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## Intercalation of wood charcoal with sulfuric acid

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**Abstract** Intercalation of wood charcoal with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was investigated. Carbonized sugi (Japanese cedar) samples were prepared by heating at various temperatures in the range 1700°–2700°C. Electrochemical oxidization was carried out in  $\text{H}_2\text{SO}_4$  and the feasibility of intercalation was determined. In potentiometric analysis, plateaus appeared for samples carbonized at temperatures above 2300°C. In their X-ray diffraction profiles, the peak at around 26° was shifted to a smaller angle of about 22.4°. These results can be considered as signs of intercalation with acid molecules. Fourier transform infrared analysis of charcoal heated at 2700°C, following washing with water and drying of the sample, showed a band at 1220  $\text{cm}^{-1}$  that was assigned to a sulfonate group. This band was not observed for samples heated at 1900°C. These observations suggest the occurrence of intercalation in the former charcoal, but not in the latter. It is concluded that wood charcoal can undergo intercalation when it has ordered stacking of hexagonal carbon layers.

**Key words** Wood charcoal · Intercalation · X-ray diffraction · Thermogravimetry · FT-IR

### Introduction

Wood charcoal is a potential source of carbon material. The main product of wood charcoalization is carbonized cell walls, which is nongraphitic carbon. Generally, nongraphitic

carbon cannot develop into perfect graphite crystals even if it is annealed at temperatures as high as 3000°C, because of restriction by the growth history of solid-phase carbonization. However, carbonized wood cell walls are expected to be a carbon source for future applications, having various allotropic structures, such as onion-like structures<sup>1</sup> and diamonds.<sup>2</sup> By using approaches considering the characteristic features of wood charcoal, novel functional materials should be obtainable. There is a concept of reducing  $\text{CO}_2$  emissions in air by returning pyrolyzed biomass to the soil as biochar.<sup>3,4</sup> In future, this concept could be extended to sequestration of carbon not only in soil, but also in industrial carbon materials. For this extended “carbon offset,” trials making carbon materials from biomass illustrate an important approach. As one such approach, we have made intercalation compounds of wood charcoal.

A well-known graphite intercalation compound is a lamellar crystal-like structure, with guest molecules inserted between the ordered stacking of hexagonal carbon layers. Predominantly, the graphite- $\text{H}_2\text{SO}_4$  intercalation compound is the source for “exfoliated graphite,” with a low bulk density. It is used in industrial materials such as coating agents, additives, and flexible graphite. At present, exfoliated graphite is considered to have potential use as an oil absorbent and in heat-resisting applications.

To date, intercalation of “nongraphitizing carbon,” including wood charcoal has scarcely been reported, while much research on graphitic carbon from petroleum sources has been carried out and applied. This is probably because synthesis of intercalation compounds requires perfect crystallinity and a large crystallite size of graphite;<sup>5</sup> in short, the driving force is the charge-transfer interaction that occurs in orderly stacked hexagonal carbon layers in highly crystalline graphite. However, by treatment at relatively high temperatures like 2000°C or higher, even nongraphitic carbon such as wood charcoal includes a mosaic graphitic portion or turbostratic portion. These portions have orderly stacked hexagonal carbon layers, but do not contain perfectly crystalline graphite. We considered that these highly ordered portions in wood may be suitable to form intercalation compounds. The aim of this study was to clarify whether

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wood charcoal can form intercalation compounds when it contains some degree of graphitic structure.

## Materials and methods

### Sample preparation

Sugi (Japanese cedar, *Cryptomeria japonica*) was precarbonized using a traditional stone kiln at a temperature of 1200°C. Samples were cut into blocks of several cubic centimeters and placed in a small carbon crucible. The crucible was placed in a furnace (SCC-30/220, Kuratagiken, Japan), where the thick-walled carbon crucible served as the electrical resistance heater element. For secondary carbonization, samples were heated at a rate of 60°C/min, held for 1 h at 1700°, 1900°, 2100°, 2300°, 2500°, or 2700°C and then cooled at a rate of 120°C/min. During the thermal treatment, the ambient pressure was kept at 10–20 Pa by evacuating the furnace, but at temperatures above 1900°C a flow of argon gas was introduced and maintained at a pressure of 0.105–0.11 MPa. After treatment, the sample was powdered and sieved to give a powder with a particle diameter of less than 63 µm. Natural graphite (Wako, Japan) was also used in subsequent tests.

### Electrochemical treatment and potentiometry

The powdered sample was stuffed into a cell in contact with a Pt electrode and was placed as the anode immersed in H<sub>2</sub>SO<sub>4</sub>. During treatment, the test tube was kept at 30°C in a thermostatic chamber and dried N<sub>2</sub> gas was purged inside to prevent absorption of moisture by H<sub>2</sub>SO<sub>4</sub>. Electrochemical treatment and potentiometry were achieved under a constant electric current of 200 µA. After 20 h for stabilization, potentiometry was started and continued until the potential reached equilibrium. The maximum increment of the potential was 2.3 to 2.5 V.

### X-ray diffraction

Diffraction was achieved by using a RINT2000 diffractometer (Rigaku, Japan) with a 40 mA/40 kV CuK $\alpha$  beam, taking 41 min to move between 15° and 35° at intervals of 0.04°. The resultant diffractogram was quite noisy due to the short measurement time, which was necessary to minimize oxidation and moisture absorption of the samples wetted with H<sub>2</sub>SO<sub>4</sub> on exposure to air. Noise in the diffractograms was reduced by Savitsky-Golay smoothing. According to a previous report,<sup>6</sup> the peaks were divided by a Gaussian-Lorentzian approximation and the thickness of carbon layer stacks ( $L_c$ ) was calculated from the half width by using Sherrer's equation.

### Thermal analysis

After electrochemical treatment, the samples wetted with H<sub>2</sub>SO<sub>4</sub> were immediately placed in a Pt pan and differential

thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed simultaneously with a Thermo Plus (Rigaku) at a heating rate of 5°C/min under a flow of dried N<sub>2</sub>. For comparison, samples not subjected to electrochemical treatment were also immersed in H<sub>2</sub>SO<sub>4</sub> prior to DTA/TG measurements.

### Fourier transform infrared spectroscopy

The electrochemically treated samples were washed with water and dried. For each sample, a small amount of less than 1 mg was dispersed in a matrix of KBr (200 mg) and pressed to form a pellet. Fourier transform infrared (FT-IR) spectra were recorded as KBr disks on a Nicolet Magna 860 FTIR spectrometer under a flux of dried air.

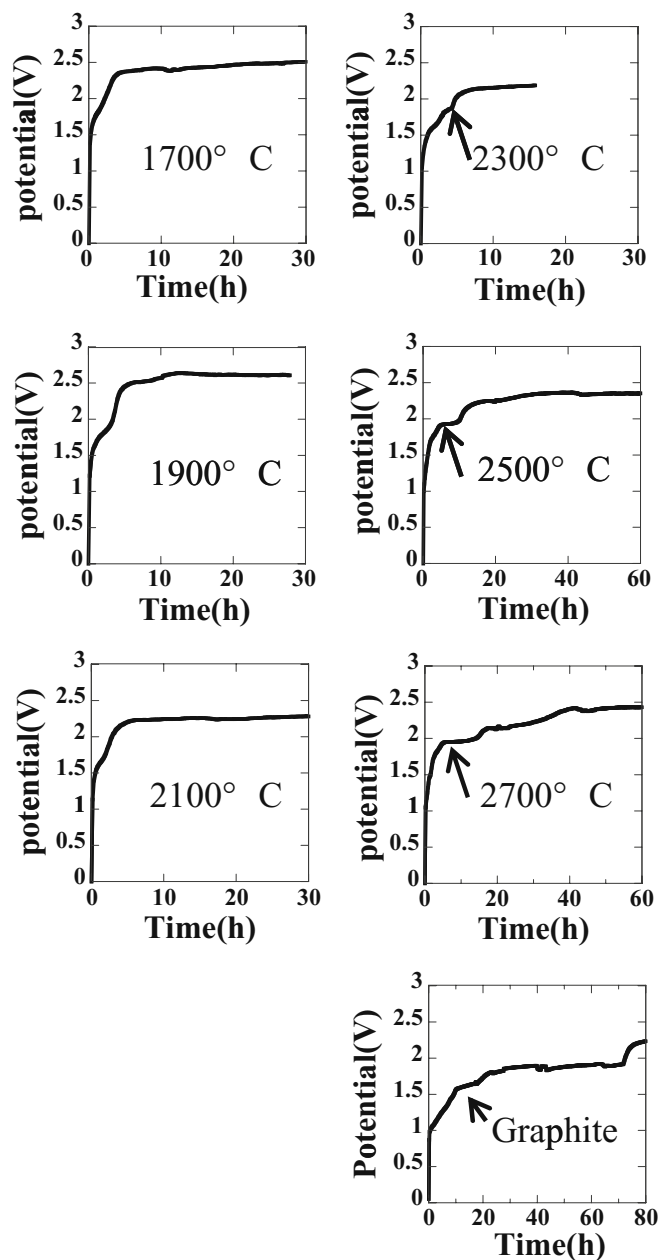
## Results

### Electrochemical treatment and potentiometry

The progress of the reaction was traced by in situ measurement of electrical potential, following the method of Iwashita and Inagaki.<sup>7</sup> Using potentiometry, intercalation should be recognized as stepwise increase of electric potential. Under such electrical treatment, graphite undergoes several stages of intercalation compounds, with different energy levels. The appearance of plateaus in the potential curve means that intercalation has advanced to the next stage. When intercalation reaches the final stage, the electric potential stops increasing. As shown for natural graphite in Fig. 1, plateaus can be observed in the potential curve in the course of reaching equilibrium. The plateaus were clearly observed for sugi samples carbonized at 2300°C or higher temperatures (arrowed regions in Fig. 1, 2300°, 2500°, and 2700°C). However, for samples carbonized at temperatures less than 2100°C, no clear plateau could be observed. The appearance of a plateau implies that for the sugi samples carbonized at 2300°C and higher temperatures, intercalation compounds with H<sub>2</sub>SO<sub>4</sub> can be formed.

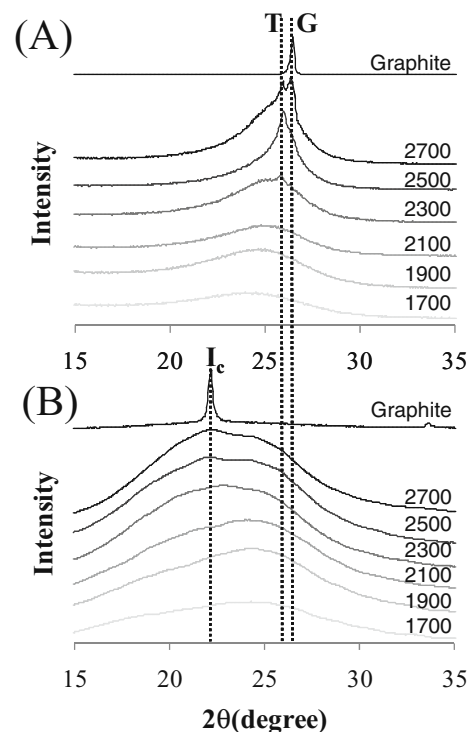
### X-ray diffraction

X-ray diffractograms of the samples before electrochemical treatment show that turbostratic and graphitic structure appeared at carbonization temperatures higher than 2300°C (Fig. 2A) as mentioned in a previous report.<sup>6</sup> Wood charcoals treated at 2300°C or higher temperatures probably have orderly stacked carbon layers that can form intercalation compounds. Iwashita and Inagaki<sup>7</sup> pointed out that H<sub>2</sub>SO<sub>4</sub> intercalation requires an orderly stack of carbon layers with a thickness of 20 nm at least in the case of graphitizable carbon. The sugi samples treated at 2500° and 2700°C had turbostratic and graphitic peaks with  $L_c$  values of 15–25 nm. These facts suggest that intercalation possibly occurred for sugi samples treated at 2500°C or higher.



**Fig. 1.** Potentiometry curves for sugi samples carbonized at various temperatures (1700°, 1900°, 2100°, 2300°, 2500°, and 2700°C) and natural graphite (Graphite), under electrochemical treatment in 98%  $H_2SO_4$ . Arrows indicate plateaus

In Fig. 2B, the (002) reflection for natural graphite just after electrochemical treatment, marked as G in Fig. 2A, disappeared and a new peak appeared at  $2\theta = 22.4^\circ$ , corresponding to 0.397 nm. This is a diagnostic peak for intercalation of  $H_2SO_4$  with a molecular size of about 0.460 nm. When  $H_2SO_4$  is inserted between the stacked carbon layers with an original separation distance of 0.335 nm, the distance increased to 0.795 nm, which is twice the original distance. For the sugi samples, although the reflection by a large amorphous region overlaps and makes the reflection of the ordered portion unclear, a new peak around  $22.4^\circ$  is

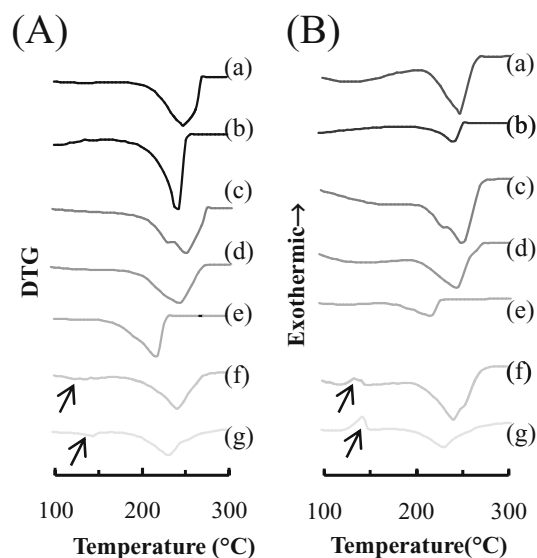


**Fig. 2A, B.** X-ray diffractograms of natural graphite and carbonized sugi samples **A** before and **B** after electrochemical treatment in 98%  $H_2SO_4$ . Bottom to the top: sugi samples carbonized at 1700°, 1900°, 2100°, 2300°, 2500°, and 2700°C, and natural graphite. G, Graphitic component; T, turbostratic component;  $I_c$ , intercalated component

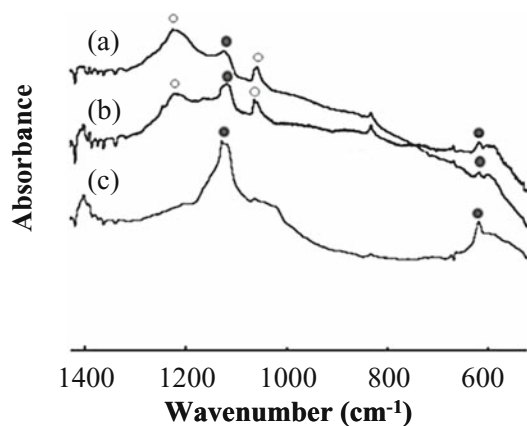
clearly observed for samples treated at 2300°C or higher. This indicates the occurrence of intercalation.

#### Thermal analysis

Figure 3 shows DTG and DTA curves, in which all samples for traces *b–g* had peaks at 200° to 250°C. These are considered to be due to evaporation of  $H_2SO_4$ , because a similar peak appeared for genuine  $H_2SO_4$  (trace *a* in Fig. 3). The shape of the peaks is very similar for DTG and DTA, but different among samples, possibly because the endothermic energy for the evaporation reaction of  $H_2SO_4$  depends on the samples. It is possible that interactions between  $H_2SO_4$  and the sample surface vary according to the carbonization temperature. The other possibility is that during the procedure,  $H_2SO_4$  may introduce water from the air in varying amounts. On the other hand, another peak was observed at around 130°C in the exothermic reaction, but only for the sugi sample carbonized at 2700°C and for graphite after electrochemical treatment (traces *f* and *g* in Fig. 3). This peak is possibly due to intercalated  $H_2SO_4$ . The peak around this temperature is known, at which point the graphite intercalation compound changes into exfoliated graphite, where the trapped  $H_2SO_4$  between the stacked carbon layers causes expansion and delamination of the stacked carbon layers.<sup>8</sup> Thus, thermal analysis indicated that the sugi sample carbonized at 2700°C could form an intercalation compound.



**Fig. 3.** **A** Thermogravimetric and **B** differential thermal analysis curves. *a*,  $\text{H}_2\text{SO}_4$ ; *b*, sugi carbonized at  $1900^\circ\text{C}$ , before electrochemical treatment; *c*, sugi carbonized at  $2700^\circ\text{C}$ , before electrochemical treatment; *d*, natural graphite before electrochemical treatment; *e*, sugi carbonized at  $1900^\circ\text{C}$ , after electrochemical treatment; *f*, sugi carbonized at  $2700^\circ\text{C}$ , after electrochemical treatment; *g*, natural graphite after electrochemical treatment. Arrows show characteristic peaks for intercalation compounds



**Fig. 4.** Fourier transform infrared spectra of residual compounds after electrochemical treatment and washing in water and drying. *a*, Graphite; *b*, sugi carbonized at  $2700^\circ\text{C}$ ; *c*, sugi carbonized at  $1900^\circ\text{C}$ . Filled circles, sulfonic acid bands; open circles, sulfonate bands

#### FT-IR spectroscopy

Figure 4 shows the FT-IR spectrum of residues after electrochemical treatment followed by washing in water and drying. In general, the residual product from the graphite intercalating compound is known as a “residual compound,” which partially keeps sulfuric acid molecules between its carbon layers. For all samples, bands for inorganic sulfuric acid were observed at around  $645$ ,  $1105$ , and  $1155\text{ cm}^{-1}$ , probably due to excess  $\text{H}_2\text{SO}_4$  that did not intercalate and remained in the sample even after washing in water (Fig. 4). On the other hand, for the natural graphite and sugi samples carbonized at  $2700^\circ\text{C}$ , additional bands due to a

sulfonate group appeared at  $1045$  and  $1180\text{ cm}^{-1}$ . This sulfonate group may have been produced via a reaction between carbon on the hexagonal carbon layer and intercalated sulfuric acid, possibly indicating intercalation of sulfuric acid between the hexagonal carbon layers (Fig. 4).

#### Discussion

Considering the results of potentiometry, X-ray diffraction, and thermal analysis, wood charcoal treated at  $2700^\circ\text{C}$  appears to intercalate sulfuric acid. The results indicate that even wood charcoal, which is categorized as nongraphitizable carbon can form an intercalation compound when the parent wood charcoal has a well-developed stacked carbon layered structure. Wood charcoal is a product of multiphased graphitization, including combination of  $\text{sp}^2$ - and  $\text{sp}^3$ -bonded carbon<sup>9</sup> and consists of a mixture of graphitic, turbostratic, and amorphous components. The graphitic component is considered to be the main body of the host for intercalation. By using  $\text{H}_2\text{SO}_4$  as a probe to investigate the wood charcoal structure, the amorphous component was revealed to be quite sparsely packed, allowing the  $\text{H}_2\text{SO}_4$  to pass through easily to reach the graphitic component. Another important point to be clarified is whether the turbostratic component can also form an intercalation compound. In this study, the possibility was implied, but not clarified. If turbostratic carbon can form intercalation structures, it will have practical uses for industry because turbostratic carbon can be systematically produced from wood using Ni catalysts.<sup>10</sup> Further investigations to identify which components of complicated wood charcoal can intercalate are expected to lead to future applications.

#### Conclusions

Sulfuric acid intercalation of sugi samples carbonized at various temperatures was investigated. After electrochemical treatment with  $\text{H}_2\text{SO}_4$ , only sugi samples carbonized at  $2300^\circ\text{C}$  or higher temperatures showed the (002) reflection in the X-ray diffractogram shifting to lower angles. This indicates that the stacking distance of hexagonal carbon layers was increased by intercalation. An exothermic peak at around  $130^\circ\text{C}$ , which is characteristic for  $\text{H}_2\text{SO}_4$ -graphite intercalation compounds, was observed by DTA for sugi samples that had been carbonized at  $2700^\circ\text{C}$  and electrochemically treated. However, this peak was not observed for sugi samples that were carbonized at  $1900^\circ\text{C}$  and electrochemically treated, or for samples not subjected to electrochemical treatment. The results of thermal analysis indicated that intercalation occurred with sugi samples carbonized at  $2700^\circ\text{C}$ . The electrochemically treated samples were washed in water and dried before FT-IR spectroscopy. For samples considered likely to show intercalation, bands due to sulfonate groups were observed and these were considered to be traces of  $\text{H}_2\text{SO}_4$  intercalation. Thus, this study revealed that wood charcoal can form intercalation

compounds when carbonized at temperatures higher than 2300°C with an ordered stack of hexagonal carbon layers.

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