Scientific Research Publishing

Journal of Power and Energy Engineering, 2021, 9, 18-25
https://www.scirp.org/journal/jpee
ISSN Online: 2327-5901
ISSN Print: 2327-588X

Porous Carbon from Corn Flour Prepared by H_3PO_4 Carbonization Combined with KOH Activation for Supercapacitors

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How to cite this paper: Li, X.Y. and Wu, G.J. (2021) Porous Carbon from Corn Flour Prepared by H_3PO_4 Carbonization Combined with KOH Activation for Supercapacitors. *Journal of Power and Energy Engineering*, **9**, 18-25.
https://doi.org/10.4236/jpee.2021.98002

Received: July 26, 2021
Accepted: August 15, 2021
Published: August 18, 2021

Abstract

Hierarchical porous activated carbon is a superior material in manufacturing supercapacitors. However, the hierarchical porous structure is hard to obtain from a single activation method. This work was carried out with the anticipation of producing activated carbon by reactivating corn flour with KOH. By employing the electrodes, the supercapacitor demonstrated a high discharge capacitance (151.2 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$), and the specific capacitance is with 3.7 times more capacitance than the activated carbon only through H_3PO_4 activation. The mechanism of improving the electrical performance has been discussed through performing SEM, XRD, EIS, and Raman analysis. The hierarchical porous and disordered structure emerge smaller charge transfer resistance, and fast electron transfer.

Keywords

Activated Carbon, Hierarchical Porous, Reactivating Corn Flour, Supercapacitors

1. Introduction

With the rapid growth of earth population and global industrialization, the demand for energy has reached an unprecedented level. Due to its high power density, the ability of quick charge and discharge, and stability and safety, the supercapacitor has become one of the most valuable and applicable potential research projects [1] [2]. Supercapacitors can be classified as electric double-layer capacitors, faraday pseudocapacitors, and hybrid supercapacitors [3] [4]. With its high power density and long life expectancy, supercapacitors are an ideal replacement for certain battery applications. Electrode materials are critical for supercapacitors, because they play an important role on the electoral chemical performance of supercapacitors. Carbon nanomaterials, such as activated carbon [5], carbon nanotubes [6], and graphene [7], are extremely suitable for electrical double-layer capacitive electrodes due to their large specific surface area and high electrical conductivity.

For supercapacitors, the performance of activated carbon based on biomasses is prominent. Biomass is the organic compound that contains carbon, and activated carbon has been made by heating organic compound in an oxygen-free environment to reduce the non-carbon components. Previous studies have shown that biomasses like argy wormwood [8], orange peel [9], ginkgo leaves [10], bougainvillea flowers [11], and perilla frutescens [12] have been used in preparing activated carbon electrode materials for supercapacitors.

Despite the diversity in biomasses, there are also many activation methods. Biomasses are activated with chemicals under high temperature. Phosphoric acid, zinc chloride, potassium carbonate, sodium hydroxide, potassium hydroxide, and other activating agents can be used to prepare activated carbon. Since macropores, mesopores, and micropores are of extreme importance to capacitor, in order to elevate the properties of the electrodes, it is necessary to construct a porous carbon structure with all three categories of pores. Nowadays, most of the studies on the activation process focus on physical activation method, chemical activation method. However, it is hard to manufacture hierarchical porous activated carbon with a single activation method. What's more, the reactivation on account of perfecting the porous carbon producing procedure has rarely been reported. In this work, synthetic methods of H_3PO_4 solution carbonization and subsequent KOH activation have been tested to prepare activated carbon from corn flour. For corn flour is an easily accessible and cheap biomass, it has been used in the experiment to test the procedure to produce hierarchical porous activated carbon. The reactivated carbon was compared with the carbon that had a single activator: H_3PO_4. Then the properties such as the crystal structure, micromorphology, and electrochemical properties were analyzed to determine the mechanism of two different methods. By employing the electrodes, the supercapacitor demonstrated a high discharge capacitance (151.2 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$). The specific capacitance is 3.7 times than the activated carbon only through H_3PO_4 activation. This investigation of activated carbon by reactivating corn flour with KOH would be valuable for development of the biomass based supercapacitor.

2. Experimental Method

2.1. Preparation of CPs

The corn flour was bought from ANGEL YEAST CO., LTD. Phosphoric acid (H_3PO_4) and corn flour were mixed together with a ratio of 1.2:1 in a beaker. The beaker was heated at 80˚C for two hours and then cooled to room temperature. Then the sample was transferred to a tube furnace at 550˚C for 90 min with an increasing rate of 5˚C/min. After that, half of the sample was obtained and named CP, and half of the sample was separated and grinded with solid potassium hydroxide (KOH) at a weight ratio of 1:2. The sample was then activated for 1 h at 800˚C. Lastly, the sample was obtained by using 0.5 molar diluted hydrochloric acid (HCl) for cleaning and deionization, and this sample was named CHP12.

2.2. Characterization

The morphology and phase structure of CP and CHP12 samples were characterized by sacanning electron microscopy (SEM, GeminiSEM 500), and X-ray diffraction (XRD, Cu Ka, 1.5418 Å), respectively. Raman scattering spectra was performed on a Renishaw System 2000 spectrometer by adopting 514.5 nm Ar^+ excitation line.

2.3. Electrochemical Measurements

Cyclic voltammetry (CV) curves were measured separately at 5, 10, 20, 40, and 60 mV/s. Galvanostatic cha-discharge (GCD) curves were studied separately at 1, 2, 5, 10, and 20 A/g. Electrochemical impedance spectroscopy (EIS) was investigated at 0.01 Hz - 100 kHz. The all electrochemical performances were measured through the electrochemical station (CHI660e).

3. Results and Discussion

Figure 1 shows the SEM images which demonstrated the morphology and microstructure of the CP and CHP12 samples. It can be observed from **Figure 1(a)** that the interior of the material has a large number of pores due to the activation by H_3PO_4. **Figure 1(b)** displays a disordered structure with a sheet and particle arrangement of CHP12 sample, implying that KOH help to form thin sheets of carbon and to create a porous structure. The difference of morphology, which resulted from various activation methods and activators, between **Figure 1(a)** and **Figure 1(b)** contributes to the difference of electrochemical performance.

In order to investigate the difference between the structure of CP and CHP12, XRD patterns of the two samples were carried out and displayed in **Figure 2**. A broad diffraction peak and a weak diffraction peak have been observed located at

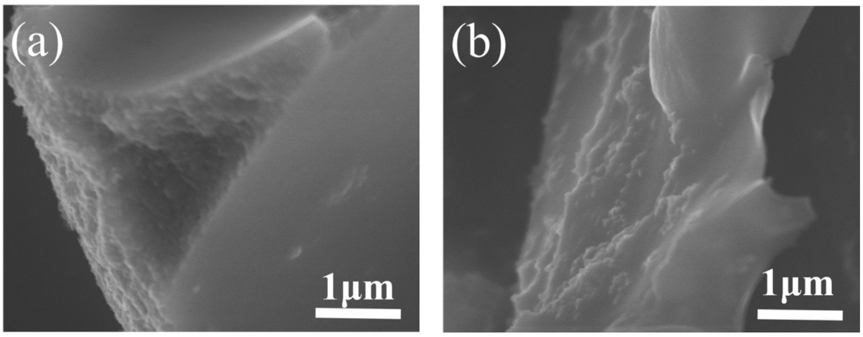

Figure 1. SEM images of (a) CP and (b) CHP12 samples.

2θ of 25˚ and 44˚ respectively, corresponding to the (2 0 0) and (1 0 0) planes of graphitic carbon layers [13]. Compared with CP, the higher intensity of CHP12 in the low angle range shows that there is an incline in the amount of micropores by the activation of KOH. These micropores, along with the pores formed by H_3PO_4, built the hierarchical porous structure [8]. CHP12 demonstrates much weaker and broader peaks belonging to carbon plane; this indicates that KOH reactivation has led to the destruction of identical structural domains and the arbitrary distribution of carbon atoms [14]. Additionally, the disordered structure of CHP12 sample can effectively improve the conductivity of materials. For further verification, Raman characterization was performed in **Figure 3**. According to **Figure 3**, there are two peaks located at about 1350 and 1597 cm^{-1} that are corresponding to D-band (matching the disorder carbon atoms with sp^2 hybridization) and G-band (matching the E_{2g} graphitic pattern for the carbon), respectively [15]. The intensity ratio between D and G bands (I_D/I_G) apparently decreases from 1.03 for CHP12 to 0.77 for CP. This shows that the KOH reactivation might result in more defects, and this result is consistent with the SEM and XRD analysis.

The electrochemical properties of CP and CHP12 samples were tested in 6 M KOH solution in three-electrode system. First, as shown in **Figure 4(a)**, CV measurements have been performed to study the supercapacitive behavior. Both of the CV curves have quasi-rectangular shape at 5 mV/s, which indicates a representative charge/discharge behavior electrical double-layer capacitance. It is noticeable

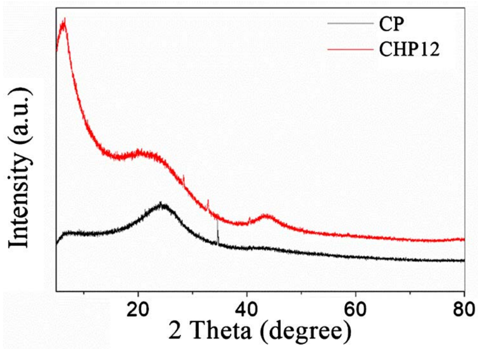

Figure 2. XRD patterns for CP and CHP12 samples.

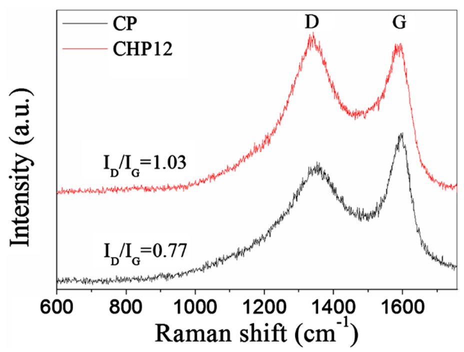

Figure 3. Raman spectra for CP and CHP12 samples.

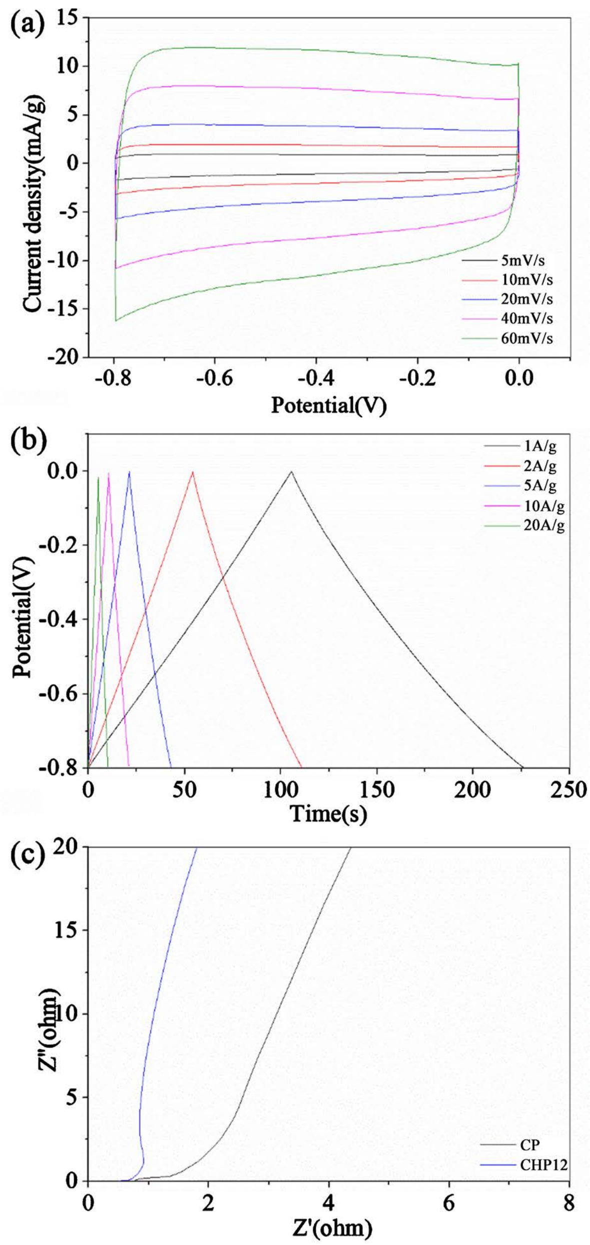

Figure 4. Electrical performance of the sample CHP12 in a three-electrode system. (a) CV curves at various scan rates. (b) GCD curves at various current densities. (c) Nyquist plots.

that the area bounded by the CV curve of CHP12 is much larger than that of CP. Due to its hierarchical porous and more disordered structure, which is caused by KOH reactivation, CHP12 sample presented much higher capacitance compared with CP sample. Next, the GCD curves for the two samples at 1 A/g are shown in Figure 4(b). Both GCD curves show triangular shapes representing electrical double-layer capacitance. The CP electrode that has only been activated by H_3PO_4 shows the shorter charge/discharge time and lower specific capacitance (40.9 $F\cdot g^{-1}$ at 1 $A\cdot g^{-1}$). Meanwhile, CHP12 sample by KOH reactivation exhibits much higher charge/discharge time and specific capacitance (151.2 $F\cdot g^{-1}$ at 1 $A\cdot g^{-1}$). EIS is a very useful technique for studying electrochemical behavior. The ideal Nyquist plot of electrochemical impedance spectroscopy for an electrical double-layer capacitor consists of a 45˚ line in the high-middle frequency region and a vertical line in the low frequency region. The inclined 45˚ line is ascribed to the consequence of the distributed resistance and capacitance in porous carbon electrode, and the slight deviation from the ideal vertical line can be interpreted as a result from the pore size distribution of porous carbon materials. The EIS has been carried out as shown in Figure 4(c). The "tails" of CP and CHP12 samples at the low frequency region are subvertical, indicating a typical supercapacitive behavior. Compared with the CP curve, the CHP12 curve has a shorter transition domain (in the high-middle frequency region) and a steeper slope (in the low frequency region), suggesting a smaller charge transfer resistance against the electrolyte penetration into the pores and channels. The EIS measurements provide an explanation for the capacitive behavior and the rate performance of the material. The influence of hierarchical porous and more disordered structure is demonstrated in the form of data.

The electrical character of CHP12 was further tested using CV and GCD under different conditions. As shown in Figure 5(a), all of the CV curves, from 5 mV/s to 60 mV/s, demonstrate quasi-rectangular shapes, even at a high scan rate. This indicates that fast electron transfer and facile ion transport on CHP12. Figure 5(b)

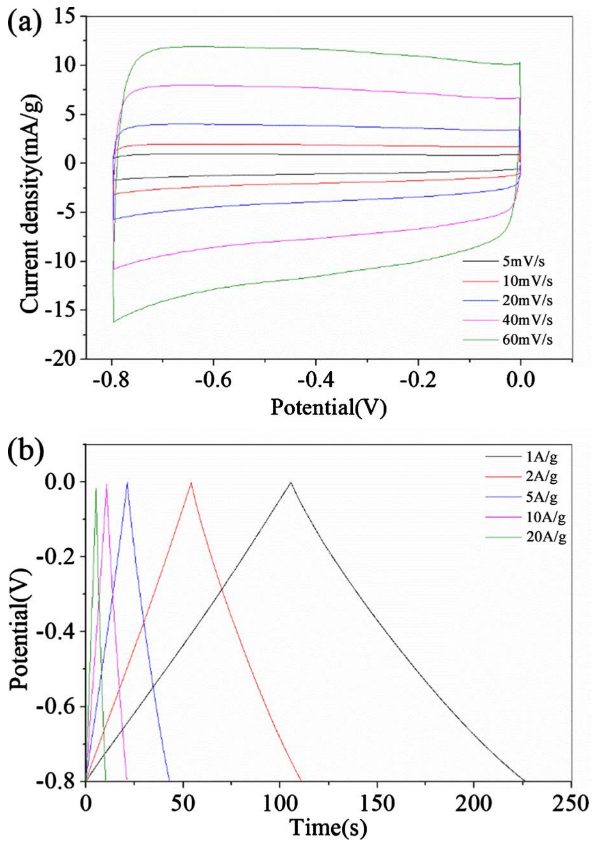

Figure 5. Electrical performance of the sample CHP12 in a three-electrode system. (a) CV curves at various scan rates. (b) GCD curves at various current densities.

shows the GCD curves of CHP12 at various current densities, from 1 to 20 A/g. All of the GCD curves stay in linear shapes, suggesting the characters of small internal resistance of the supercapacitor based on CHP12.

4. Conclusion

In summary, corn flour based porous carbon electrode material for high-performance supercapacitor was prepared by activation of H_3PO_4 and reactivation of KOH. The reactivated carbon was compared with the carbon that had a single activator: H_3PO_4. The activated carbon obtained through the process has hierarchical porous and disordered structure. The properties of CHP12 are different from that of CP. Based on the analysis, CHP12 has higher charge/discharge time, higher specific capacitance, smaller charge transfer resistance, and fast electron transfer. As a result, CHP12 material is a fabulous and superior choice to reuse and process corn flour as electrode material for supercapacitor. The simple and low-cost method for obtaining high performance hierarchical porous activated carbon would be valuable for development of the biomass based supercapacitor.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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