Effect of Biochar Loading on Carbon Nanofibrous Sponge Produced from Biochar and Electrospun Polymer Nanofibers

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ABSTRACT

This study aims to process a specific waste product. Particularly, the 3D carbon nanofibrous sponges are prepared by using the commercial biochar from Black Owl Biochar™, where the electrospun polymer (i.e., polyacrylonitrile - PAN and polyimide - PI) nanofibers work as the skeleton support. In the precursor sponge, biochar's weight ratio to polymer varies from 4:1 up to 20:1. The heat treatment of the precursor sponge includes the stabilization in air and carbonization in argon. This process transforms it into a carbon nanofibrous sponge. It is observed that the carbonization increased the elasticity of the sponge and also the mechanical stability. In addition, the electrochemical study of the manufactured carbon nanofibrous sponge indicates its potential use in making supercapacitor electrodes. Besides, the increase in the biochar weight ratio could be effective in increasing the energy density of the supercapacitor.

Keywords: Electrospinning, electrospraying, biochar, carbon nanofibrous materials, Energy storage, and conversion

1 INTRODUCTION

The 3D sponges made of short electrospun nanofibers or nanofibrous membranes have growing attention due to their lower density, large porosity, exceptional mechanical stability, and high mass transport capabilities. The sponges made from biochar are reported in [1]. The thermochemical production [2] of the biochar is carried out in several ways, for example, conventional carbonization, i.e., slow pyrolysis, fast pyrolysis, hydrothermal treatment [3-5] with and without catalyst, etc.

The biochar from hydrothermal treatment is a waste byproduct and is often used for heat generation and soil fertility improvement [6]. Therefore, the fabrication of advanced 3D nanofibrous structures/sponges using biochar would be economically advantageous [1].

However, the biochar cannot be readily used to make a biochar sponge. It requires support to form the sponge structure. The electrospun carbon nanofibers (ECNFs) can be used as the skeleton support. The ECNFs are known for their excellent chemical, electrical, and mechanical properties [7, 8]. Therefore, ECNFs have adopted a variety of application areas, for example, energy storage, catalysis, sensors, etc. [9, 10]

Polyacrylonitrile (PAN) can be used to produce ECNFs. However, the elasticity/robustness of sponges fabricated using PAN nanofibers alone is poor and can be improved with a combination of different electrospun polymer nanofibers. For example, polyimide (PI) nanofibers can be mixed with PAN nanofibers [11].

Here we report the 3D carbon nanofibrous sponges prepared by using the commercial biochar from Black Owl Biochar™ and hydrothermal liquefaction. In the precursor sponge, biochar's weight ratio to polymer varies from 4:1 up to 20:1. The heat treatment of the precursor sponge transforms it into a carbon nanofibrous sponge. In addition, the electrochemical study of the carbon nanofibrous sponge is presented.

2 MATERIALS AND METHODS

2.1 Materials

Polyacrylonitrile (PAN, Mw = 150,000), poly(vinyl alcohol) (PVA, Mw = 13,000–23,000), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), poly(amic acid) (PAA) solution, ethanol, acetone, and were purchased from Sigma-Aldrich and used without further purifications. The biochar sample was purchased from Black Owl Biochar. The Black Owl Biochar (TM) products have 85% Organic Carbon.

2.2 Mechanical Breaking of Biochar

The biochar (in the form of grain, with particle sizes of millimeters) was first dispersed in deionized water and then put into a high-speed blender (i.e., a Waring Laboratory Blender). After being blended for 10 min, the suspension of biochar particles was filtered using the vacuum filtration process and then dried for further use.

2.3 Fabrication of Biochar-Containing Sponge

A block flow diagram of the fabrication of the biochar-containing sponge is shown in Figure 1. The PAN and PI nanofibrous membranes acquired after electrospinning was initially treated with oxygen plasma (Plasma Etch, Inc., Carson City, NV, USA) for 3 min to make the nanofiber surfaces more hydrophilic. 1.2 g PAN and 0.3 g PI (i.e., PAN/PI weight ratio of 4/1) nanofibrous membranes were first to cut into small pieces and then put into the high-speed blender with ~ 750 g deionized water. After being blended for 10 min, a uniform suspension of shortened/fragmented PAN and PI nanofibrous membranes was acquired. Subsequently, 0.1 g ethanol and 1.6 mL PVA aqueous solution (0.05 g mL^{-1}) was added per 30 g suspension. Later, various biochar loading was used to prepare the uniform suspension containing biochar particles and shortened/fragmented electrospun nanofibrous membranes. The biochar loading was varied to have the weight ratio of nanofibers to biochar being 1:4, 1:8, and 1:12. A sample dataset for the biochar sponge formulation is provided in Table 1.

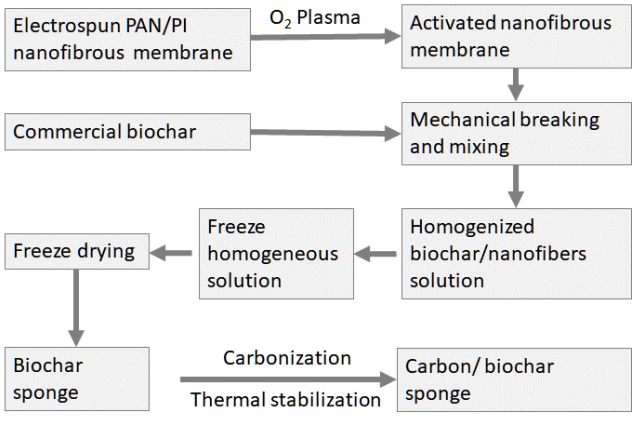

Figure 1: Block flow diagram of manufacturing the carbon/biochar sponge.

Finally, each suspension was sonicated using a 100 W ultrasonic probe (Branson Ultrasonics Corp., Danbury, CT) for 30 min to mix different components in the suspension.

Table 1: Sample data for biochar sponge with PAN/PI/PVA to biochar ratio of 1:12.

Trial	*Homogenous solution + biochar (g)	Sponge weight after freeze-drying (g)	Calculated PAN/PI/PVA in the sponge	Calculated biochar in the sponge
1	3.4884	0.2132	0.0174	0.1958
2	3.4803	0.2217	0.0174	0.2043
3	3.5082	0.2104	0.0175	0.1929
4	3.5595	0.2271	0.0178	0.2093
5	3.5310	0.2232	0.0177	0.2055
6	3.5536	0.2220	0.0178	0.2042
7	3.5418	0.2208	0.0177	0.2031
	*Homogeneous solution: PAN/PI/PVA + water + ethanol			

The uniform suspension was then transferred into 8-10 molds, each with 3.5 g of suspension, and placed in a freezer. After that, the obtained sample was put into a pre-cooled glass flask and freeze-dried at room temperature for 72 hours. The carbon nanofibrous sponge is shown in Figure 2.

Figure 2: Carbon nanofibrous sponge before carbonization and thermal stabilization from PAN/PI/PVA to biochar ratio of 1:12.

2.4 Thermal Stabilization and Carbonization

Thermal stabilization and carbonization were carried out in a Lindberg 54453 Heavy Duty Tube Furnace (TPS Co., Watertown, WI, USA). During the stabilization process, a constant airflow was maintained through the furnace. Freeze-dried sponges were first heated from room temperature to 100 °C at the rate of 1 °C min^{-1} and then held at the temperature of 100 °C for 1 h; thereafter, the sponge was heated to 230 °C at the rate of 0.5 °C min^{-1} and then held the temperature at 230 °C for 3 h. The stabilized sponge was then carbonized at the rate of 5 °C min^{-1} to 600, 800, 1000, and 1200 °C, respectively; at each temperature, the samples were kept for 1 h.

3 RESULTS AND DISCUSSIONS

The BET surface area for the Black Owl Biochar TM is 27.82 m^2/g. On the contrary, it is 51.7 m^2/g hydrothermally

treated biochar in the lab. Here we report the electrochemical properties of the commercial biochar from Black Owl Biochar™. The results from the hydrothermally treated biochar can be found in [1].

Electrochemical properties of the fabricated carbon nanofibrous sponge were studied by the Nyquist plot and the cyclic voltammetry (CV) tests in 6 M KOH aqueous electrolyte from − 0.6 to 0.6 V (vs. SCE). The impedance plot of the sample having the PAN/PI/PVA to biochar being 1:12 is shown in Figure 3. The impedance is measured before and after cyclic voltammetry (CV), carbonization, and thermal stabilization (CT). It is observed that each impedance plot before and after carbonization and thermal stabilization (CT) has a noticeable arc at higher frequency regions and a nearly vertical line at lower frequencies. The vertical lines indicate faster ion diffusions in the electrolyte. The cyclic voltammetry (Figure 4) of the sample with a 1:12 ratio of PAN/PI/PVA to biochar was measured at scan rates of 10, 30, and 50 mV/s. A distinct redox peak can be identified in each of the CV curves that is indicative of the pseudo-capacitive behavior of the carbon nanofibrous sponge.

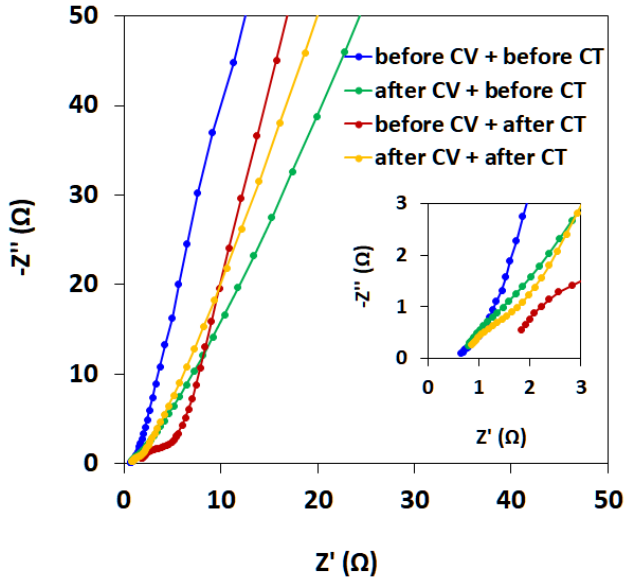

Figure 3: Impedance plot of the sample having the ratio of PAN/PI/PVA to biochar being 1:12 before and after cyclic voltammetry (CV) and carbonization and thermal treatment (CT) of commercial Black Owl Biochar™.

In Figure 5, impedance plots of the carbon nanofibrous sponge electrode before and after the cyclic voltammetry of samples S1, S2, and S3 where PAN/PI/PVA ratios to biochar are 1:4 (S1), 1:8 (S2), and 1:12 (S3) are provided. It is observed that the impedance curves obtained from the commercial carbon nanofibrous sponge after CV are identical, indicating stable electrochemical properties. The current density vs. active loading of commercial biochar is shown in Figure 6. The current density of the biochar sponge increases with the increase of the active loading of the biochar.

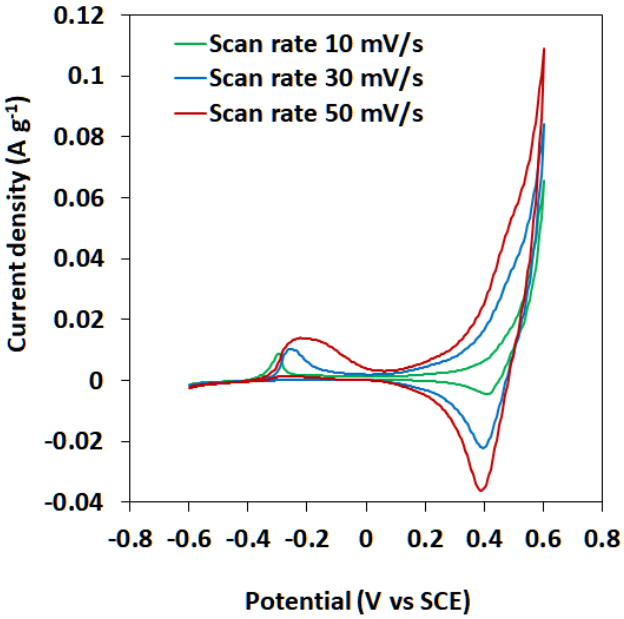

Figure 4: Cyclic voltammetry of the sample from commercial Black Owl Biochar™ having the ratio of PAN/PI/PVA to biochar being 1:12 before carbonization and thermal treatment (CT).

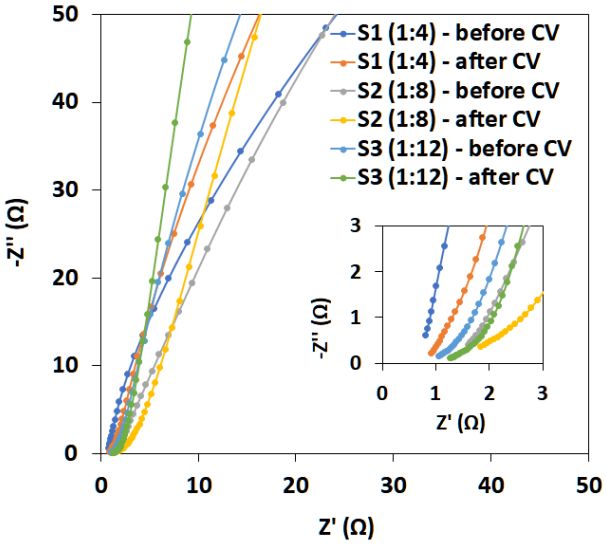

Figure 5: Impedance plots of the carbon nanofibrous sponge electrode after the cyclic voltammetry of samples S1, S2, and S3 where PAN/PI/PVA ratios to biochar are 1:4 (S1), 1:8 (S2), and 1:12 (S3).

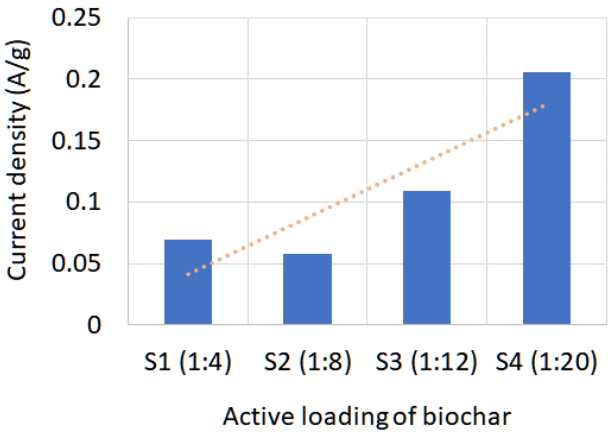

Figure 6: Current density vs active loading of commercial biochar.

4 CONCLUSIONS

The 3D carbon nanofibrous sponges prepared by using the commercial biochar from Black Owl Biochar™ are reported. In the precursor sponge, biochar's weight ratio to polymer varies from 4:1 up to 20:1. The heat treatment of the precursor sponge transforms it into a carbon nanofibrous sponge. In addition, the electrochemical study of the manufactured carbon nanofibrous sponge indicates that the current density increases with an increase in the active loading of the biochar as expected.

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