Bamboo-based activated carbons as an electrode material for Electric double layer capacitors (EDLCs)

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Introduction

After Honda commercially released the FCX4, the first FCEV (fuel cell electric vehicle) with incorporated supercapacitor for power source assistance, increased investigation and experimental research has been carried out in order to create and improve novel power sources for pollution-free vehicles such as HEV (hybrid electric vehicle), FEV (full electric vehicle) and FCEV. And also interest has been focused on the application of carbon as an electrode material in EDLCs [1], especially activated carbons (ACs) [2,3], due to their ease of process and relatively low production costs.

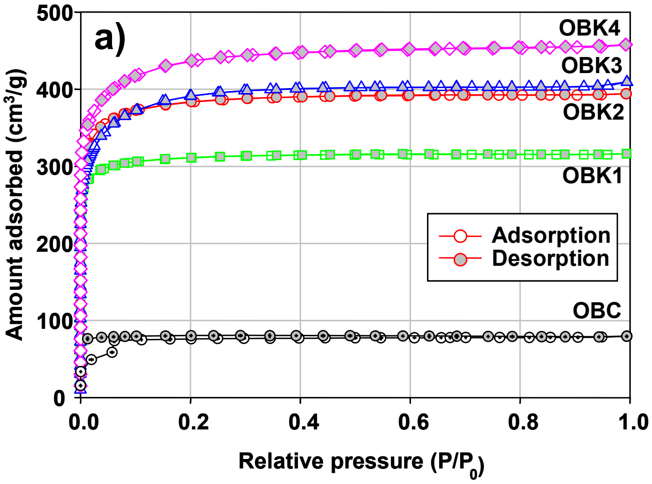
Materials of biological origin such as wood, coconut shell, agricultural wastes and lignite have been produced for commercially activated carbons due to cheap and easy process and their abundance [4,5]. Wastes are generated from bamboo after consumption can be recycled into activated carbon as an adsorbent material for multi-purpose [6] and electrode material. In this work, bamboo-based ACs have been prepared by chemical activation using potassium hydroxide (KOH) for use as electrodes in electric double layer capacitors (EDLCs). Bamboo-based ACs shows a high microporous structure with a large concentration of small mesopores (presumption is *ca.* 2-5nm), act as a highway for the mobility of ions thus increasing the permeability of the electrolyte, proportional to the KOH addition.

Experimental

Carbonization of the bamboo (Kagoshima, Japan) precursor was carried out from room temperature to 700 ºC at 10 ºC/ min in an argon flow (500 ml/ min) and maintained at 700 ºC for 2 h. The resulting bamboo char was ground and sieved to a size range of 150 ~ 300 μm. The bamboo char (OBC, 1 g) was mixed at various ratios with dry potassium hydroxide powder (KOH) (Bamboo char:KOH ratios; OBK1 (1:1), OBK2 (1:2), OBK3 (1:3) and OBK4 (1:4)). In order to examine the effect of the various bamboo char:KOH ratios, chemical activation was carried out under the following fixed conditions; room temperature to various target temperatures (600 ~ 900 ºC) at 5 ºC/ min, 800 ml/min argon flow, and then maintained at each target temperature for 1 h. The resultant material was washed repeatedly with deionized water to remove the KOH and residual organic and mineral species until *ca*. pH 6.5. Purified samples dried at 70 ºC for 24 h under vacuum. In order to determine the electric properties (*i.e.* the capacitance of the samples with the various KOH ratios), the electrodes in the test cell were prepared by mixing the bamboo-based ACs and 5 wt.% of PTFE (polytetrafluoroethylene) acts as a binder, the current collector used was glassy carbon and separator, all of which were immersed in an aqueous electrolyte (30 wt.% H_2SO_4/H_2O) and organic electrolyte (1M of Et_4NBF_4/PC). Thermogravimetric analysis (TGA, DTG-50 Shimadzu), gas adsorption using N_2 at 77K (Micromeritics, ASAP2010), specific capacitances (F/g and F/cc) in aqueous/organic electrolytes, cyclic voltammograms (CVs, Potentiostat/Galvanostat, Hokuto Denko Co., Ltd., HA-15) and equivalent series resistance (ESR, a fixed frequency at 1kHz) were carried out and also field emission scanning electron microscope (FE-SEM, JEOL JSM-6335FS) was used to validate the macro structure of bamboo-based ACs.

Results and Discussion

Figure 1a shows N_2 adsorption isotherms of the bamboo-based ACs at 77K. All samples show typical type 1 behavior, a microporous material demonstrates high amounts of adsorption at very low relative pressure ($>P/P_0=0.1$) resulting from the filling effect of micropores, except OBC, which is nonporous material. The amount of adsorbed N_2 increases as a function of the KOH/bamboo char ratio. It is found that the increase of adsorbed N_2 in OBK3 and OBK4 after $P/P_0 = 0.1$ due to the high ratio of small mesopore concentration resulting from the capillary condensation of N_2. The S_{BET} increases with increasing KOH concentration, however, the sample OBK3 shows the lowest micropore area and the highest ex-micropore (small mesopores) resulting in the lowest electrode density as shown in 1b (Table).



b)	S_{BET} (m²/g)	$S_{mi.}$ (m²/g)	S_{BET} - $S_{mi.}$ (m²/g)	$D_{electrode}$ (g/cm³)
OBC	246.8	225.4	21.3	0.950
OBK1	1010.2	913.4	96.8	0.768
OBK2	1251.7	1027.2	224.4	0.678
OBK3	1293.2	894.6	398.6	0.599
OBK4	1413.2	1034.3	378.9	0.631

Figure 1. Adsorption isotherms of N2 at 77K (1a) and the BET surface area and electrode density (1b) of bamboo-based ACs.

Figure 2 shows the variation of specific capacitance (F/g), in aqueous electrolyte (30 wt.% H_2SO_4/H_2O) 2a and organic electrolyte (1M of Et_4NBF_4/PC) 2b as functions of discharge current density (mA/cm^2) and variation of KOH ratio. The specific capacitance can be compared with PVDC + CSCF (addition of purified 20 wt.% cup-stacked carbon nanofiber (CSCF) as a conductive filler [7]) and coconut shell (CS), which are widely used electrode materials for aqueous systems and biomass-based activated carbon, respectively (Figure 2a). It is found that the specific capacitance of bamboo-based AC electrodes is much higher than that of the CS electrode, and it is worth noting that the specific capacitance of all types of bamboo-based AC electrodes are surpassing those of PVDC+CSCF as approaching the range of high discharge current density (>100 mA/cm^2). OBK1/OBK2 and OBK3/OBK4 depending on the small mesopores concentrations, OBK3/OBK4 have a relatively high percentage of small mesopores show higher capacitance in high discharge current density range (>300 mA/cm^2). A clear relation is evident; the higher small mesopore concentration, the higher specific capacitance in high discharge current density range, which is due to effective mobility of ions through the small mesopores. The OBK3 sample shows that the maximum specific capacitance in organic system differs from that of the aqueous system in Figure 2a. The OBK3 sample has a minimum micropore area, however, it has the highest percentage of small mesopores. The ion size of the organic electrolyte is larger than that of aqueous ions [2], which means that the role of small mesopores is important. It is confirmed that the high specific capacitance of the small mesopores does not degrade in EDLCs.

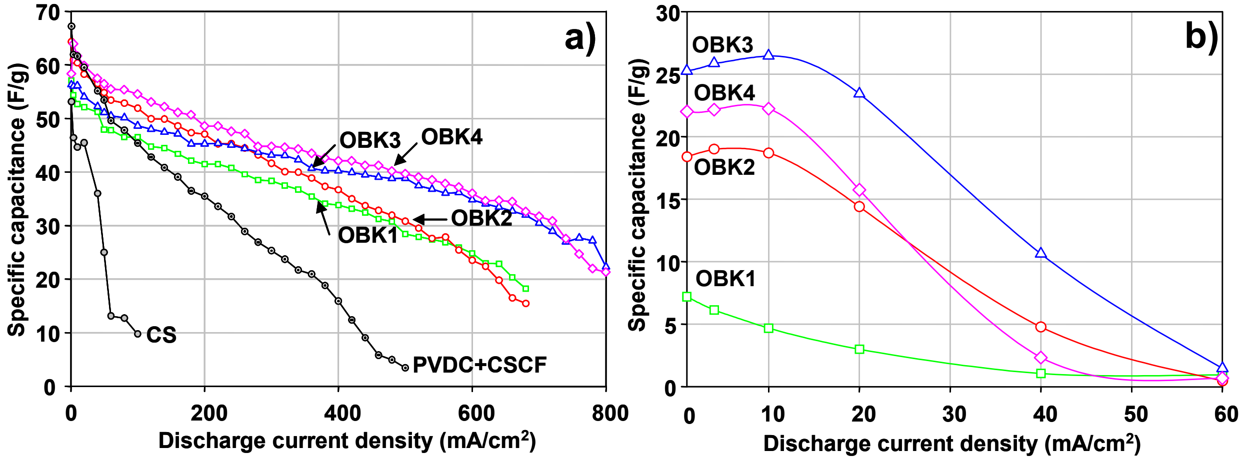


Figure 2. Variation of specific capacitances per gram, in aqueous electrolyte (30 wt.% H_2SO_4/H_2O) in 2a and organic electrolyte (1M of Et_4NBF_4/PC) in 2b, as functions of discharge current density (mA/cm^2) and variation of KOH ratio.

Conclusions

Bamboo-based ACs is a microporous structure with a relatively high percentage of small mesopores as function of bamboo char:KOH ratio. The total surface area and pore volume increase with increasing KOH addition. However, the ex-micropore (small mesopore) surface area and volume are at a maximum in the OBK3 sample. Using an aqueous electrolyte, the OBK3/OBK4 samples, which have a high concentration of small mesopores, shows higher specific capacitance in the high-discharge current density range. In the organic electrolyte system the OBK3 sample shows the greatest specific capacitance with the maximum small mesopore concentration among samples derived from bamboo char. It is found that the concentration of small mesopore is an important factor for specific capacitance due to the influence of electrolyte permeation and ion mobility within the pores of the structure. Due to the abundance of cheap bamboo waste, it is worth to produce value-added materials such as an activated carbon for electrode materials for energy storing devices and adsorbent materials for air and water cleanup.

References

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