

Facile Fabrication of N-doped Carbon Derived from Kiwi Fruit Peel for Advanced Supercapacitor

Hanbo Wang¹, Ziqi Zhang¹, Yiduo Li¹, Dongyu Pei¹, Sheng Wan¹, Yingying Li¹, Haiyan Lu^{1,2,3,*}

¹College of Chemistry, Jilin University, Changchun 130012, Jilin, China

²Key Laboratory of Physics and Technology for Advanced Batteries of Ministry of Education, Jilin University, Changchun 130012, Jilin, China

³Zhuhai Zhongli New Energy Sci-Tech Co., Ltd., Zhuhai 519175, Guangdong, China

Abstract: As a potential material, biomass material has become a hot spot for energy storage equipment because of its enhanced properties and environmental-friendly features. Waste kiwi fruit peel is a kind of biomass material with a natural macroporous structure. After carbonization, acid pickling and activation, the kiwi fruit peel carbon (KFPC) with a 3D porous structure composed of macropores, mesopores and micropores on its surface and inner channels, respectively. The morphology and structure of the KFPC are studied by scanning electron microscopy (SEM). The electrochemical properties were analyzed in a three-electrode system. The cyclic voltammetry (CV) measurement at the scan rate of 5-100 mV s⁻¹ in 2 M KOH aqueous electrolyte. The *Galvanostatic charge/discharge (GCD)* and Electrochemical Impedance Spectroscopy (EIS) are used to calculate the specific capacitance and resistance, respectively. The KFPC exhibits a 2290 m² g⁻¹ specific surface area. The capacitor has a specific capacitance of 249.8F g⁻¹ at 1 A g⁻¹ and a capacity retention rate of 89.22 % after 5000 cycles at 5 A g⁻¹, indicating that the KFPC is relatively stable. After assembling the materials into a symmetric supercapacitor, it delivered a high energy density of 9.75 Wh kg⁻¹, which reveals the promising application of KFPC in high-performance supercapacitors.

Keywords: Biomass materials, N-doped functional groups, High electrochemical performance.

1. Introduction

With the development of society, fossil energy is overused constantly, which leads to the depletion of fossil fuels and the production of a large number of harmful gases such as carbon dioxide and nitrogen dioxide causing serious environmental damage. The notion of green and sustainable development, the utilization of renewable sources and the innovation of new resources for energy storage applications has been popular recently. Hence, hot spots were concentrated on oxygen/hydrogen evolution [1], water splitting [2], lithium ion batteries [3], especially supercapacitor electrode materials [4]. As a kind of promising material, biomass has lots of advantages such as low cost, easy preparation and environmental-friendly, thus some common biomass materials, such as rice husk [5], straw cellulose [6], household waste [7] have been widely commercialized. Moreover, biomass materials is rich in various elements such as O, N [8], P [9], S [10] and so on. Therefore, it is expected that high temperature carbonization of nitrogen-rich biomass can produce nitrogen-doped carbon without introducing additional nitrogen sources which could be used as electrode materials for batteries and high performance supercapacitors [11] (SC).

Hierarchical porous structured carbon materials have been extensively studied nowadays because it can be fabricated easily from biomass materials. It has advantages of high specific surface area, well-developed pore structure and long cycle stability [12]. It is a material containing at least two or more of the three structures of macroporous, mesoporous and microporous. Macropores are “ion reservoirs”, providing abundant ion and electrons for the rapid adsorption and desorption reactions. Mesopores provides accessible channels for rapid transfer of electrolyte ions and fasten ion migrations. Micropores provide a large number of active sites and are

dominant in providing construction of electric double layer capacitance [6].

These three pores are distributed inside and outside the carbon materials, all of which play a crucial role in the performance of the supercapacitor and improve the cycle stability and rate capability of the supercapacitor to a certain extent.

Kiwi fruit peel (KFP) is a kind of biomass materials contain a large amount of organic compounds, including carbohydrates polyphenols, flavonoids, polysaccharides, etc [13]. After carbonization, these compounds decomposed and formed N-doped carbon. The mixing of nitrogen atoms and nitrogenous functional group not only change the electronic distribution but also enhance the synergistic effect by inducing defects, enhancing the porosity, and optimizing the interlayer of carbon. Furthermore, improving the capacitance and rate capability of KFPC [14]. After carbonization, the nature of carbon materials was also determined by the activation process. The choice of activation reagent is very important, such as alkali [15], ZnCl₂ [16], CO₂, which has different effects on rate of porosity, morphology, and electrochemical performance [17].

In this paper, N-doped activated carbon was successfully modified from KFP as materials. With a simple thermal treatment, acid pickling and activation. N-doped carbon with abundant pores was obtained. The prepared kiwi fruit peel carbon (KFPC) has excellent electrochemical properties for supercapacitors both in two-electrode and three-electrode test systems, which is mainly owing to its 3D porous structure and introduced N-functional groups [18].

2. Experimental

2.1. Raw materials

The kiwi fruit was purchased from Jilin University

supermarket, Changchun, China. Hydrochloric acid, potassium hydroxide, carbon black, poly tetra fluoroethylene (PTFE) and ethanol were purchased from Beijing Chemical Works. Deionized water (resistivity of 18.25 M Ω cm) was used for all experiments.

2.2. Sample preparation

The rinsed kiwi fruit peel was dried in an oven at 100 $^{\circ}$ C for 24h. After drying the KFP followed by a carbonization process in N₂ atmosphere at 400 $^{\circ}$ C for 1 h with a heating ramp of 5 $^{\circ}$ C min⁻¹. The carbonized KFP was removed to a mortar for full grinding, and then stirred with 50ml 3M HCl several times. The rinsed carbonized KFP was centrifuged before dried in an oven at 60 $^{\circ}$ C overnight. Subsequently, the as-prepared sample was further activated with KOH (carbonized KFP: KOH=1:3, weight ratio) in N₂ atmosphere. During the calcination process, the heating rate was 5 $^{\circ}$ C min⁻¹ until reaching up to 800 $^{\circ}$ C and the calcination process time was 1h. The obtained sample was washed repeatedly with deionized water and ethanol until pH=7, followed by a drying process at 60 $^{\circ}$ C for 24h to obtain kiwi fruit peel carbon.

2.3. Preparation of KFPC electrode

After mixing the KFPC, carbon black and PTFE at a mass ratio of 8:1:1, about 30 ml of ethanol was added into the mixture, and then heated and stirred at 80 $^{\circ}$ C in a water bath. After vaporizing most of the ethanol, the samples were pressed into sheets with a few drops of ethanol, and dried at 60 $^{\circ}$ C for 12 h. The dried sheet was cut into 1 \times 1cm², and then pressed the stainless steel and sheet together under 10 Mpa for 30 s.

2.4. The physical and electrochemical characterization

X-ray diffraction (XRD) of products was measured on a Ragaku X-ray diffractometer with Cu K α radiation source (λ = 1.541874 \AA) at 50.0 kV and 200.0 mA, with a range of 10 $^{\circ}$ -80 $^{\circ}$. Scanning electron microscopy (SEM) was used to analyze the morphology of the electrode material, using a Hitachi SU8020 at 3 kV.

2.5. Electrochemical characterization

The electrochemical tests of KFPC electrode was carried out in three-electrode and two-electrode systems. The three-electrode system was assembled with a working electrode, Pt counter electrode and Hg/HgO reference electrode and 2 M KOH electrolyte. The two-electrode system applied for symmetric supercapacitor tests, was assembled with two same slice of KFPC as both positive electrode and negative electrode. Cyclic voltammetry test (CV), Chronopotentiometry test (CP), open circuit potential-time test (OCPT), and electrochemical impedance spectroscopy (EIS) were performed by CHI660E workstation (Chenhua CO., Ltd., PR China). The galvanostatic charge-discharge test (GCD), cycling stability test and rate test were operated via the BTS system (CT-4008-5V-50 mA-164, Neware CO., Ltd., PR China).

3. Result and Discussion

3.1. Microstructure characterizations of KFPC

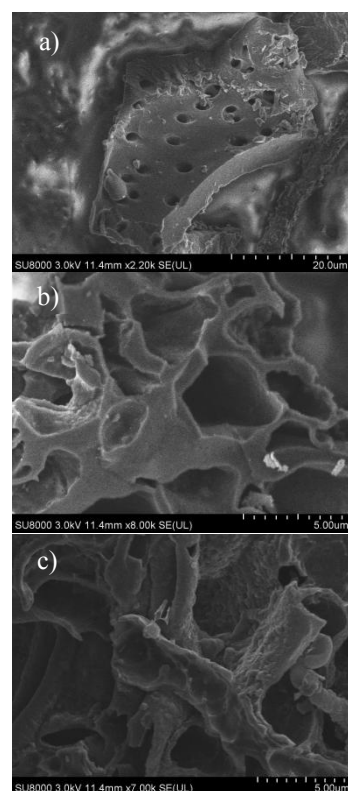


Figure 1. SEM images of a) KFPC (scale bar: 20 μ m), b) KFPC (scale bar: 5 μ m), c) KFPC (scale bar: 5 μ m), respectively.

Fig. 1(a–c) show the morphological properties of KFPC respectively, suggesting the structural characters are loose and porous. Also the morphology was seriously affected by carbonization and activation process. Firstly, the KFP seems to be an ordinary biomass material with very little pore structure, and most of the pore structure without any regular shape. After carbonization and activation, as shown in Fig.1(a-c), there exhibit large networks structure and exist structured porous morphology. During the carbonization process at 400 $^{\circ}$ C, large amounts of organic compounds in KFP were transferred to amorphous carbon dominates the composition with small amounts of inorganic mineral salt and slight organic materials that have not been transformed¹¹. After acid pickling, the carbonization product was mixed with KOH and activation at 800 $^{\circ}$ C. As the temperatures are elevated higher, the dynamic of carbon increased. When increasing the activation temperature to about 800 $^{\circ}$ C, KOH melt and etched on the hollow tube wall of carbonized product, existed a large amount of macropores, mesopores and micropores. Eventually lead to the specific surface areas of KFPC increase dramatically. However, when the activation temperature is elevated beyond 800 $^{\circ}$ C, the reaction between the KOH and the carbon may overreaction, which causes excessive ablation of the carbon material, part of the pore structure collapse and the ionic nature of the electrostatic adsorption decreases resulting in a small decline of the capacity. Therefore, the activation temperature was set to be 800 $^{\circ}$ C⁵. The reaction is not only good for the electric double-layer, but also form a relatively regular structure with large specific surface area.

3.2. Electrochemical properties of KFPC

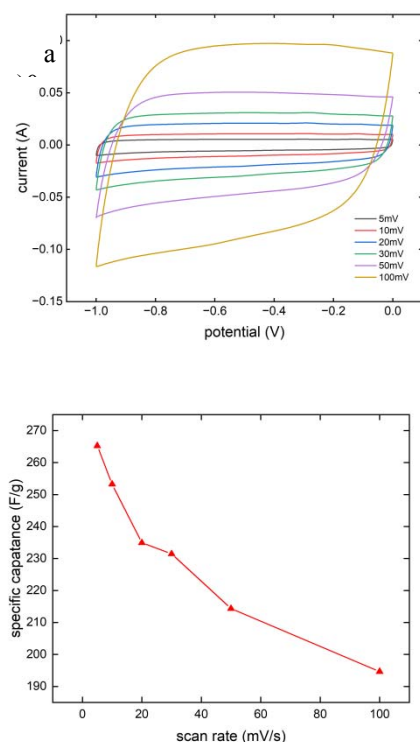


Figure 2. a) CV curves of KFPC at various scan rate, b) specific capacitance of KFPC electrodes at different scan rates.

To explore the electrochemical properties of KFPC, the CV and CP curves were measured in an aqueous electrolyte of 2M KOH using a three-electrode configuration. The working electrode, reference electrode and counter electrode were KFPC, Hg/HgO electrode, 1cm x 1cm Pt foil, respectively. As shown in Fig. 2a, all the profile displayed quasi-rectangular shapes, revealing a swift electrochemical response and a dominated electric double layer capacitance behavior. Nearly no peaks were observed over the cyclic voltammetry cycles either high or moderate scan rate, which indicates that there is no Faraday reaction and all capacitance derived from the electric double layer capacitance, because of the thoroughly acid pickling. Very little humps were observed over the cyclic voltammetry cycles under low scan rate, which may caused by some nitrogenous functional group result in some reversible redox reaction.

The specific capacitance was calculated from cyclic voltammogram via equation (1)

$$C = \int i du / 2m v \Delta u \quad (1)$$

where i is the instantaneous current, u is the instantaneous voltage, m is the activated materials mass of one electrode, and v is the scan rate, Δu is the voltage change. As illustrated in Fig.2b, the specific capacitance of KFPC was calculated to be 265.25, 253.26, 239.91, 231.46, 214.35, 194.66F g⁻¹ at the scan rate of 5, 10, 20, 30, 50, 100mV s⁻¹, respectively. And the capacitance retention of KFPC reached 73.39%, higher than many biomass carbon materials and commercial activated carbon. The high capacitance retention further proofed that various size pores in the carbon material coordinated excellent with each other.

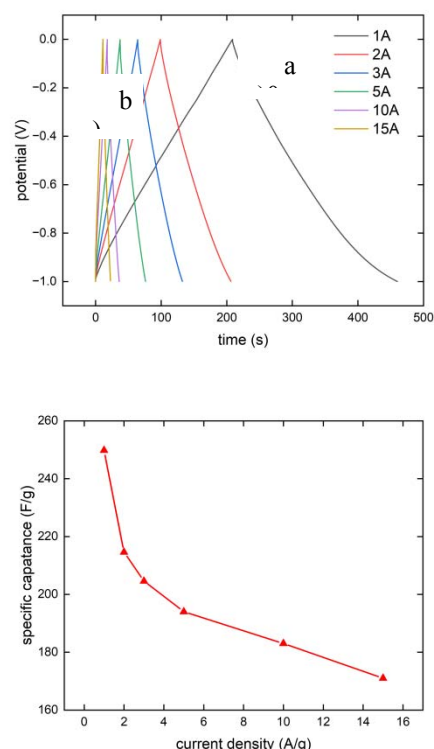


Figure 3. a) charge-discharge curves of KFPC at a current density of 1A g⁻¹ -15A g⁻¹, b) specific capacitance of KFPC electrode at a current density ranging from 0.5A g⁻¹ to 15 A g⁻¹

The specific capacitance was calculated from Chronopotentiometry test via equation (2)

$$C = \frac{It}{mV} \quad (2)$$

where I is the discharge current, m is the mass of active material in one electrode, Δt is the time of discharge, V is the voltage change. Moreover, as shown in Fig. 3a, CP curves were measured at current densities from 1A g⁻¹ to 15 A g⁻¹ to examine the specific capacity and rate capability of KFPC in 2 M KOH. CP curves exhibit a linear and near-symmetrical shape with a relatively low IR drop, revealing a typical electric double-layer capacitor behavior and good charging efficiency.

The very small IR drop is possibly attributed to the lower internal resistance and rapid ion diffusion as well as flexible charge transfer, which further proof that KFPC with porous structure. As shown in Fig. 3b, the KFPC reached a high specific capacitance of 249.8, 214.6, 204.6, 194.0, 183.0, 171.0F g⁻¹ and a good rate capability with the capacity retention of 68.5% when the current density increased from 1 to 15 A g⁻¹. The specific capacitance calculated from CV and CP curves were almost the same, indicated that KFPC was an excellent biomass materials and different pores in and out the materials exhibited good performance. These pores with different sizes played different roles in the formation of electric double layer capacitance. In the charge–discharge process, macropores can played an important role as an “ion reservoir” to provide abundant ion sources for the rapid ionic adsorption and desorption reaction. Mesopores can provide ions with sufficient channels for fast ion migration.

Micropores provided a large amount of ion adsorption active sites and play the main role for the construction of electric double layer capacitance. That's one of the reasons why the material has better properties.

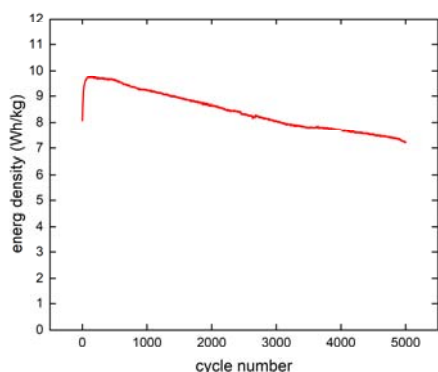


Figure 4. Stability test for KFPC at 5A g⁻¹ for 5000 cycles in 2M KOH.

As shown in fig.4, KFPC was assembled to be a symmetrical supercapacitor and had a charge-discharge test at 5A g⁻¹ for 5000cycles in 2M KOH. It can be understood that the KFPC electrode possessed larger energy density and long-life cycle stability. Firstly, KFPC exhibited 8.07Wh kg⁻¹, after about 100cycles, the energy density reached the maximum of 9.75Wh kg⁻¹, that was because the KOH electrolyte was fully penetrated into pores and channels in KFPC. The Faraday efficiency also reached nearly 100%, when the cycle number was 100, indicated the ionic adsorption and desorption react adequately. Additionally, the KFPC has a high cycling stability with a capacitance retention of 89.21% for 5000 charge-discharge cycles at 5 A g⁻¹ in 2M KOH. Hence, KFPC supercapacitor device displays a better stability owing to its electric double layer nature and abundant active sites for ion interaction inside pores and channels [19].

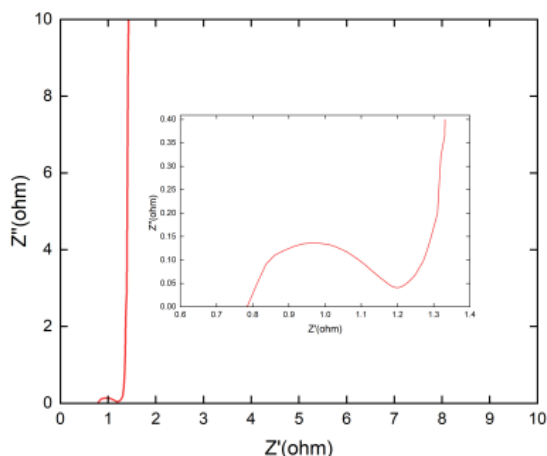


Figure 5. Nyquist plots of KFPC

The EIS of KFPC electrode was tested to explore the capacitive behaviour in Fig. 5. At

high frequency, the intersection point on the real axis represents the electrical conductivity of the electrode, the radius of the curve demonstrated the electron transfer rate during charging and discharging. It is obvious that the KFPC electrode has a lower charge transfer resistance of 0.34Ω and inherent resistance was 0.79Ω, confirming the ideal

capacitive behavior and ion diffusion within the hierarchically porous N-doped network. Sufficient pores, channels and some N-doped functional groups enlarged the presence of KFPC, shorten the ions transfer pathways and improved the conductivity of activated carbon electrode.

4. Conclusion

In this study, a kind of N-doped porous nanostructured carbon material was successfully synthesized from kiwi fruit peel biomass via a facile three-step method, carbonization, acid pickling and activation. The N-doped porous nanostructure of as prepared carbon electrode materials was responsible for electrochemical performance. a very high specific surface area of 2290 m² /g with macropores, mesopores and micropores. The sample also showed superior specific capacitance (265.25 F g⁻¹ at 50 mV s⁻¹ and 249.8 F g⁻¹ at 1 A g⁻¹) and the energy density reached 9.42 wh kg⁻¹ and remained over 80% of when the current density was at 5 A g⁻¹ for 5000 cycles. Every electrochemical performance was higher than commercial activated carbon. The excellent performance of fabricated supercapacitors based on KFPC demonstrated the potential of applying the novel N-doped porous KFPC as an effective supercapacitor electrode.

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