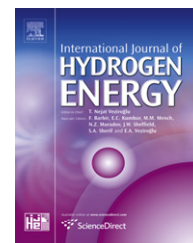


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# Hydrogen storage ability of porous carbon material fabricated from coffee bean wastes

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## ABSTRACT

The hydrogen storage ability at 298 and 77 K of porous carbon materials with microporous structures fabricated from coffee bean wastes through KOH activation was investigated regarding pore structure. The dependence of hydrogen storage ability on the pore structure of porous carbon materials was investigated at 298 and 77 K to clarify the storage mechanism of carbon materials. Hydrogen storage ability at 298 K was increased linearly with increasing of specific surface area increasing. The maximum amount of stored hydrogen was 0.6 wt.% on porous carbon material with 2070 m<sup>2</sup>/g specific surface area. The hydrogen storage ability at 77 K was 4.0 wt.% on the same sample. The hydrogen storage ability showed a linear relationship with the micro-pore volume size. These changes in the dependence of the hydrogen storage ability on pore size suggested that the storage configuration changed from two- to three-dimensional. The stored hydrogen densities in porous carbon materials calculated from these values were 5.7 and 69.6 mg/cm<sup>3</sup> at 298 and 77 K, respectively. The change in density indicated that the state of stored hydrogen in porous carbon materials was filled up aggregational state, which is extremely close to the liquid state, and suggested the realizing of high hydrogen storage ability on carbon materials fabricated from agricultural waste.

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## 1. Introduction

Recently, hydrogen energy has attracted attention as a countermeasure to the depletion of petroleum resources and to the global environmental problems associated with fossil-fuel use, because hydrogen is the cleanest fuel. The gravimetric energy density of hydrogen is 33 kW h/kg, and its calorific value is three times as high as that of petroleum [1]. Once hydrogen energy with excellent characteristics can be produced cheaply, it is considered that common energy systems will change from being fossil-fuel based to being

hydrogen-fuel based. Important challenges in achieving a hydrogen energy economy are not only hydrogen production but also hydrogen transport and storage. In particular, innovative hydrogen storage technology has not yet been established, although the production and transport of hydrogen have, to some extent, been established. Until now, hydrogen storage development has been explored using various strategies such as compression, liquefaction, metallic hydrides, and carbon materials. The hydrogen storage mechanism should involve physical adsorption to enable repeated use of hydrogen storage equipment. High specific surface areas are

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required for high-efficiency physical adsorption of hydrogen. Furthermore, light weight is also necessary for these storage materials to ensure low energy consumption during transport.

Because of the above requirements, carbon materials are superior materials for hydrogen storage. Carbon-based hydrogen storage materials, using carbon nanotubes [2], graphite nanofibers [3], and porous carbon, have been reported. Kojima et al. reported that activated carbon having a specific surface area of 3220 m<sup>2</sup>/g adsorbed 1.3 wt.% of hydrogen at room temperature [4]. It is known that porous carbon materials with a high specific surface area can be prepared by chemical activation with metallic compounds. Various chemical agents for porous carbon material activation have been studied, such as zinc chloride [5], and acid [6,7]. Recently, higher-specific-surface-area porous carbon materials with alkaline activation have attracted attention [8]. Porous carbon materials with specific surface areas have been produced by the reaction between alkali metal and graphite during alkaline activation with NaOH and KOH. Also, micropores in porous carbon materials with a high specific surface area have been fabricated [9–11]. Although there are mechanism theories for alkaline activation above 800 °C, almost the KOH activation mechanism for the porous carbon material synthesis from carbon materials was explained by the gasification and the elimination of CO or CO<sub>2</sub> [12–16]. These carbon materials for the hydrogen storage should be fabricated from wastes for genuine resolving of the environmental problems. And the research on specific storage mechanisms can lead to the identification of the best structure for hydrogen storage carbon materials fabricated from wastes. Some reports for porous carbon materials suggest that these storage mechanisms depend on temperature [4,17]. For example, the hydrogen storage ability is 0.7 wt.% at 296 K, which increased to 5.0 wt.% at 77 K [4]. The dependence of the hydrogen storage ability of porous carbon materials fabricated from waste on temperature has not been researched sufficiently in an orderly manner. Coffee beans wastes as raw materials for porous carbon materials were selected, because these wastes of 400,000 T had been discarded by beverage-manufacturer at 2007 in Japan. These coffee beans wastes exist all over the world in high volume. Hence, coffee beans wastes are appropriate for raw materials of hydrogen storage carbon materials. In this work, the relationship between the hydrogen storage ability and the structure of porous carbon materials fabricated from coffee beans waste as factory wastes was investigated at room and low temperatures to prove the fabrication hydrogen storage materials from waste and to clarify the storage mechanism.

## 2. Experimental

Carbon materials were prepared from waste coffee beans by steam activation using furnace heating. Waste coffee beans were dried in an oven at 120 °C for 24 h to remove moisture. Steam activation was applied in two phases: carbonization and activation. In carbonization, the dried coffee bean waste was placed into an SUS container with a bottom composed of mesh. Steam gas was introduced at 45 g/min into the container and heated at 500 °C for 1 h. After carbonization,

steam activation was performed with 45 g/min steam and 10 L/min CO<sub>2</sub> gas. Then, carbon materials were prepared by heating at 800 °C for 2 h. For KOH activation, the carbon materials to which KOH was added were placed into a SiC crucible. The weight ratios of KOH to carbon materials were from 1:1 to 5:1. Then, porous carbon materials were fabricated by heating at 850 °C for 2 h.

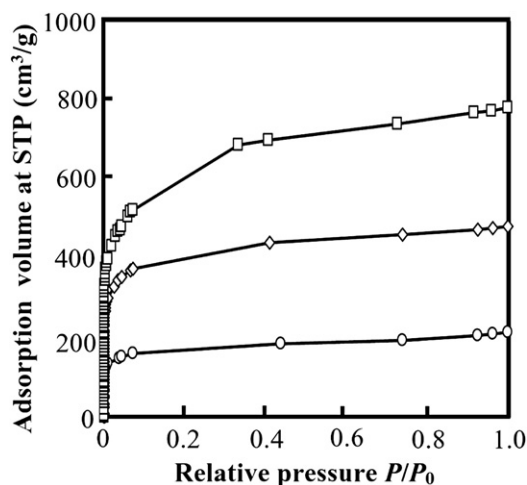
Pore characteristics, specific surface area, pore size distribution and pore volume were estimated by analyzing of the N<sub>2</sub> adsorption isotherm profiles of the carbon materials at 77 K. The isotherm profiles were obtained using Belsorp-max (BELL Japan). Before the N<sub>2</sub> adsorption measurement, absorbed gases were baked out at 200 °C for 10 h under vacuum pressure. After that, the balance pressure at each pressure for the samples was measured, and relative pressure was defined by the ratio of these balance pressures to the pressure of saturated vapor at 77 K. The specific surface area  $S_{\text{BET}}$  was calculated on the basis of the Brunauer–Emmett–Teller (BET) model [18]. The pore size distribution (PSD) was obtained by the micro-pore analysis method (MP-method) [19]. These pore sizes were calculated with assuming gas-sorption on the both inner side of slit-like pore model.

The crystal structures were estimated by the  $\theta$ – $2\theta$  method with X-ray diffraction (XRD) analysis. MO3XHF MXP3 (Mac Science) was used for the XRD analysis with Cu K $\alpha$  (1.54 Å) X-ray sources; these sources were powered by a current of 40 mA and a voltage of 40 kV.

The stored hydrogen content of the porous carbon materials was measured using the volumetric analysis defined by the JIS H 7201 “Method of determining the PCT relation of hydrogen absorbing alloys”. Prior to the analysis, a powder sample with the desired weight (0.5 g) was placed in a pressure vessel. In the pressure vessel, the sample was degassed under 10<sup>–2</sup> Torr at 423 K for 10 h, and then maintained at 298 K or 77 K. The stored hydrogen content of the sample under these conditions was assumed to be 0 wt.%. After closing the valve connected to the pressure vessel, the pressure in the hydrogen reservoir was controlled in the range of 0–12 MPa adjusting by the valve for hydrogen introduction. After closing the valve for hydrogen introduction and opening the valve connected to the pressure vessel, equilibrium pressure was obtained in the hydrogen reservoir and sample cell. The stored hydrogen content of the sample was calculated using the pressure drop measured with a high-pressure gauge. Temperatures at measurement were 298 and 77 K. 77 K was achieved by liquid nitrogen cooling.

## 3. Results and discussion

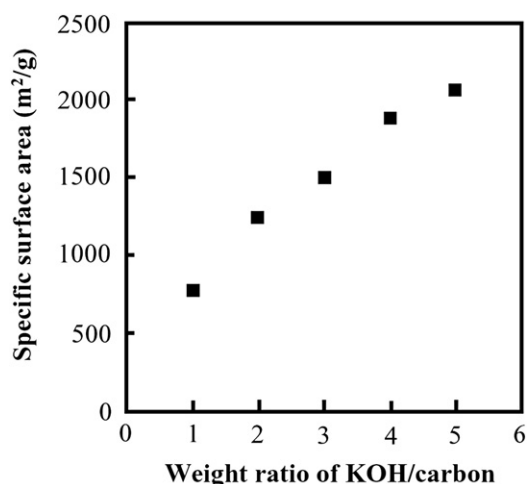
Fig. 1 shows that the N<sub>2</sub> adsorption isotherms of the porous carbon materials fabricated from carbon materials prepared from coffee beans wastes by KOH activation. The N<sub>2</sub> adsorption volume of porous carbon materials activated by KOH increased considerably at a relative pressure of less than 0.1. The N<sub>2</sub> adsorption capacity at the pressure of saturated vapor increased from 215 to 760 cm<sup>3</sup>/g as the weight ratio of KOH to carbon materials was increased from 1 to 5. The adsorption isotherms of all porous carbon materials indicated the Langmuir type [20]. Adsorption isotherms of the Langmuir type



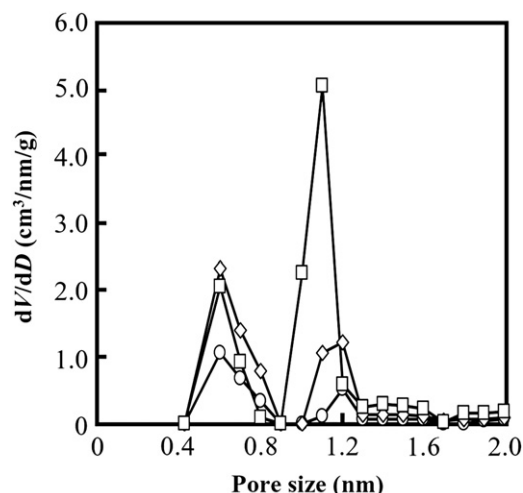
**Fig. 1** – Nitrogen adsorption isotherms of porous carbon activated with KOH. Weight ratio of KOH and carbon materials; 1:1 (○), 3:1(◇), 5:1(□).

were observed when the pore size of the carbon materials was micron order and the interaction potential between the carbon surface and  $N_2$  was high. Therefore, these results indicate that micro-pore structures were developed to porous carbon materials from waste to functional material by KOH activation.

Fig. 2 shows that the relationship between the specific surface area,  $S_{BET}$ , calculated using the BET model, and the weight ratio of KOH to carbon.  $S_{BET}$  was distributed in the range from 780 to 2070  $m^2/g$  as a function of the KOH percentage at activation.  $S_{BET}$  increased to 2070  $m^2/g$  as the weight ratio of KOH to carbon materials increased from 1 to 5. The maximum specific surface area of the obtained porous carbon material was higher than specific surface area of 200–1315  $m^2/g$  for carbon nano-materials such as carbon nanotube [21–25]. The PSD in all porous carbon materials indicated that the diameters of pores range from approximately 0.6–1.1 nm for all the materials, as shown in



**Fig. 2** – Relationship between specific surface area and weight ratio of KOH/carbon.



**Fig. 3** – Pore diameter distribution of porous carbon activated with KOH. Specific surface area of porous carbon materials; 780  $m^2/g$  (○), 1500  $m^2/g$  (◇), 2070  $m^2/g$  (□).

Fig. 3. Thus, these  $N_2$  adsorption characteristics showed that micropores were developed in porous carbon materials by alkalic activation. When  $S_{BET}$  values ranged from 780 to 1500  $m^2/g$ , the pore volume of approximately 0.6 nm increased from 1.06 to 2.34  $cm^3/g/nm$ . On the other hand, this increase was not observed in the  $S_{BET}$  range of 780–2070  $m^2/g$ . In addition, the volume of pore size with approximately 1.1 nm significantly increased from 0.58 to 5.07  $cm^3/g/nm$  at the range of 780–2070  $m^2/g$ . Average pore size of porous carbon calculated from the PSD also changed from 0.81 to 1.1 nm when  $S_{BET}$  increased to 780–2070  $m^2/g$ . Thus, it is considered that  $S_{BET}$  increased because the micropores with a diameter of approximately 1.0 nm formed in carbon materials upon KOH activation.

Fig. 4 shows the XRD patterns of the porous carbon materials fabricated through KOH activation. The large width pattern of  $2\theta = 24$  corresponds to the (002) plane of graphite from ICDD card No. 00-056-0159 (graphite hexagonal). Because the peaks in the diffraction patterns were broadened and such broadening was observed at a lower angle than that in the highly oriented polygraphite, it is clear that the graphite cluster in porous carbon was small and the order of graphene layers was short. The peaks assigned at (002) on the diffraction pattern became broader with an increase in specific surface area from 780 to 2070  $m^2/g$ . The extremely broad peaks at 44 were assigned to (10). Upon KOH activation, the diffraction peaks for (10) have a smaller effect than the diffraction peaks for (002).

Hydrogen storage capacity at 298 K was investigated in these porous carbon materials fabricated from coffee beans wastes by the KOH activation. In all the samples, the stored hydrogen content increased with the equilibrium pressure of hydrogen, as shown in Fig. 5. The maximum stored hydrogen content was obtained at 12 MPa. The stored hydrogen was decreased with reducing of hydrogen pressure, and almost stored hydrogen was desorbed from these porous carbon materials. Hence, the type of stored hydrogen on these carbon

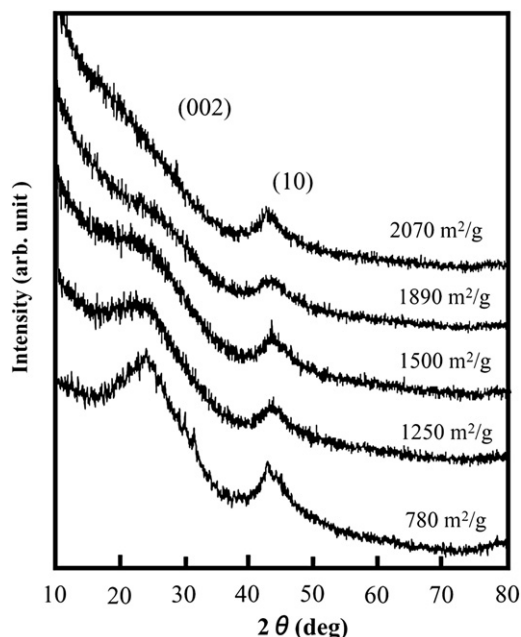


Fig. 4 – XRD patterns of porous carbon activated with KOH.

materials is the physisorption. Fig. 6 shows the maximum stored hydrogen content of the sample as a function of the specific surface area of porous carbon materials. The stored hydrogen content increased at a rate proportional to the specific surface area. The stored hydrogen content reached 0.6 wt.% a specific surface area of 2070 m<sup>2</sup>/g. These results indicate that the hydrogen storage ability at 298 K is affected by the specific surface area.

The hydrogen storage capacities at 77 K were investigated on these porous carbon materials fabricated from coffee beans wastes by the KOH activation, as shown in Fig. 7. In all samples, the stored hydrogen content was approximately 4 MPa in equilibrium pressure of hydrogen. The stored hydrogen content reached 4.0 wt.% at the specific surface area of 2070 m<sup>2</sup>/g. The amounts of stored hydrogen at 77 K for all

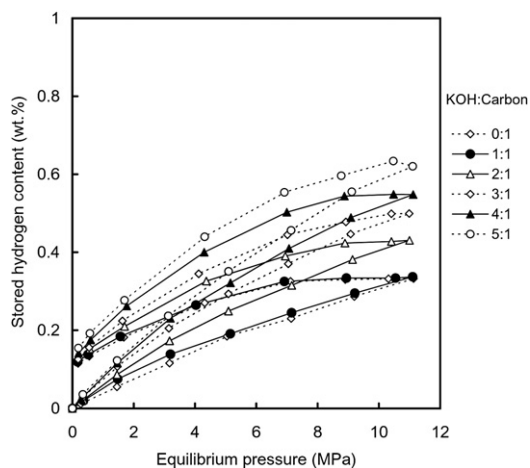


Fig. 5 – Stored H<sub>2</sub> content in porous carbon as a function of equilibrium pressure at 298 K.

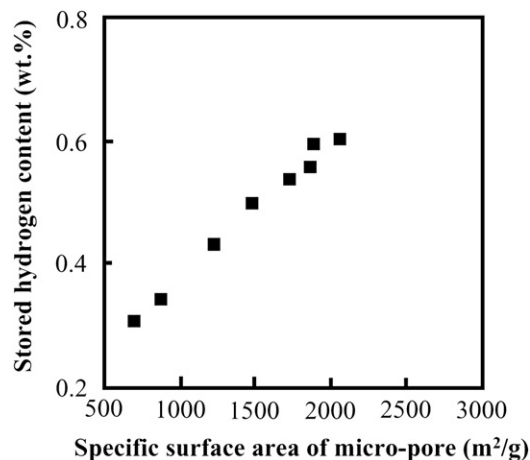


Fig. 6 – Relationship between maximum stored H<sub>2</sub> content and specific surface area of micro-pore in porous carbon at 298 K.

samples were larger than those at 298 K. The same trend of hydrogen storage ability with temperature is shown in other reports [4,17]. The relationship between the maximum amount of stored hydrogen and the specific surface area in porous carbon materials did not show a proportional relation, and we tried to find another relationship. Fig. 8 shows the maximum amount of stored hydrogen in the sample as a function of the pore volume size in porous carbon materials calculated from PSDs. The amount of stored hydrogen content increased with increasing pore volume size, which was controlled by the graphite structure in porous carbon materials. These results indicate that the hydrogen storage ability at 77 K is affected by the pore volume size. The change in the dependence of the amount of stored hydrogen from the specific surface area to pore volume size suggests that the stored hydrogen configuration changed from two-dimensional to three-dimensional storage.

To understand the condition of the adsorbed hydrogen, the density of adsorbed hydrogen was estimated. Zuttel et al.

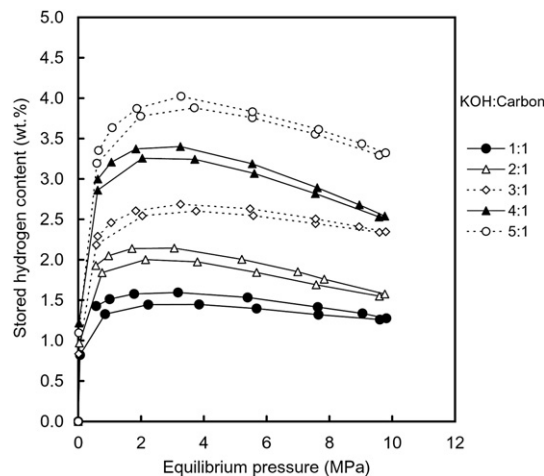
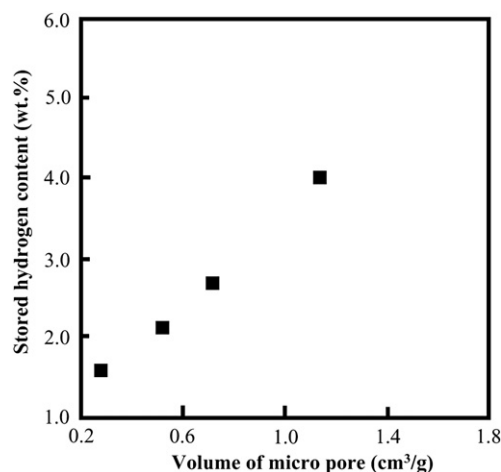


Fig. 7 – Stored H<sub>2</sub> content in porous carbon as a function of equilibrium pressure at 77 K.





**Fig. 8 – Relationship between stored maximum H<sub>2</sub> content and volume of micro-pore in porous carbon at 77 K.**

proposed a theoretical expression for the relationship between the graphite surface and adsorbed hydrogen under the assumption that hydrogen atoms adsorb as a monolayer on the graphite surface [25].

$$W_0 = \frac{M \cdot s}{\left(\frac{\sqrt{3}}{2}\right) \cdot \left(\frac{\sqrt{2 \cdot N_a \cdot M}}{\rho}\right)^{\frac{2}{3}}} \quad (1)$$

$W_0$  is the amount of adsorbed hydrogen,  $M$  is the molecular mass ( $=2$ ),  $s$  is the specific surface area of the sample,  $N_a$  is the Avogadro constant and  $\rho$  is the density of adsorbed molecules. From our results, the densities of adsorbed hydrogen were 3.2–5.7 mg/cm<sup>3</sup> at 298 K and 47.4–69.6 mg/cm<sup>3</sup> at 77 K. The density at 69.6 mg/cm<sup>3</sup> suggested that the state of adsorbed hydrogen in porous carbon materials was the filled up aggregational state, which is extremely close to the liquid state, because the theoretical density of hydrogen on liquid is 70.8 mg/cm<sup>3</sup>. The kinetic energy of hydrogen molecules at 77 K is low compared with 298 K, and causes the hydrogen molecules to be easily adsorbed to the walls of carbon micropores by van der Waals force. Hydrogen molecules agglomerate inside the micro-pore because the interaction between hydrogen molecules at 77 K was also greater than that at 298 K. Hence, the amount of stored increased linearly increasing of the micro-pore volume. This trend on temperature dependence was also reported carbon materials fabricated such as carbon nanofiber from other raw materials by several methods [26–29]. These results about porous carbon materials fabricated from coffee beans waste indicated that porous carbon materials which had same quality level on hydrogen storage ability could be fabricated from wastes which are unstable quality on raw material.

#### 4. Conclusions

The hydrogen storage ability at 298 and 77 K of the porous carbon materials with microporous structures fabricated from coffee beans wastes through KOH activation was investigated

with respect to pore structure. At 298 K, the hydrogen storage ability of porous carbon materials increased linearly with specific surface area. The hydrogen storage ability of the material with a specific surface area of 2070 m<sup>2</sup>/g was 0.6 wt.% at 12 MPa. The hydrogen storage ability of this sample at 77 K was 4.0 wt.% at 4 MPa and showed linear relationship with the micro-pore volume size. These dependences of stored hydrogen suggest that the storage configuration changed from two-dimensional to three-dimensional storage. The stored hydrogen densities in porous carbon materials calculated from these values were 5.7 and 69.6 mg/cm<sup>3</sup> at 298 and 77 K, respectively. These results indicated that porous carbon materials which had hydrogen storage ability could be fabricated from wastes which are unstable quality on raw material.

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