Biomass derived carbon materials for electrochemical energy storage devices

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Abstract. This paper presents water hyacinth and sensitive plant derived carbon as a biomass carbon with utility for electrochemical energy storage. The prepared samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Electrochemical properties of the carbon materials were investigated by using cyclic voltammetry and galvanostatic charge-discharge. The specific capacitance value of 38 and 16 F g\textsuperscript{-1} were observed for biomass carbon of water hyacinth and sensitive, respectively.

1. Introduction

Supercapacitors are electronic devices which are widely used to store extremely large amounts of electrical charge. They are also known as electric double-layer capacitors (EDLC) or ultracapacitors. Supercapacitors may be used in a variety of applications such as vehicles, electric power distribution, railways telecommunications, and other consumer electronic products etc. [1 – 4]. In particular, carbon-based EDLC materials are used to electrode for supercapacitors because of their good cycle lifetime, high maximum power density, considerable energy density, and environmental friendliness [1, 5 – 7]. Water hyacinths (WHs) and sensitive plant (SP) are two of the fastest growing plants known. It is traditionally considered as a weed and found to affect water bodies across the globe [8, 9]. It will rapidly and thoroughly cover entire surfaces of lakes and ponds – dramatically impacting water flow, blocking sunlight to native submerged plants, and starving the water of oxygen often killing wildlife such as fish.

In this paper, a low-cost biomass carbon derived from WHs and SP are prepared by carbonization process and then employed as electrode materials for EDLC. The microstructures and characterization were described using well-known techniques. The electrochemical properties of the biomass carbons have been discussed.

2. Experimental procedure

The fresh WHs and SP were cuted into small pieces, washed using water to remove the mud and other dirt, and dried in an oven at 80 °C. The clean and dried water hyacinth and sensitive plant were carbonized at 400 °C in a tubular furnace for 2h without an oxygen. The prepared samples were...
characterized by X-ray diffraction (XRD) using a CuKα radiation with λ = 0.154060 nm (D2, Bruker, Germany). The morphology of the as-prepared materials was investigated using field emission scanning electron microscopy (FE-SEM, Carl Zeiss, Auriga).

The electrochemical measurements were performed on an Metrohm Autolab (PGSTAT302N). The electrochemical performance of the electrodes was tested by using a standard three electrode configuration comprising a platinum wire counter electrode, an Ag/AgCl reference electrode, and a working electrode. The working electrodes were prepared by mixing active materials, a polyvinylidene difluoride (PVDF) binder and acetylene black at a weight ratio of 8:1:1 using 

\[\text{NMP}\] as a solvent to form a slurry. The mixture solution was painted onto nickel foam and dried at 80 °C for 24 h in air. The Ni foam was pressed at 20 MPa before serving as the working electrode in a three-electrode system. The KOH 6M was used as the electrolyte solution in this study. Cyclic voltammetry (CV) measurements were performed at different scan rates (2 to 100 mV s\(^{-1}\)) from -0.9 to 0.1 V. Galvanostatic charge-discharge (GCD) measurements were operated at different current densities ranging from 0.2 to 1 A g\(^{-1}\) with cutoff voltage of -0.9 to 0.1 V. The specific capacitance, energy density, and power density of the cells were calculated by the following equations [10 – 13].

\[
C_{CV} = \frac{1}{m \Delta V} \int I dV
\]  

(1)

\[
C_{CD} = \frac{I \Delta t}{m \Delta V}
\]  

(2)

\[
E = \frac{1}{2} C_{CD} \Delta V^2
\]  

(3)

\[
P = \frac{E}{\Delta t}
\]  

(4)

where \(C_{CV}\) (F g\(^{-1}\)) and \(C_{CD}\) (F g\(^{-1}\)) are the specific capacitance from CV and GCD techniques, respectively. \(I\) is current (A), \(m\) is active mass (g), \(E\) is energy density (mWh g\(^{-1}\)), \(\Delta V\) is potential windows (V), \(\Delta t\) is discharge time (s), and \(P\) is power density (mW g\(^{-1}\)).

3. Results and discussion

The SEM image of WHc and SPc are shown in Figure 1(a) and (b), respectively. It was clearly seen that the carbon has sheet-like shape with a large uniform rough surface. It can be observed that the bulk size several micrometres was observed in both prepared. Figure 2 shows the XRD patterns of the WHc and SPc samples. The as synthesized samples exhibit two broad diffraction peaks at 2θ = 23.12° and 44.34°, which may be attributed to the (002) and (100) crystal planes of partially graphitised carbon [14 – 15].

Figure 3(a) and (b) shows CV curves of WHc and SPc at different scan rates of 2 to 100 mV s\(^{-1}\). Apparently, the current increases with increasing of scan rate. The voltammogram area of WHc larger than that of SPc as seen in Figure 3(c). Figure 3(d) shows the corresponding specific capacitance of all as a function of scan rate. The specific capacitance decreased with increasing of scan rate. At low scan rates there is enough time for ions to penetrate deeply into pores producing high charges and higher specific capacitance. As the scan rate increases the diffusion of electrolyte ion into electrode internal structure and pore become difficult and ineffective interaction between the electrolyte and electrode materials occurs therefore the specific capacitance is decrease. At a scan rate of 2 mV s\(^{-1}\), all the electrodes shown the highest specific capacitance. The maximum value of 38 and 16 F g\(^{-1}\) were observed for Whc and SPc, respectively. However, the values are much lower than Figure 4(a) and (b) show the GCD curves of WHc and SPc, respectively at different current densities (0.2–1.0 A g\(^{-1}\)). The asymmetry...
with distortion curvature indicates a pseudocapacitive contribution coupling with a weak EDLCs reaction.

Figure 1. SEM images of (a) the water hyacinth carbon (WHc) and (b) the sensitive plant carbon (SPc).

Figure 2. XRD patterns of water hyacinth and sensitive plant derived carbons.

The charge/discharge curves of WHc and SPc at 1 A g\(^{-1}\) are presented in Figure 4(c). The WHc electrode show longer charge and discharge time than that of SPc electrode. The specific capacitance calculated from the discharging time is shown in Figure 4(d). It was found that, the specific capacitances decreased with an increasing of current densities. A comparison of power and energy density of both electrodes is displayed by the Ragone plot as shown in Figure 5. The WHc electrode still outstripped the efficiency of the SPc electrode, because it stores energy of \(~1.8\) mW h g\(^{-1}\) at a high-power density of \(~562\) mW g\(^{-1}\) demonstrating faster charging/discharging. The corresponding specific capacitance (\(C_s\)) energy densities (\(E\)) and power densities (\(P\)) are listed in Table 1 and presented as Ragone plot (Figure 5).
Table 1 Summary of the electrochemical performance of WHc and SPc.

| Sample | Current densities (A g\(^{-1}\)) | \(C_s\) (F g\(^{-1}\)) | \(E\) (mW h g\(^{-1}\)) | \(P\) (mW g\(^{-1}\)) |
|--------|---------------------------------|-----------------|-----------------|-----------------|
|        | 0.2                             | 38.5            | 8.5             | 126             |
|        | 0.4                             | 17.4            | 3.6             | 245             |
| WHc    | 0.6                             | 13.4            | 2.6             | 357             |
|        | 0.8                             | 11.3            | 2.1             | 463             |
|        | 1.0                             | 10.1            | 1.8             | 562             |
|        | 0.2                             | 7.7             | 1.8             | 129             |
|        | 0.4                             | 4.4             | 1.0             | 255             |
| SPc    | 0.6                             | 3.5             | 0.8             | 382             |
|        | 0.8                             | 3.0             | 0.7             | 509             |
|        | 1.0                             | 3.1             | 0.7             | 638             |

Figure 3. CV curves of (a) WHc (b) SPc electrodes between -0.9 to 0.1 V at different scan rates from 2 to 100 mV s\(^{-1}\) (c) comparison of the CV curves of WHc and SPc obtained scanning rate of 2 mV s\(^{-1}\) and (d) comparison of the specific capacitance as a function scan rate of samples.
Figure 4. GCD curves of (a) WHc (b) SPc electrode at different current densities (c) The comparison of GCD curves between WHc and SPc electrodes at a current density of 1.0 A g\(^{-1}\) and (d) The specific capacitances of WHc and SPc electrodes as a function of current density.

Figure 5. Ragone plots of WHc and SPc electrodes.
4. Conclusions
We have successfully prepared biomass carbon from WH and SP raw materials by using carbonization process. The maximum specific capacitance value of 38 and 16 F g\(^{-1}\) at 2 mV s\(^{-1}\) using CV, 38 and 7 F g\(^{-1}\) at 0.2 A g\(^{-1}\) (using GCD) were observed for WHc and SPc, respectively. The biomass carbon has a deliver a desirable capacitance and rate performance in EDLCs. The results indicate that the prepared biomass carbon can be used as an alternative electrode material in energy storage devices.

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