

Biochar as a raw material for supercapacitor manufacture

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Introduction

World production growth and increasing urbanization have resulted in various effects for society including the production of large amounts of organic industrial and human wastes. These various carbon rich residuals include crop debris, biosolids, food and wood processing waste, etc. Biomasses are considered to be a very important feedstock for fuel manufacture in virtue of especially two facts: they are renewable sources and low cost materials. On the other hand, biomass processing plants and bio-oil refineries generate a lot of biochar, which is, in turn, is considered to be a waste of no economical value. The disposal/utilization of these residues has become an increasing problem and a growing expense for industry and society. To protect our natural resource base for the future, these residues should be converted directly into value-added products or into the precursors of such products [1,2].

This work demonstrates how a char derived from pine processing waste by pyrolysis can be converted by controlled physical activation with CO₂ into a value-added activated carbon suitable for fabrication of the electrodes for supercapacitors.

The activated carbon prepared from the pine processing waste by physical activation with CO₂ at 880 °C has been characterized by the following methods: BET surface area (liquid N₂, Autosorb 1), iodine number (ASTM D4607), acidity (Boehm titration [3]) measurements; ultimate chemical (Vario MICROcube), thermogravimetric (TA Q500) analyses; and X-ray photoelectron spectroscopy (XPS, Axis 165). Supercapacitor charge/discharge experiments and impedance measurements were performed with a Solartron 1255B frequency response analyzer.

Results and Discussions

The raw biochar had a surface area of 340 m²/g and contained 83.7 weight % of carbon, 2.71% of hydrogen, 0.27% of nitrogen, and

0.18% of sulphur. The results of TGA presented in Figure 1 revealed the presence of volatiles in the raw material. To remove them, the sample was heated at 1000 °C, 2h in forming gas (FG, 5% of H₂ balanced with Ar) following by physical activation in dry CO₂. This preliminary heat treatment remarkably increased the surface area of the biochar but decreased the oxygen content and, therefore, acidity of the material.

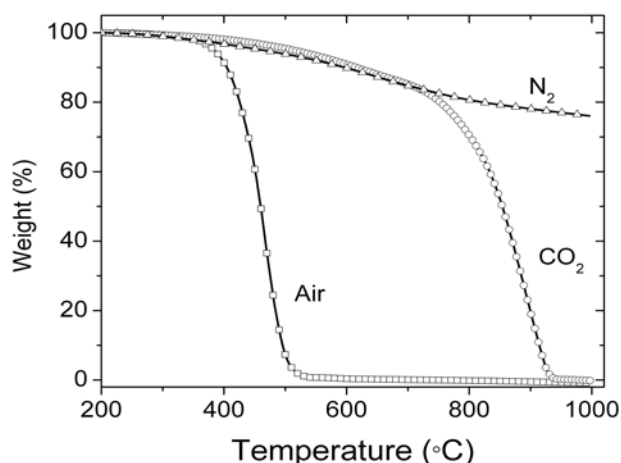


Figure 1. Thermal behavior of as-received raw biochar under different atmospheres; heating rate is 10 °C/min

The general properties of the activated carbons prepared are presented in Table 1.

Table 1. Some properties of activated carbons prepared at 880 °C in CO₂

Samp.	Activation time, min	Burn-off, %	Iodine #, mg/g	Acidity, mmol/g
AC-FG*	-	-	380	0.086
AC-1	30	3.8	770	0.275
AC-2	60	5.9	800	0.282
AC-3	120	9.7	870	0.302
AC-4	180	13.8	1050	-
AC-5	300	21.3	1180	0.454
AC-6**	300	39.9	1240	0.396

*Sample prepared in forming gas at 1000 °C, 2h

**Sample prepared in wet CO₂ (3 vol% of H₂O)

It has been found that for reduced in FG sample the iodine number was almost two times lower than that for BET number (see Tables 1, 2). For CO₂ treated samples both numbers correlated almost 1:1. It has been also found that the surface area of activated carbon increased with treatment time in dry flowing CO₂ (20 cm³/min) up to 1220 m²/g for 5h treatment. Carbon's acidity also increased, however, the fabrication of electrodes suitable for supercapacitor was quite challenging due to low wettability of the surface of activated carbon prepared in dry CO₂. To improve wettability one sample (AC-6) was treated at 880 °C in wet (3% of H₂O) CO₂.

Table 2. Surface area and pore volume of carbons activated by CO₂ at 880 °C

Samp.	S _{BET} , m ² /g	V _{total} , cm ³ /g	V _{micro} , cm ³ /g	S _{micro} , cm ² /g
AC-FG*	650	0.293	0.255	630
AC-1	800	0.351	0.309	786
AC-2	760	0.329	0.292	744
AC-3	860	0.367	0.332	849
AC-4	990	0.424	0.380	969
AC-5	1220	0.526	0.473	1195
AC-6**	1530	0.718	0.605	1474

*Sample prepared in forming gas at 1000 °C, 2h

**Sample prepared in wet CO₂ (3 vol% of H₂O)

The electrodes were prepared from AC-6 carbon using a water-based Teflon suspension (60 wt%) from Dupont as a binder. The geometric area of electrode was 0.32 cm² and the thickness was 0.6 mm. The weight of activated carbon in each electrode was 20.0 mg. A plain Ni-foil of a thickness of 25 µm was used as a current collector. To minimize the contact resistance the carbon pellet was attached onto the Ni current collector with a carbon conducting glue and the electrode was finally heated at 200 °C, 1h. The test supercapacitor was composed of pair of carbon electrodes separated by a thin (50 µm) Nafion disk. 5 M KOH : LiOH (4:1) aqueous solution was used as an electrolyte. The voltage limits were set between 0 and 1 Volts to avoid the decomposition of aqueous electrolyte. The results of current discharge measurement are presented in Figure 2.

By measuring the slope of V-T curve, the gravimetric specific capacitance of a single electrode C₁ can be calculated through the formula: C₁ (F/g) = 2 x I/slope x m, where I is a current and m is a mass of carbon in one electrode. The specific capacitance measured at 1 mA was found to be as high as of 130 F/g, which is a typical value for electrochemical

double layer capacitance of carbonaceous materials [4]. This fairly good performance can be attributed to both a sufficiently high surface area (~1500 m²/g) and suitable surface functional groups. XPS analysis showed a progressive increase in alcoholic, phenolic, and etheric groups located on the carbon surface as a function of treatment time in CO₂. The oxygen containing functional groups can allow electrolyte to penetrate into small pores more rapidly; they may react reversibly and behave like a "pseudo-capacitor", therefore, the total "apparent" capacitance would increase.

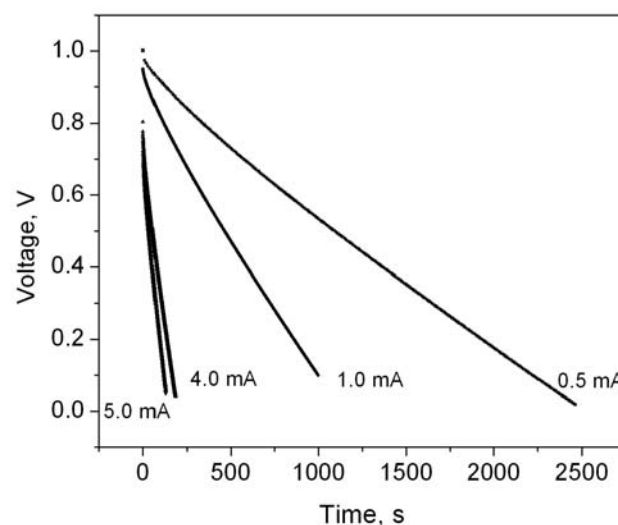


Figure 2. The galvanostatic discharge curves recorded at 0.5-5.0 mA current for a capacitor built from AC-6 in 5 M KOH/LiOH

Conclusions

The activated carbon from pine processing waste prepared in CO₂ exhibits a quite good capacitance characteristic (130 F/g). The surface area and functional groups can be easily tailored by controlling temperature and activation time. This carbon derived from waste can be used as an electrode material for supercapacitor manufacture.

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