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Investigations on pore structures and surface functional groups of activated carbon fabricated by microwave irradiation

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A new method for fabrication of activated carbons by using microwave heating is developed. In general, activated carbon with high specific surface area is being manufactured using potassium hydroxide in the presence of inert gas. The heating method uses conventional equipments such as electric furnace and gas combustor. In this report, the fabrication of activated carbon by microwave irradiation is investigated. High-quality activated carbons with specific surface area over 3000 m^2/g and pore size distribution of 1 – 2 nm were obtained. The surface acidic functional groups, determined by Boehm's titration method, reduced due likely to microwave effect. Results of the performance test of the capacitors, giving stable capacitance (about 80 F/g) over 100 charge-discharge cycles, showed that the activated carbons fabricated by microwave heating were well suited for electric double layer capacitor.

Key words: activated carbon, pore structure, surface functional group

1. Introduction

Activated carbons have been widely used as industrial absorbents and solid catalysts due to their high specific surface area, microporous structure and special surface reactivity [1-3]. They are also used as electrode for rechargeable battery and electric double layer capacitor (EDLC) because of their good electric conductivity and electrochemical stability [4, 5].

Wood, coconut shell, coal, etc. are selected as raw materials for activated carbons. Generally, they are prepared by two methods. One is a physical activation method consisting of two steps, carbonization of a carbonaceous precursor and activation under H_2O or CO_2 atmosphere at high temperatures (800 – 1100 °C). The other is a chemical activation method consisting of carbonization and activation performed in one step at relatively low temperatures (400 – 800 °C) with reaction agents ($ZnCl_2$, H_3PO_4) [3]. In 1970s, Wennerberg [6] invented a new technique for preparation of activated carbons with higher specific surface area using potassium hydroxide.

In this work, carbonization and activation of carbons were carried out by microwave irradiation. Nowadays, microwaves are used in various technological fields for heating dielectric materials [7]. Microwave heating reduces the energy consumption as a result of less reaction time [8]. Conventional heating and microwave heating differ with respect to heat generation. In conventional heating the heat source is located outside the sample which is heated by conduction and/or convection. In the sample a temperature gradient is generated before reaching a steady state. In microwave heating, however, microwave is converted to heat inside the carbon sample by dipole rotation and ionic conduction. This effect results to less decomposition products adhering at the surface of activated carbons. Moreover, microwave treatment in an inert environment is an efficient and attractive way of removing oxygenated functionalities from carbon surfaces and of increasing the hydrophobicity and basicity of carbons [9].

There are a few studies that describe the use of microwave for producing activated carbon [10]. The objective of this report is to fabricate activated carbons for EDLC by microwave irradiation and to investigate the pore structures and surface functional groups of activated carbons.

2. Experimental

Activated carbons were prepared from PET (polyethylene terephthalate) mixed with KOH at weight ratio of PET / KOH = 1 : 5. The mixture was heated up to 800 °C by microwave irradiation under N_2 flow, and held for 10 – 60 min. After cooling, the product was neutralized with dilute HCl, followed by washing with distilled water to remove soluble salts.

The pore structures of activated carbons were measured by using an automatic adsorption apparatus (AUTOSORB-1, Quantachrome). Nitrogen gas (99.99%) was used as probe and liquid nitrogen was used as cold bath (-196 °C). Before starting the measurement, the sample was degassed at 200 °C for 4 h below 10^{-8} torr vacuum. The specific surface area was calculated by the BET equation. Among the many sophisticated physical models for gas adsorption, models based on density functional theory

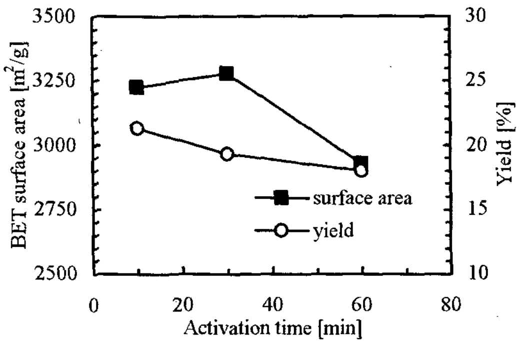

Fig. 1 BET specific surface area and yield of activated carbons prepared as a function of activation time.

(DFT) [11] have recently gained increasing acceptance. Therefore, the pore size distribution reported in this paper was taken from DFT data.

Base-acid titration of the carbons based on Boehm's method [12] was performed to measure the surface functional groups of the samples. About 0.1 g of samples was placed in three 200-ml Erlenmyer flasks, each containing 50 ml solution of 0.1 mol dm^{-3} sodium bicarbonate ($NaHCO_3$), 0.05 mol dm^{-3} sodium carbonate (Na_2CO_3) and 0.1 mol dm^{-3} sodium hydroxide (NaOH), respectively. The flasks were sealed and shaken in water bath kept at 25 °C for 48 h. The carbons were filtered and 20 ml of filtrates were back-titrated with aqueous hydrochloric acid.

Two-electrode cell was used to examine the capacitance of the activated carbon. The cell was constructed with two facing carbon electrodes, sandwiching a piece of separator. All measurements were performed at ambient temperature, by soaking the cell in an electrolyte solution of 30 wt% H_2SO_4. The capacitance of the cell was measured by charging the capacitors from 0 to 0.9 V at a constant current of 0.5 mA. After keeping the voltage at 0.9 V for 30 min, the cell was discharged at a constant current of 0.1 mA until the voltage was reduced to 0 V. This operation was repeated for 100 cycles. The specific capacitance (F/g-carbon) was calculated from the slope of time vs. voltage curve in the discharge process (BTS-2004W, NAGANO).

3. Results and Discussion

Fig. 1 shows BET specific surface area and yield of activated carbons fabricated by microwave heating method as a function of activation time (activation temperature = 800 °C). The yield decreased with an increase in activation time. The specific surface area of activation time for 10 to 30 min reached above 3200 m^2/g, however, at 60 min it was below 3000 m^2/g. At higher temperatures, KOH reproduced in the dehydration is considered to react with carbon atoms. It can cause gasification into CO or CO_2, thus decreasing the yield. As the activation proceeds, micropore grows into meso or macro pore. Therefore, high degree of activation leads to decrease of specific surface area.

Table I Properties of activated carbons

	Heating method		Commercial (C)
	Microwave (A)	Conventional (B)	
Surface area [m^2/g]	3140	2770	3280
Ash content [wt%]	< 0.2	< 0.2	< 0.1

The properties of the activated carbons used in this report are listed in Table I. Three samples are prepared: by microwave heating (A), conventional heating (B) and commercial activated carbon with the highest surface area (C). Ash contents of all samples were below 0.2 wt%.

Fig. 2 shows the nitrogen adsorption-desorption isotherms of activated carbons. A large amount of N_2 was adsorbed at low relative pressure (P/P_0), and the N_2 adsorption was saturated again at high relative pressure. Therefore, all the samples present type I isotherms, characteristic of microporous carbons. The drastic adsorption increase in the low relative pressure range is due to the micropore filling effect. Sample B exhibits hysteresis between the adsorption and desorption isotherms associated with mesoporosity. Various carbon materials have unique pore distribution resulting from the precursor and process involved. Fig. 3 shows the pore size distribution of three types of samples. Sample

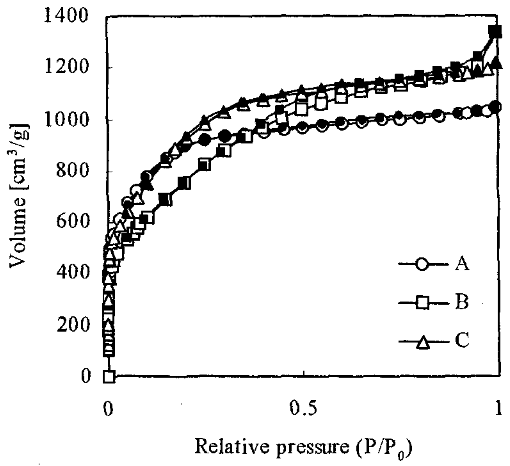

Fig. 2 Adsorption and desorption isotherms of N_2 on activated carbons at -196 °C (open symbols: adsorption, closed symbols: desorption).

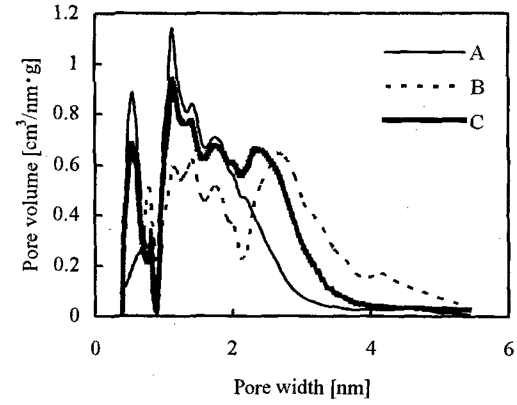

Fig. 3 Pore size distributions of activated carbons calculated from DFT.

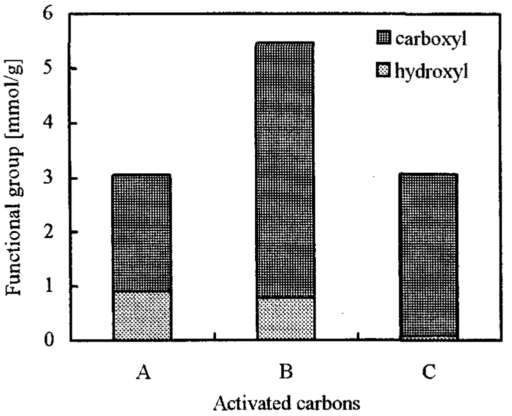

Fig. 4 Surface acidic functional groups of activated carbons by Boehm's titration.

A has sharp distribution compared to other samples. This result may suggest that less decomposition products adhere to the surface of activated carbons.

The surface functional groups based on weight of the activated carbons are shown in Fig. 4. The three bases used in the titration are regarded as approximate probes of surface acidic functional groups: $NaHCO_3$ (carboxyl), Na_2CO_3 (carboxyl and f-lactone), NaOH (carboxyl, f-lactone and phenolic). The functional groups of sample A, especially carboxyl group, were lower than other samples. The microwave effect on reducing the surface acidic functional groups was confirmed.

Fig. 5 shows the chronopotentiograms (potential-time curves) of the activated carbons in 30 wt% H_2SO_4. All potentiograms indicates a typical behavior of capacitance electrodes. Based on the results, the specific discharge capacitance in the capacitors can correspond to the inverse of the gradient of the potentiogram. Therefore, sample A with gentle slope has a larger capacitance (about 90 F/g) than sample B. The stability of the prepared capacitors can be measured by repeating charge-discharge cycle. The discharge capacitances with cycle number are shown in Fig. 6. The results show that the capacitor has stable capacitance over 100 cycles.

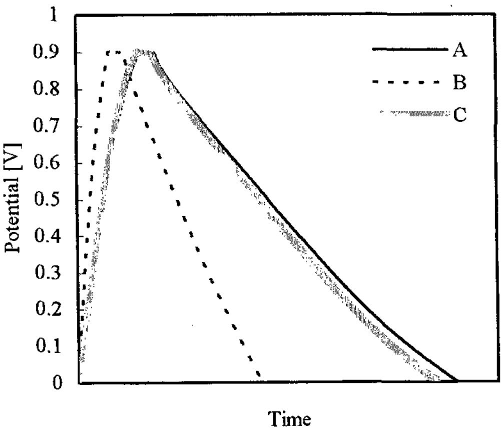

Fig. 5 Chronopotentiograms (potential-time curves) for the activated carbons in 30 wt% H_2SO_4.

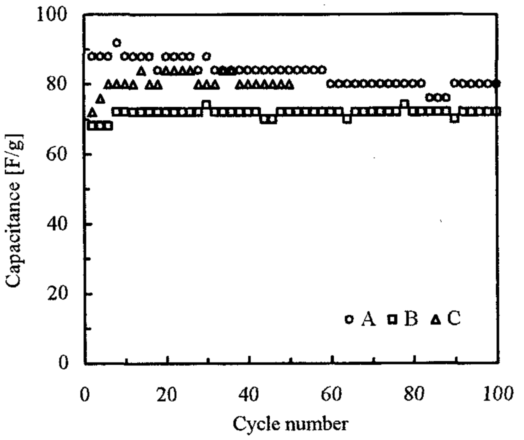

Fig. 6 Capacitance stability with cycle number for activated carbons charged at 0.5 mA and discharged at 0.1 mA in 30 wt% H_2SO_4.

These results indicate that the EDLC depends upon the characteristics of activated carbons, the BET surface area, pore size distribution and surface functional groups.

4. Conclusions

A new method for making high-quality activated carbons with high specific surface area by using microwave heating was successfully developed. The activated carbons prepared by this method had specific surface area over 3000 m^2/g and pore volume distribution of 1 – 2 nm. The surface acidic functional groups, especially carboxyl group, were lower than that obtained by conventional heating. Moreover, they had a larger capacitance (about 90 F/g) and stable over 100 cycles. Results showed that the activated carbons fabricated by microwave heating were well suited for electric double layer capacitor.

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