

Electrochemical Modification of Surfaces of Carbonaceous Materials

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1 Abstract

This paper deals with the fundamental study of electrochemical modification of the charcoal surface. It is necessary to find the efficient utilization of unused biomass. Electrochemical cell to modify a charcoal surface was studied. Three types of cells were fabricated. Result from the reaction ratio of carbon, surface area and IR spectrum suggested that the cell in which charcoal was used as anode was adapted to electrochemical modification of charcoal. Electrochemical modification of charcoal was indirect radically mediated reaction. Electrochemical reactions of the cell occurred onto the surfaces of carbon. Therefore the modification occurred efficiently and much more carbon was consumed.

2 Introduction

Carbonization process is widely used to obtain charcoal from unused biomass e.g., pruning branches, lumbering wastes and agriculture residues. Because design and operation of carbonization processes has been well discussed, the installation of the process is not difficult. The use of charcoal has a long history; however, some historical use, such as cooking and heating energy, are replaced to electricity, gas and oil. The market of charcoal is limited. There are many techniques to make a carbonaceous material valuable, improving its functions. surface.

One of the most popular ways is surface modification. By surface modifications, the pore structure is developed, the surface area is enlarged, and functional groups are introduced onto the surface. On the other hand, surface modification of carbon in liquid phase has been reported. Hydrothermal activation [1] is pyrolysis reaction in pressurized liquid water at temperatures around 300°C. The study of electrochemical oxidation of carbon nanotube composites is also reported [2]. In that study, carbon nanotube composites are used as electrode. By electrochemical oxidation of the electrode, their capacitance was increased. We adapt relatively cheap material to electrochemical modification. In this study, fundamentals of the electrochemical modification of the surface of charcoal were examined. The effect of fabrication of electrochemical cell on the electrical modification of charcoal is discussed. We also evaluated the treated charcoal samples by the changes in the surface area and FTIR spectrum.

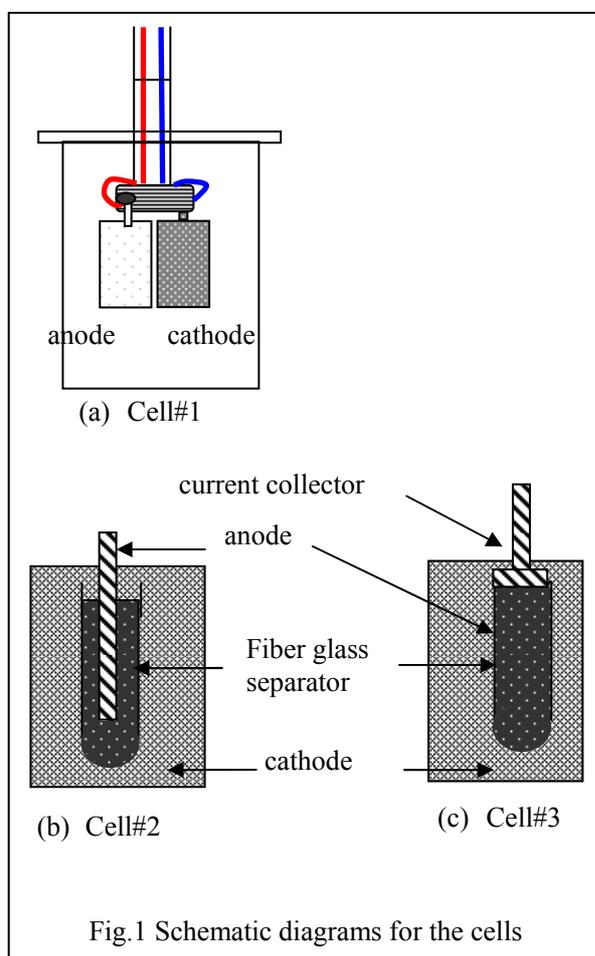
3 Experimental

A charcoal sample was obtained from a demonstration plant to recycle lumbering waste by carbonization (Togane-shi, Chiba, Japan). At the facility charcoal was produced at a high temperature around 1000°C. Raw material was Japanese cedars back board. The charcoal has a large surface area.

ELECTROCHEMICAL MODIFICATION OF SURFACES OF CARBONACEOUS
MATERIALS

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Then 100g of carbonaceous materials were washed with 1L of 1M KOH aqueous solution to remove alkali soluble substance. After neutralized with 0.1 M HCl, the sample was washed with deionized water. Three types of electrochemical cell were assembled (Cell#1, Cell#2 and Cell#3). Schematic diagrams of the cells are shown in Fig.1. Anode and cathode of Cell#1 was Ni solid plate (purify 99.9+%) . KOH aqueous solution in which powdered carbon sample was suspended. Anode and cathode of Cell#2 was Ni solid plate and Ni screen (40 mesh) respectively. To increase carbon concentration, the charcoal sample was loaded within the fiber glass separator in Cell#2. While both the anode and cathode were Ni, charcoal sample was used as anode in Cell#3 (the cathode was Ni screen).



Electrochemical modification proceeds along with the application of voltage. The changes in electric current were recorded. Sample was taken out and washed by deionized water after neutralized with 0.1M HCl aqueous solutions. BET surface areas of treated samples were

measured by an automatic surface area analyzer (BELSORP-mini: BEL JAPAN INC). Functional groups of the surfaces were measured by a FTIR spectrometer (AVATER 370: ThermoNicolet, USA)

4 Results and discussion

Electrochemical reaction at the surfaces of charcoals is expressed as follows. It is expected two reactions at anode.

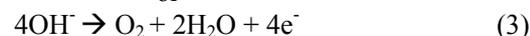
Cathode reaction



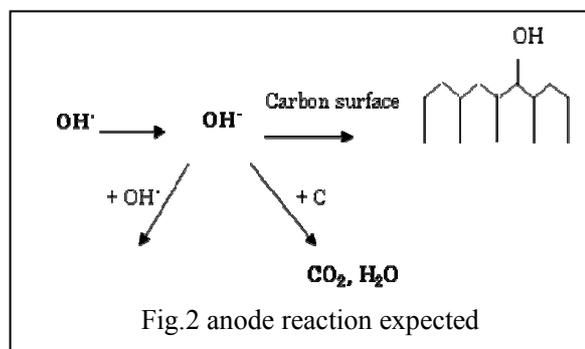
Anode reaction



or



When carbonaceous materials are electrochemically oxidized, reaction expressed as eq (2) occurs and carbon can be consumed with current flow . More detailed anode reaction is shown in Fig.2. A hydroxyl ion releases an electron and form hydroxyl radical. This radical react with other radical, carbon or the carbon surface. Then O_2 , CO_2 or oxygenated functional group respectively generated.



The electrical quantity (Q) flowing the circuit can be defined as follows

$$Q = I \cdot t \quad (4)$$

(I [A]; electrical current, t [sec]; reaction time)

The reaction time and the mass change can be written in eq (5); i.e. Faraday's raw.

$$m = \frac{Q}{z F} \quad (5)$$

(m [mol]; mole number of materials consumed, z; number of electron concerned reaction F[C/mol]; Faraday constant = 96465)

Reaction ratio of charcoal sample is defined as follow in this study.

$$\text{Theoretical reaction ratio} = \frac{\text{Theoretical weight loss of sample}}{\text{mass of pretreatment sample}} \quad (6)$$

$$\text{Experimental reaction ratio} = \frac{\text{experimentally weight loss of sample}}{\text{mass of pretreatment sample}} \quad (7)$$

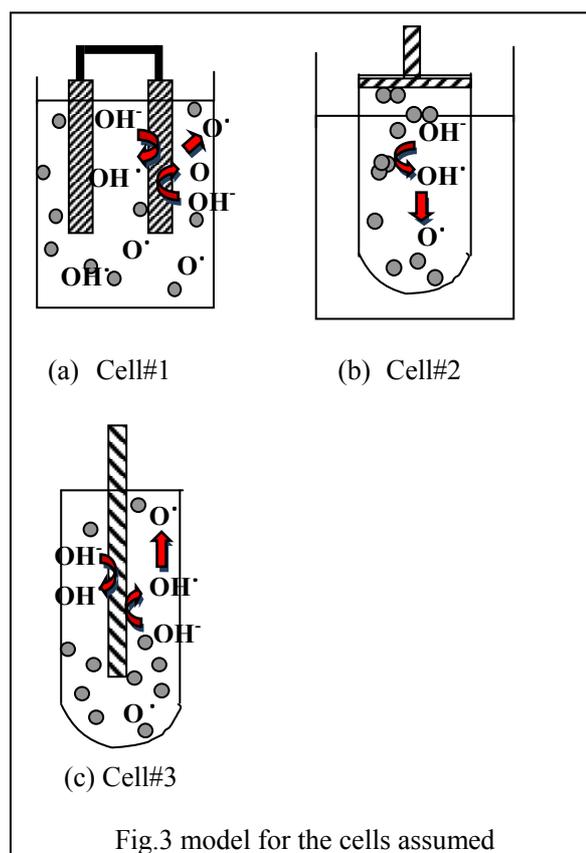
The results for electrochemical treatment were shown in Table 1. The experimentally obtained reaction ratio for Cell#1 and Cell#2 was much smaller than the theoretical ones. On the other hand, Cell#3 showed a reaction ratio similar to the theoretical ratio.

Table 1 Results of electrolyte in 3M KOH about each cell.

	current [mA]	weight loss of sample [g]		reaction ratio[%]	
		theoretical	experimental	theoretical	experimental
cell#1	150	0.403	0.0578	13.4	1.9
cell#2	125	0.335	0.0473	5.8	1.6
cell#3	110	0.296	0.335	4.1	4.2

As shown in Fig. 3 (a), OH⁻ ions released electrons on the surface of Ni anode in Cell#1. Activated species such as hydroxyl radical and oxygen radical generated. These activated species reacted with other free activated species or carbon. In Cell#2, the reaction mechanism was the same as Cell#1. Because the carbon sample was loaded within the fiber glass separator, the carbon concentration was much higher than that of Cell#1. Because of the higher carbon concentration, reaction ratio is expected larger than Cell#1. The carbon sample was used as anode in Cell#3. Reaction was occurred at the carbon surfaces. In this point, Cell#3 was different from others. Electrochemical modification of carbonaceous materials was indirect radically mediated reaction, as described in Fig. 2. Electrochemical reactions in Cell#1 and Cell#2 occurred at the surfaces of Ni anode, on the other hand, the active species were produced at the surface of the carbon anode for Cell#3.

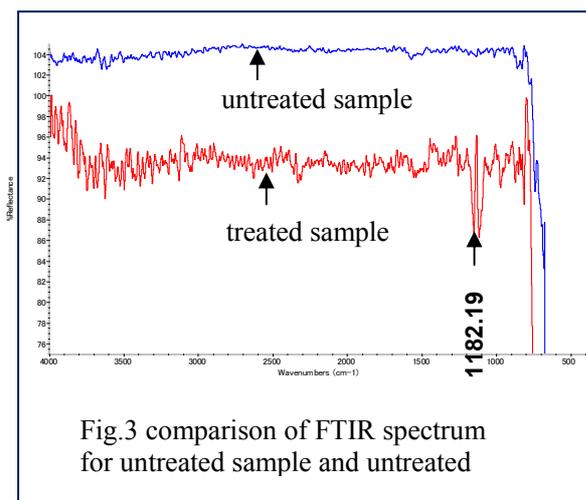
Therefore, the oxidation of carbon proceeded much more efficiently in Cell#3.



After the electrochemical treatment, the samples were evaluated. BET surface areas for the samples were shown in Table 2. From this result, surface areas became smaller after electrical modification. It was found that the electrochemical oxidation was hard to enlarge the BET surface area under the condition tested in this study. FTIR spectrum of the sample for the Cell#3 (Fig. 4) suggested the formation of oxygenated functional groups onto the surface of electrochemically modified sample, because the peak spectrum of 1182.19cm⁻¹ indicates the existence of C-O, C-C, OH. It was suggested that both the oxidation of carbon to produce carbon dioxide and the addition reactions to form oxygen-containing functional group onto the carbon surface occurred.

Table 2 Results of measurement of BET surface area [m²/g]

	untreated carbon sample	treated carbon sample
cell#1	462.8	354.2
cell#2	462.8	448
cell#3	416.5	302



5 Conclusion

The electrochemical oxidation of the charcoal sample was observed and the reaction mechanism was suggested to be indirect reaction mediated by oxygenated radicals. Although the amounts of carbon consumed did not agree with the theoretical values estimated from the current flow for the experiments with Cell#1 and Cell#2, the reaction with a carbon anode in Cell#3 proceeded as expected. The electrochemical reaction increased the surface functional group, as well as the consumption of the carbon. However, the consumption did not contribute to the enhancement of the BET surface area. Under the condition tested in this study, the electrochemical oxidation was hard to develop the microporous structure of the carbon sample.

6 Acknowledgement

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7 Reference

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