\)). After taking out the sample, carbonization was continuing at 800 °C, heating for a period of 2 h in an argon atmosphere at 5 °C min\(^{-1}\) as the heating rate; then, stable BHC-800 is obtained (Figure 1a). According to the different sintering temperatures, the samples were recorded as BHC-700, BHC-800, BHC-900, and BHC-1200.

Morphology and Structural Characteristics: The characterization results show that the BHC has an outstanding morphological structure. Field-emission scanning electron microscopy (MIRA3 LMH, 20kV) and TEM (Titan G12) were used for observation. The crystal structure of BHC is characterized by XRD (Bruker AXS, D-76187, Karlsruhe, Germany). Using a Renishaw inVia system, the Raman spectra of BHC samples could be clearly measured, while applying an aperture analyzer to the nitrogen adsorption-desorption isotherm and pore size analysis of BHC.

Electrochemical Measurements: We scraped the surface of the block BHC and used it as the anode electrode of PIBs. The electrolyte was a 0.8 M KPF\(_6\) dissolved in a mixture of EC and DEC with a volume ratio of 1:1. The 2032 coin batteries were assembled in an argon environment in a glove box. Via Arbin 2000 battery tester was used to test the galvanostatic charge/discharge process of constant current. The CV curve was tested with CHI660E electrochemical workstation. Calculate the capacities according to the weight of the active substance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords

binder-free, biomass carbon foam, freestanding anodes, high stability, potassium-ion batteries

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