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SHORT COMMUNICATION

Feasibility of bamboo-based activated carbons for an electrochemical supercapacitor electrode

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Abstract−This study focused on the preparation and electrochemical properties of bamboo-based activated carbons (ACs) through carbonization and subsequent activation with steam and non-aqueous electrolyte solutions. The specific surface areas and the capacitances of samples ranged from 445 to 1,025 m^2/g and from 5 to 60 F/g, respectively, depending on the activation conditions. The sample activated at 900 °C for 60 min under our experimental conditions exhibited the highest capacitance and the largest specific surface area.

Key words: Bamboo, Activated Carbon, Electrochemical Supercapacitors

INTRODUCTION

Though various materials have been tried as electrochemical double-layer capacitors, the application is still limited due to the low energy density [Lee et al., 2001]. Recently, in order to enhance the energy density of capacitors, many researchers have put much effort in developing and modifying carbonaceous materials, such as controlling the pore size distribution, introduction of electroactive metallic particles or electrical conducting polymers and fabrication of the hybrid-type cell. Various forms of carbonaceous materials, i.e., powder, fiber, paper (fabric or web), carbon nanotubes and the related nanocomposites are candidates for capacitor electrodes [Frackowiak and Beguin, 2001; Kim and Yang, 2003]. Many naturally occurring materials such as coconut, bamboo, wood, cotton and man-made polymers like phenolic-resin, pitch, polyacrylonitrile (PAN) etc., have been tried as possible precursors for manufacturing activated carbon (AC) [Lee et al., 2004; Yang, 1986]. Among them, bamboo is a very attractive material for the bio- and AC industry in Korea and other countries, due to its excellent properties of the antibacterial and deodoration effect of the vinegar (by-product), and the refine distilled liquor industry [http://www.jinro.co.kr]. However, the structural characterizations and the electrochemical properties of bamboo-based ACs have not been reported yet. In the present study, the AC samples were prepared from bamboo with steam. The properties of the double-layer capacitance for the bamboo-based AC are discussed in detail in order to confirm the feasibility for the electrical device industry.

EXPERIMENTAL

The bamboo was obtained from Damyang (2-3 years old, Phyllostachys, Korea). The samples were crushed and then washed with distilled water, and dried in a vacuum oven at 150 °C for 24 hrs. The raw materials were carbonized at 1,000 in a N_2 flow for 1 h. The carbonized samples were ball-milled into powder by using an alumina milling ball with average diameters of 40 mm. Then, samples were treated with 3 M HCl solution, in order to remove the ash compounds. The carbonized-milled samples were activated by supplying 30 vol% of steam in the carrier gas of N_2 at 700, 800 and 900 °C for 60 min. Specific surface areas and pore size distributions of the samples were evaluated by using the Brunauer-Emmett-Teller (BET) equations. The samples were preheated at 423 K for 2 hours under vacuum prior to the adsorption measurements. X-ray diffraction (XRD, CuK_α λ=1.54056 Å Ultima-, Rigaku, Japan) analysis was used to investigate crystallites.

The electrodes were prepared in the form of disks with 80 wt% contents of bamboo-based ACs, 10 wt% of acetylene black and 10 wt% of binding substance (polytetrafluoroethylene, PTFE). Two-electrode supercapacitors cells were fabricated with two 3.14 cm^2 electrodes in 1 M tetraethylammonium tetrafluoroborate (Et_4NBF_4, TEA)/propylene carbonate (PC), in an nonaqueous electrolyte solution, a polypropylene separator (Cellgard 3501, Scimat Co., UK), and an Al foil 20 m in thickness as a current collector. Cyclic voltammetry of the unit cell was performed in the potential range of 0 to 2.5 V at a scan rate ranging from 1 to 500 mV/sec. The capacitance is calculated from the CV curves. Assuming the total weight of both positive and negative electrodes except for the current collectors is W, the capacitance, C, for a two electrode system is:

$$C = \int i dt/dv \tag{1}$$

where i is the current, t is the time and v is the voltage. The specific capacitance is calculated as follows:

$$C_{spec} = \frac{4C}{W} \tag{2}$$

All the electrochemical measurements were carried out at 25 °C using 1 M TEA as an electrolyte.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the bamboo-based carbonized

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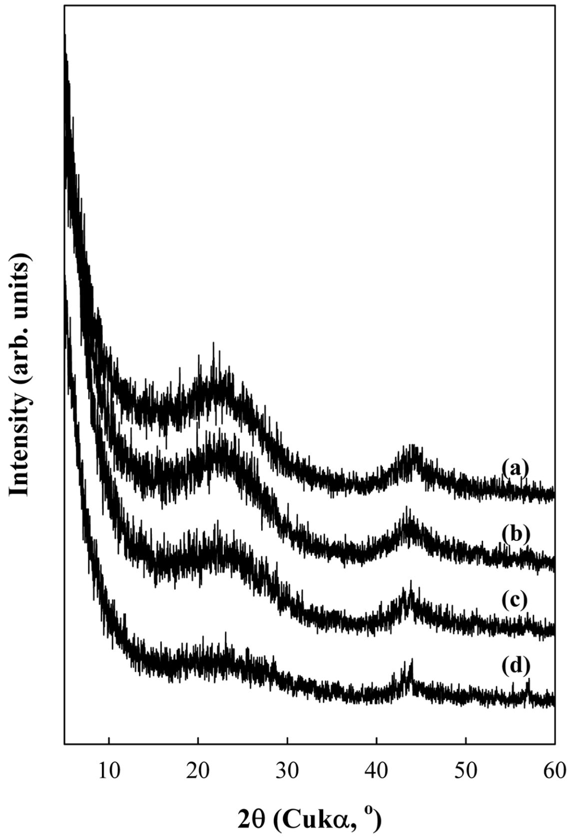

Fig. 1. XRD patterns of bamboo-based carbonized and activated samples: (a) carbonized at 1,000, (b) activated at 700, (c) 800 and (d) 900 °C.

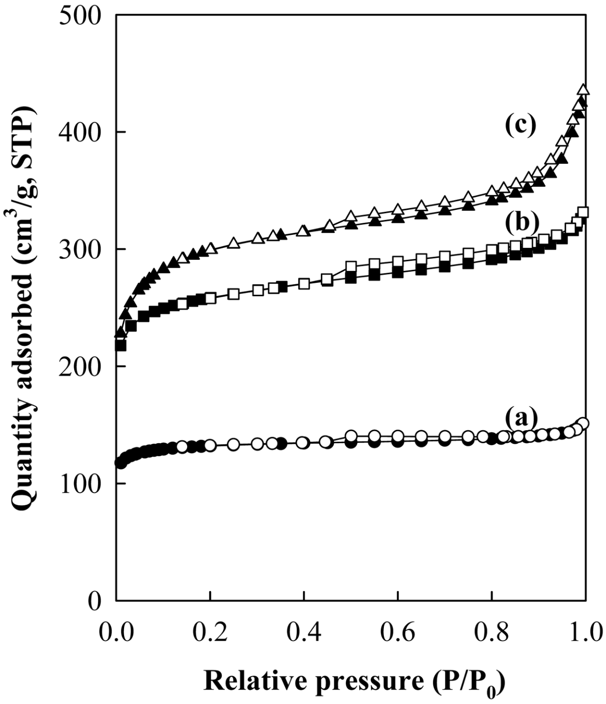

Fig. 2. Nitrogen adsorption isotherms at 77 K for bamboo-based ACs: (a) 700 °C, (b) 800 °C, and (c) 900 °C.

and activated samples as a function of activation temperature. The XRD patterns of carbonized samples showed two broad peaks near 2θ=25° and 43°, corresponding to the crystalline graphite. The peaks representing (002) and (100/101) plane slightly broaden with increasing activation temperature due to the creation of porous structure in AC surface. In the case of activated samples, all patterns were typical of amorphous carbon, composed of a broad (002) peak and (10) peak attributed to micrographite structure. To characterize the structural changes of ACs, structural parameters including porosity parameters are summarized in Table 1. The effect of pore rearrangement on the adsorption properties of bamboo-based ACs was investigated by nitrogen adsorption measurements at 77 K. The volume of adsorbed nitrogen appeared to have a tendency to increase with increasing activation temperature in the range of 700 to 900 °C. All results are typical of type I isotherms with negligible hysteresis effect. The types of isotherms gradually change to another form with larger pores. With increasing activation temperature, the angle of the round knee between the initial steep branch and the plateau became wider, and the plateau dramatically further increased with a slope along the pressure axis. These results may be related to the variation of the pore size distribution, that is, the induction of wider micropores and creation of mesopore with increasing in the activation temperatures. The BET specific surface areas and total pore volumes were linearly increased with an increase in evaluated activation temperature (Table 1).

Potential cyclic voltammetric measurements of the bamboo-based AC electrode supercapacitors were conducted within a potential window of 0.0 V to 2.5 V to analyze the electrochemical behavior of the electrodes. The typical cyclic voltammograms (CV) of the capacitor cells at 5 mV/s scan rate are shown in Fig. 3. The figures demonstrate that the electrodes are stable in the TEA non-aqueous

Table 1. Surface characterization of the bamboo-based ACs

Activation temp. (°C)	d_{002} (nm)	L_{c002} (nm)	BET S.S.A (m^2/g)[a]	Micro S.S.A (m^2/g)	Pore volume distribution (%)		V_{meso} (cm^3/g)[b]	V_{micro} (cm^3/g)[c]	T.P.V. (cm^3/g)	W_{micro} (nm)[d]
					Micro	Meso				
700	0.386	1.02	445	383	82	18	0.045	0.202	0.247	1.03
800	0.394	0.93	874	673	69	31	0.188	0.418	0.606	1.02
900	0.396	0.92	1,025	675	61	39	0.311	0.486	0.797	1.02

[a]BET S.S.A calculated by BET method.
[b]V_{meso}: mesopore (1.7-300 nm) volume calculated with Barret, Joyner and Halenda (BJH) method based on the Kelvin equation.
[c]V_{micro}: micropore volume calculated with Horvath-Kawazoe (HK) method.
[d]W_{micro}: average micropore width calculated with HK method.

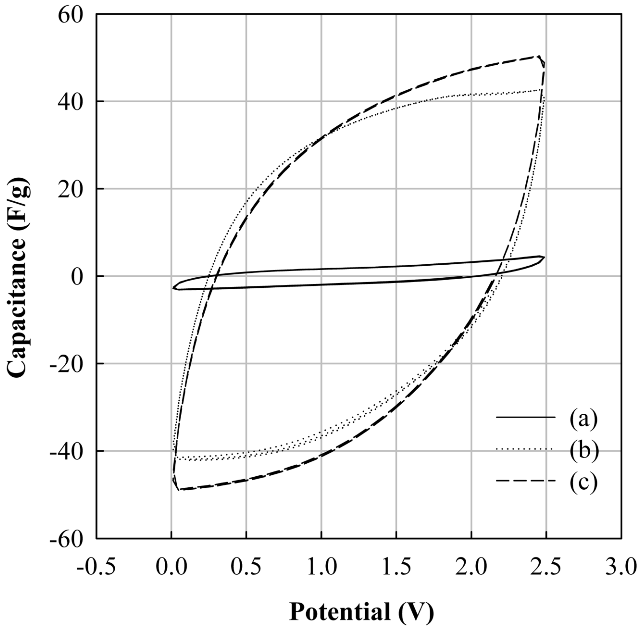

Fig. 3. Cyclic voltammograms of bamboo-based AC electrodes at various activation temperatures: (a) 700 °C, (b) 800 °C, and (c) 900 °C in 1 M TEA electrolyte at potential sweep rate of 5 mV/s.

solution within the potential range employed, and the peaks from faradic current were not observed for the capacitor cells. An ideal EDLC affords a rectangular CV profile without a pseudo (redox) peak. The voltammograms also exhibit that the induced current increased with the activation temperature. Those activated at 700 °C sample possessed a low capacitance due to small specific surface area. In contrast, the activated at 800 °C and 900 °C samples showed extremely large capacity in comparison with activated at 700 °C

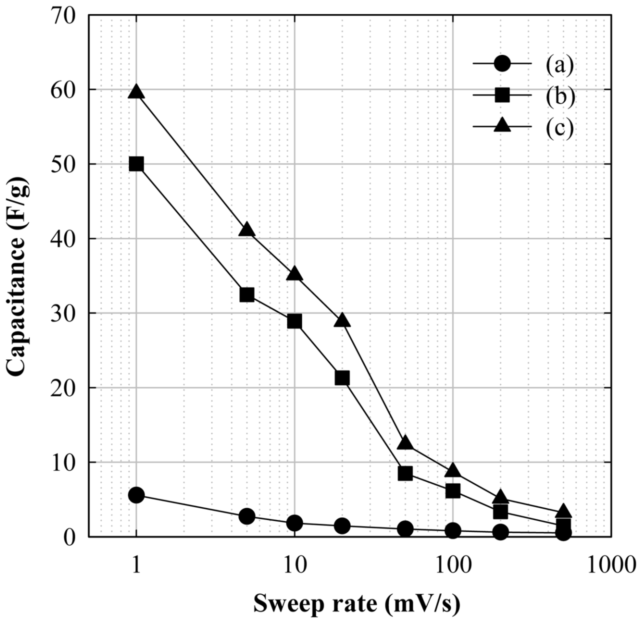

Fig. 4. Dependence of specific capacitances on the sweep rate of samples activated at various times: (a) 700, (b) 800 and (c) 900 °C.

sample. Generally, it is believed that the specific capacitance of porous carbons is a direct relation to the BET surface area of ACs [Yang, 1986]. It was found that the specific capacitance is linearly increased with an increase in BET specific surface area. Fig. 4 shows the specific capacitance as a function of the sweep rate for the samples activated at various activation temperatures. In general, the specific capacitance decreases gradually with increasing potential sweep rate. Larger ions compared with pore size may block the entrances of the micropores and thus reduce the specific capacitance. The specific capacitance of AC electrodes activated at 800 and 900 °C showed similar performance at the whole sweep rate range, the electrode activated at 900 °C exceeded than the one activated at 800 °C. Consequently, the electrode with larger BET surface area would introduce higher specific capacitance at higher sweep rate. High capacitance at a high sweep rate proposes practical importance for applications in various devices.

CONCLUSIONS

The bamboo-based AC as a nonaqueous EDLC electrode was firstly investigated. All samples have about 445-1,025 m^2/g of BET specific surface area, which was linearly increased with an increase in activation temperature. The bamboo-based ACs activated at 900 °C for 60 min exhibited the highest capacitance and the largest specific surface area value. The specific capacitances of activation temperature 700, 800 and 900 °C were about 5, 50 and 60 F/g, respectively, at a scan rate of 1 mV/s. Cyclic voltammetric measurements indicated that the electrodes are stable in the 1 M Et_4NBF_4/PC nonaqueous solution within the potential range employed, and the peaks from a faradic current were not observed in the case of the capacitor cells. It was found from the voltammograms that the induced current increased with the activation temperature.

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