

A new route for the fabrication of corn starch-based porous carbon as electrochemical supercapacitor electrode material



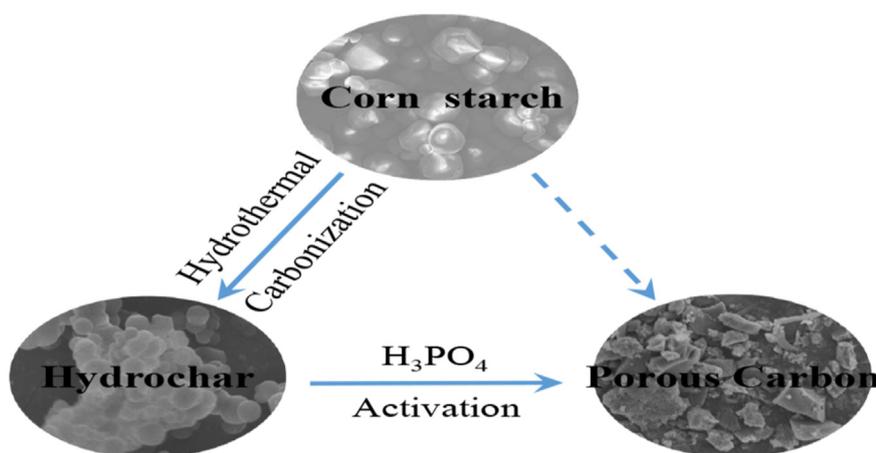
Liyun Pang, Bo Zou, Yongcun Zou, Xue Han, Liyuan Cao, Wei Wang, Yupeng Guo*

College of Chemistry, Jilin University, Qianjin Street 2699, Changchun 130012, China

HIGHLIGHTS

- A new route could convert corn starch to high-performance porous carbon.
- This new route coupled with hydrothermal carbonization and H_3PO_4 chemical activation.
- The porous carbon presented a specific surface area as large as $1239 \text{ m}^2 \text{ g}^{-1}$.
- The specific capacitance of the porous carbon was as high as 144 Fg^{-1} at 0.625 Ag^{-1} .

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 March 2016

Received in revised form 7 May 2016

Accepted 18 May 2016

Available online 19 May 2016

Keywords:

Corn starch

Hydrothermal carbonization

H_3PO_4 activation

Porous carbon

Supercapacitor

ABSTRACT

A new route has been developed for the fabrication of porous carbon from corn starch by a two-step process: hydrothermal carbonization and chemical activation with H_3PO_4 . The as-prepared porous carbons were characterized by scanning electron microscopy, powder X-ray diffraction, fourier transform infrared spectra, C, H, N, O, S analyzer, N_2 adsorption, zeta potential measurements, cyclic voltammetry and galvanostatic charge/discharge techniques. A blocky structure morphology of the porous carbon was achieved. The porous carbons showed a high specific surface area of $1239 \text{ m}^2 \text{ g}^{-1}$ and a large pore volume of $1.40 \text{ cm}^3 \text{ g}^{-1}$. The electrode delivered higher specific capacitance (144 Fg^{-1}) and energy density (19.9 Wh kg^{-1} at a power density of 311 W kg^{-1}) than commercial porous carbon at a current density of 0.625 Ag^{-1} in 6 mol L^{-1} KOH electrolyte. Also, the supercapacitor device exhibited superior cycling stability. The results demonstrated that corn starch-based porous carbons will be a kind of promising electrochemical supercapacitor electrode materials.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Supercapacitor, as a type of state-of-the-art energy storage and supply device, has been attracted increasingly growing attention recently owing to its attractive properties such as high power

* Corresponding author.

E-mail address: guoyupeng@jlu.edu.cn (Y. Guo).

density, large energy density, good rate performance, long cycle lifetime and wide range of applications in electrical vehicles, electric power distribution, digital devices, pulsing techniques, etc [1–3]. The electrode material is a critical factor to determine the performance of the supercapacitor. Up to now, the porous carbon is widely favored as electrode material for electrochemical supercapacitor because of its relatively low cost, high surface area, large pore volume, good electrical conductivity, good chemical stability and environmental compatibility [4–6]. The charge-storage mechanism for the porous carbon can be described as a double-layer model, which is a reversible ion adsorption onto the carbon surface, the charge is reserved in the interface between the carbon electrode and the electrolyte, so leading to the so-called 'double-layer capacitance'.

However, the practical applications of the porous carbon for supercapacitor, whose electrochemical performance mainly depends on the raw material itself and activation method. Nowadays, since high-grade commercial porous carbon specific to electrical double layer capacitor is relatively expensive compare to common grade activated carbon, various natural carbon-rich materials such as coal, coffee beans, palm shells, coconut shells and other lignocellulosic materials have been successfully used as the inexpensive raw materials for the porous carbon preparation in the activation process [7–11]. Biomass has become excellent carbon sources of preparing the porous carbon materials lately. As is well-known, starch, as a green, inexpensive and renewable natural polymer being rich in carbon and can be achieved from large amounts renewable plant resources. It is also the cheapest biopolymer, which is completely biodegradable [12,13]. Corn starch is derived from the fruit of corn, which is one of the highest yield crops. As a high yield crop, corn is widely cultivated in the north of China, where is known as the gold corn belt of the world. Nowadays, the deep processing of corn is the key point of the whole economy and many companies are making use of corn and its byproducts for the preparation of chemical products. Furthermore, corn starch is a relatively pure precursor compared with other types of biomass, so the corresponding products with less impurity and high yield. Thus, corn starch can be used as green carbon source to synthesize materials and the corn starch-based products will be developed rapidly. Chemical activation is a prefer method to obtain high-performance porous carbon from different raw materials compared with physical activation. The most often used chemical activation agents are H_3PO_4 , KOH, NaOH, ZnCl_2 , K_2CO_3 and Na_2CO_3 [14–19]. From both economical and environmental perspectives, H_3PO_4 is a desirable chemical activation agent and it has been reported in many researches. During the activation process, the precursor is impregnated in the H_3PO_4 and is dehydrated, cross-linked along with the increase of the temperature [20]. The micropores and mesopores/macropores come into being as well as high specific surface area and large pore volume in the porous carbon. Moreover, H_3PO_4 can be recovered, the activation condition is milder and the corresponding porous carbon with well-developed porosity and high yield [21–24].

In the previous works, the preparation of corn starch-based porous carbon spheres have been investigated [12,25]. However, the fabrication of porous carbon from corn starch by using H_3PO_4 as activating reagent for supercapacitor electrode material has been seldomly reported. In the present work, we propose a new route to synthesize high-performance porous carbon as electrode material for supercapacitor through a two-step process coupled with hydrothermal carbonization and H_3PO_4 activation by using corn starch as the raw material. Hence, the main objective of this paper is to achieve a two-step process for preparing the porous carbons from corn starch by hydrothermal carbonization and chemical activation with H_3PO_4 . Furthermore, the electrochemical performance of the porous carbons was also studied in detail.

2. Experimental

2.1. Materials

Corn starch was achieved from local supermarket (Changchun, China). Sulfuric acid (98 wt.%) and phosphoric acid (85 wt.%) were purchased from Beijing Chemicals Co. Ltd., which were of analytical grade. Commercial porous carbon (CPC) was high-grade carbon specific to electrical double layer capacitor, which was provided by Kuraray Chemical Company (Japan, YP-80F). Distilled water was used in all experiments.

2.2. Preparation of the porous carbon

Fig. 1 shows the schematic diagram of the preparation process of the porous carbon. A two-step process coupled with hydrothermal carbonization and chemical activation was used for preparation of the porous carbon. Corn starch was hydrothermal carbonized at 95°C for 6 h with 40 wt.% H_2SO_4 , the ratio of starch mass (g) to 40 wt.% H_2SO_4 solution volume (mL) was 1:10, the solid product was collected and washed to neutral and dried in an oven at 120°C overnight to obtain the hydrochar. Then the hydrochar was impregnated with 85 wt.% H_3PO_4 , the impregnation mass ratios of H_3PO_4 to hydrochar were varied from 2:1 to 6:1, the samples were heated up to the activation temperature $400\text{--}600^\circ\text{C}$ for 0.5–2.5 h. Finally, the solid products were washed to neutral and dried in an oven at 120°C for 12 h to obtain the final porous carbons. The porous carbons will be denoted according to the expression: HPC/Temperature ($^\circ\text{C}$)/Time (h)/ H_3PO_4 :hydrochar, for example, the porous carbon obtained at 500°C 1 h when the H_3PO_4 :hydrochar ratio was 4:1, the porous carbon was denoted as HPC/500/1/4:1. All the porous carbons prepared from the above process were heated to 800°C for 1 h under N_2 atmosphere.

2.3. Characterization

The morphology of corn starch, hydrochar and the porous carbon were observed by a JSM-6700F scanning electron microscope (SEM). The crystal structures were analyzed by powder X-ray diffraction (XRD). The surface chemical properties were examined by Fourier transform infrared spectra (FTIR). The elemental analysis of the samples were performed on PerkinElmer 2400C, H, N, O, S analyzer. The Brunauer-Emmett-Teller (BET) surface area and the pore structure were measured by N_2 adsorption at a Micromeritics ASAP 2420 surface analyzer. The specific surface area (S_{BET}) and pore size distribution were determined according to the BET equation and the Density Functional Theory (DFT) method, respectively. The microspore area (S_{mic}) and volume (V_{mic}) were analyzed by the t-plot method. The external area (S_{ext}) was the deduction of S_{mic} from S_{BET} . Zeta potential was measured by using a Malvern Instrument Nano-ZS90 Zeta potential analyzer.

2.4. Electrochemical measurements

The electrochemical performance measurements were carried out on a CHI 660D electrochemical workstation with a conventional three-electrode configuration in 6 mol L^{-1} KOH aqueous electrolyte. The working electrodes were prepared by mixing the sample, acetylene black and polytetrafluoroethylene (PTFE) at a mass ratio of 8:1:1 and then spreaded onto a nickel foam with a coating area of 1 cm^2 . Finally, the as-prepared electrodes were dried at 50°C overnight and pressed at 10 MPa for 3 min. Saturated calomel electrode was used as the reference electrode and platinum foil was used as the counter electrode. The cyclic voltammetry (CV) measurement was conducted at different scan rates from 10 to 50 mV s^{-1} , the galvanostatic charge/discharge measurement was

Download English Version:

<https://daneshyari.com/en/article/591437>

Download Persian Version:

<https://daneshyari.com/article/591437>

[Daneshyari.com](https://daneshyari.com)