PREPARATION OF CYPRESS CHARCOALS USING SUPER-HEATED STEAM AND THEIR APPLICATION TO ELECTRIC DOUBLE LAYER CAPACITOR

Eiki Ito and Michio Inagaki, Aichi Institute of Technology, Toyota 470-0392, Japan

Abstract

Cypress charcoals were prepared by using super-heated steam at 700~950 ^{o}C. A high total surface area of about 1000 m^2/g was obtained at temperatures above 850 ^{o}C. At around 800 ^{o}C, external surface area was found to increase abruptly from 50 to about 300 m^2/g, and then microporous surface area of the charcoal increased to about 700 m^2/g. Capacitance in electric double layer capacitor (EDLC) was measured on the sheet containing these cypress charcoals with carbon black and binder in mass ratio of 80:10:10 and in 3-electrode test cell with 1 M H_2SO_4 electrolyte. EDLC capacitance measured was discussed in the relation to carbonization conditions and pore structure of the resultant cypress charcoals. EDLC capacitance of cypress charcoal reached 270 F/g with a current density of 20 mA/g, about 200 F/g with 50 mA/g and about 140 F/g with 1000 mA/g. Their performance rating measured by capacitance with 1000 mA/g to that with 50 mA/g was relatively high as 0.7~0.8.

Introduction

The conservation of forest resources was pointed out to be important for the remediation of the environment of the globe. For that purpose, thinning of the forest has to be done periodically. However, this thinning is usually laboring, particularly in steep slope, which is suitable for planting trees, cypress and Japanese cedar in Japan [1]. In promoting thinning works, effective usage of thinned woods has to be established. Production of charcoals from various woods has been carried out since prehistoric era and charcoals produced have been used in various applications, such as a heating source, an adsorbent, a medicine, etc. Some of these charcoals have been converted to activated carbons in order to expand their application for modern technology, a typical example being activated carbon from coconut shells, which has widely been used in various applications [2].

Recently, special attentions have been paid on carbon materials contributing to our ecological circumstances and their preparation through the processes gently for our earth, by calling "eco-carbons" [3]. The production of activated carbons has been carried out from various biomass resources, not only thinned woods but also sawdust, waste woods and bamboos [3-7], which is thought to be one of eco-carbon activity. For the production of activated carbons from various precursors, including woods, we developed a carbonization furnace using super-heated steam, where carbonization and activation were possible to be carried out at the same time [8].

In the present work, carbonization of cypress, which had been planted in wide area in Japan and was needed to be thinned periodically, was performed under super-heated steam using the carbonization furnace developed. The pore structure and electric double layer performance of resultant carbons were investigated.

Experimental

Preparation of carbons from cypress

For the carbonization under super-heated steam a pilot-plant scale apparatus was constructed, consisted of the generator of super-heated steam, the carbonization furnace using high-temperature steam, the pre-drying furnace for cypress chips using low-temperature steam, and the pyrolytic incinerator for wasted gases, In the carbonization furnace and pre-drying furnace, cypress and its carbonized chips were pushed further by rotating paddles with a constant rate, where super-heated steam was flowing in contrary direction. For comparison, carbonization in a flow of Ar was performed by using a tubular-type laboratory scale furnace with the diameter of 60 mm.

The original cypress chips had a size of about 10~20 mm x 10~60 mm x 2~10 mm. Temperature for the carbonization under super-heated steam was determined at its inlet to the carbonization furnace. In the present work, carbonization temperature employed was in the range of 700 ~ 1000 ^{o}C. Under super-heated steam, the cypress chips of 30 kg during 1 or 2 hours (*i.e.*, supplying rate of 30 kg/h or 15 kg/h) by rotating the paddle with 4.7 and 9.4 rpm (rotating rate) were employed. For the carbonization in Ar gas flow, cypress chips of about 1 g were placed at the center of the furnace tube, heated with a rate of 5 ^{o}C/min and then kept at the programmed temperature for 1 h. Flow rate of Ar gas was 70 mL/min. After carbonization, the carbon obtained was pulverized in a ball mill to the particle size less than 75 μm and subjected to different examinations.

Characterization of pore structure

Pore structure was evaluated through the analysis of adsorption/desorption isotherm of N_2 gas at 77 K by using BET, α_s and BJH methods. By BET analysis on the data measured at the relative pressure P/P_0 of N_2 gas below 0.3, surface area S_{BET} was determined, to make the comparison with other activated carbons easier. From α_s plot referring to a standard carbon black, total surface area S_{total}, external surface area $S_{ext.}$ and micropore volume $V_{micro.}$ were determined. From the balance between S_{total} and $S_{ext.}$, microporous surface area $S_{micro.}$ was calculated. External surface area $S_{ext.}$ was the surface area due to the pores larger than 2 nm, but its main part is caused by the surface area due to mesopores (2 ~ 50 nm size). The carbons prepared were also analyzed by BJH method using desorption branch of the isotherm of N_2 gas, in order to evaluate surface area and volume of mesopores. From the cumulative curves, surface area and pore volume due to mesopores $S_{meso.}$ and $V_{meso.}$ were determined by separating from those due to micropores $S_{micro.}$ and $V_{micro.}$.

Measurement of the performance in electric double layer capacitor

For the determination of the performance of electric double layer capacitor (EDLC) for the cypress charcoals, the electrode was prepared by mixing the carbon powders with acetylene black as an electrical conductor and PTFE as a binder in a mass ratio of 80:10:10, which were blended to be homogeneous by using N-methyl-2-pyrrolidone as a solvent. The mixture was pressed to get the film in approximate thickness of about 100 μm and then dried at 100 °C for 1 h under vacuum. Three-electrode test cell was used with 1 mol/L H_2SO_4 as electrolyte, Ag/AgCl as a reference electrode and a platinum plate as a counter electrode. For these sample electrodes the charge-discharge cycles in the potential window from 0.0 to 1.0 V were carried out at room temperature. The capacitance of the sample electrode was calculated from charge-discharge curves at 0.2 to 0.8 V. The current density employed for the measurement of capacitance was 20 ~ 1000 mA/g. The change in capacitance with current density during charge-discharge cycle was expressed as the ratio of the capacitance measured with a current density of 1000 mA/g, C_{1000}, to that with 50 mA/g, C_{50} C_{1000}/C_{50} (performance rating).

Results

Pore structure

In **Figure 1**, BET surface area S_{BET} of cypress charcoals prepared under super-heated steam (30 kg/h and 9.4 rpm) and also in Ar gas flow was plotted against carbonization temperature. S_{BET} increases at around 800-850 °C in two steps under super-heated steam and reaches 900 m^2/g before 900 °C, although charcoals prepared in Ar gas flow gave S_{BET} of about 400 m^2/g, irrespective of carbonization temperature. This result suggests that the activation process proceeds above 800 °C under super-heated steam, together with carbonization.

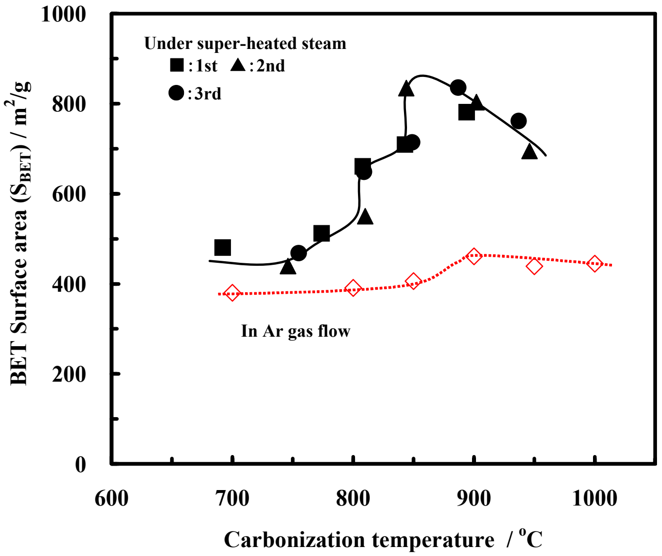

Figure 1. Changes in surface areas of cypress carbonized under super-heated steam and in Ar gas flow.

In order to understand the pore structure in the cypress charcoals prepared under super-heated steam with supplying rate of 30 kg/h and rotating rate of paddles with 9.4 rpm, changes in microporous and external surface areas $S_{micro.}$ and $S_{ext.}$ are shown in **Figure 2a**, together with total surface area S_{total}. $S_{ext.}$ increases at about 800 °C in advance of the increase in $S_{micro.}$ above 850 °C. The reproducibility in pore structure during the carbonization in 3 runs seems to be excellent.

In **Figure 2b**, changes in S_{total}, $S_{micro.}$ and $S_{ext.}$ are plotted for the cypress charcoals prepared with a slow supplying of the chips and a slow moving speed in the furnace (*i.e.*, supplying rate of 15 kg/h and a rotating rate of paddles with 4.7 rpm). By comparing with those prepared with a high supplying rate and a high rotating rate (*i.e.*, 30 kg/h and 9.4 rpm) shown in **Figure 2a**, it has to be pointed out that $S_{ext.}$ became very high, around 450 m^2/g,

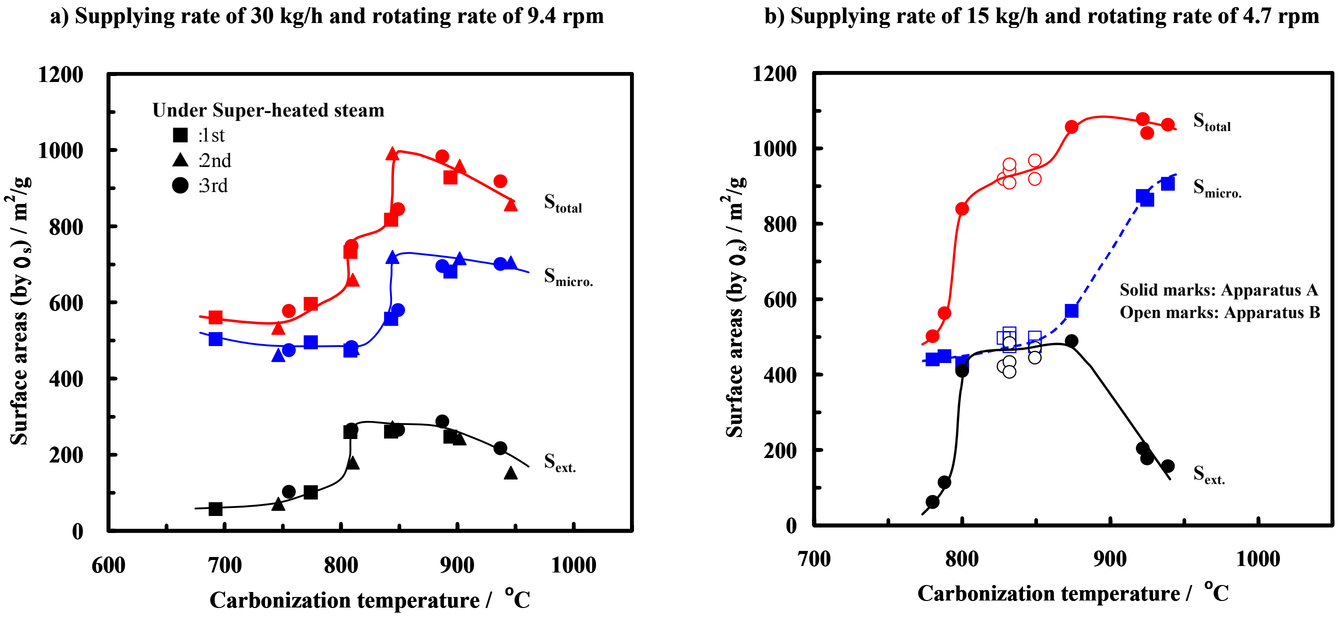

Figure 2. Changes in surface areas of cypress charcoals prepared under super-heated steam with slow conditions.

Performance in electric double layer capacitors

Cypress charcoals prepared under super-heated steam with different conditons gave relatively high EDLC capacitance in 1 M H_2SO_4 electrolyte: about 270 F/g with a current density of 20 mA/g, about 200 F/g with 50 mA/g and about 140 F/g with 1000 mA/g.

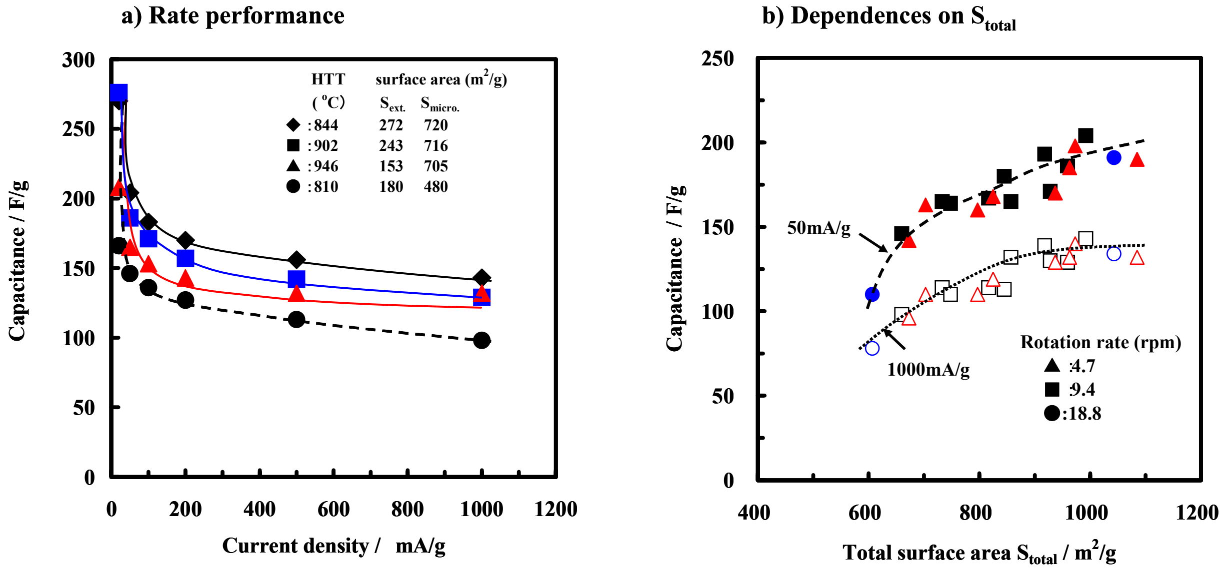

Figure 3. Capacitance of cypress charcoals prepared under super-steam

In **Figure 3a**, rate performance is shown for some cypress charcoals. Up to the current density of 200 mA/g, capacitance decreases very rapidly, but the decrease in capacitance becomes small above 200 mA/g. The performance rating C_{1000}/C_{50} was around 0.7-0.8.

In **Figure 3b**, capacitances measured with current density of 50 and 1000 mA/g are plotted against total surface area S_{total} on the cypress charcoals prepared under super-heated steam with different conditions (supplying rate of 15 and 30 kg/h, and different rotating rate of the paddle with 4.7–18.8 rpm). Capacitance increases gradually with increasing S_{total} and tends to saturate at a high S_{total}. This figure shows that the dependences of capacitances with different current densities are common for the cypress charcoals which have different pore structure, as shown in **Figure 2**, revealing that capacitance is mainly governed by pore structure. The fact that two dependences with 50 and 1000 mA/g are almost parallel suggests almost constant rate performance.

Conclusion

Cypress charcoals were successfully prepared under super-heated steam, which had relatively high surface area of about 1000 m^2/g and were mesoporous. Activation was found to occur by super-heated steam with a temperature above 800 ^oC together with carbonization. By selecting carbonization conditions, temperature of steam, supplying rate of cypress chips and rotating rate of paddle in carbonization furnace, mesoporous and microporous carbons were prepared from cypress chips. In mesoporous charcolas, external surface area reached about 400 m^2/g, being comparable with microporous surface area. These charcoals were found to give relatively high capacitance and high performance rating in electric double layer capacitor with 1 M H_2SO_4 electrolyte.

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