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Influence of milling conditions on hydrogen storage capacities of activated carbon mechanically milled in an H_2 atmosphere

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Abstract

We investigated whether the hydrogen storage capacity of activated carbon (AC) powder prepared by mechanical milling in an H_2 atmosphere is influenced by the milling conditions. The hydrogen storage capacity of AC milled for more than 20 h using a 30 ml pot tended to be larger than that obtained when using a 45 ml pot. This suggests that the number of trapping sites for hydrogen storage increased as the nanostructure progressed because milling using a smaller pot might produce greater acceleration than that using a large one. In addition, the applied force exerted on powders on the mill wall by the mass of balls in the smaller pot might be stronger than that in the larger one because the ball filling fraction of the former is larger than that of the latter. The intensities of (0 0 2) diffraction of AC milled for more than 20 h using the 30 ml pot were weaker than those obtained when using the 45 ml pot. The hydrogen storage capacity increased as the initial H_2 pressure in the milling pot increased. This indicates that physisorption might contribute to the hydrogen storage mechanism of AC mechanically milled in an H_2 atmosphere. However, we assume that the physisorption capacity might be small because the hydrogen storage capacity showed little dependence on the specific surface area of the host AC. The hydrogen storage capacity might also be independent of the particle size of the host AC.

Keywords: Hydrogen storage capacity; Activated carbon; Mechanical milling condition; Pot volume; Initial hydrogen pressure

1. Introduction

Nanostructured graphite, as reported by Orimo et al., can store 7.4 wt.% H_2 [1] and has attracted attention as a promising hydrogen storage material of the future. This large hydrogen storage capacity is related to the number of defect structures produced by mechanical milling [2]: that is defect structures might act as trapping sites for hydrogen storage. Although we tried to prepare a better hydrogen storage material by using activated carbon (AC) powders with many defects, the maximum capacity of AC hydrogenated by mechanical milling was only 2.6 wt.% [3]. Furthermore, the hydrogen storage capacities of natural graphite (NG) and activated carbon fiber (ACF) showed little dependence on their host structures in our studies and were both about 3.0 wt.% [4]. We believe that the difference between the capacities of the nanostructured graphite reported by Orimo et al. [1,2] and our nanocarbons [3,4] might be related to the milling conditions. Table 1 shows the principal differences between their and our milling conditions. We focused on the volume of the milling pot, the initial H_2 pressure introduced into the milling pot, and the particle sizes of the host AC.

We investigated the influence of the above milling conditions on the hydrogen storage capacity of AC prepared by mechanical milling in an H_2 atmosphere.

2. Experimental

2.1. Sample preparation

We used activated carbon (AC) powders (Maxsorb; The Kansai Coke and Chemical) with different specific surface

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Table 1
Comparison of milling conditions

Condition	Ours	Orimo et al.s [1,2]
Pot volume (ml)	45	30
Number of balls	22 (ϕ7)	20 (ϕ7)
Initial H_2 pressure (MPa)	0.8	1.0
Particle size of host (μm)	35	∼200

Table 2
Several kinds of activated carbon

Sample name	Particle size[a] (μm)	Specific surface area[a] (m^2/g)
AC-1	35	1470
AC-2	40	2400
AC-3	200	2500
AC-4	30	3100

[a] Catalogue value.

areas, as shown in Table 2. Each AC (0.3 g) was degassed below 1×10^{-3} Pa at 300 °C using a turbomolecular pump and placed in 30 and 45 ml steel pots with 22 steel balls each 7 mm in diameter. The pots were housed in a glovebox filled with purified argon. These pots were equipped with a connection valve for the introduction and evacuation of hydrogen. The pots were then removed from the glovebox and degassed using a rotary pump, and high-purity H_2 (99.9999%) was introduced at initial pressures 0.2–0.8 MPa. The pots were then mounted in a planetary ball mill apparatus (Fritsch, P7) and the host was mechanically milled at 400 rpm for 1–100 h at room temperature. All the samples were handled in the glovebox before and after mechanical milling.

2.2. Analysis and characterization

We undertook a structural analysis using X-ray diffraction (XRD) measurements (Rigaku, MultiFlex, with Cu Kα radiation) and Brunauer–Emmett–Teller (BET) adsorption measurements (YUASA IONICS, NOVA 2200, under a relative pressure $P/P_0 < 0.06$). The hydrogen desorption and concentration were characterized by thermal desorption mass spectroscopy (TDS) (NTT-AT, custom made) and the inert gas fusion-thermal conductivity method (HORIBA, EMGA-621W).

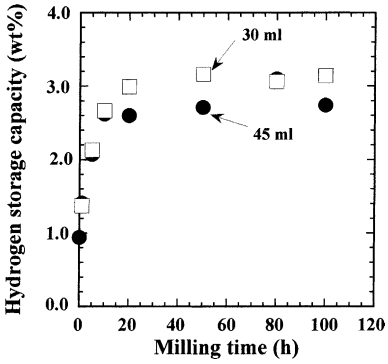

Fig. 1. Dependence of hydrogen storage capacities on milling pot volume (□, 30 ml pot; ●, 45 ml pot).

3. Results and discussion

3.1. Pot volume dependence

We consider the milling process to be dependent on the volume of the milling pot. That is, we expect nanocarbons milled using different milling pots to have different structures [5] and to bond differently with hydrogen. First, we examined whether the volume of the milling pot influenced the hydrogen storage capacity.

Fig. 1 shows dependence of the hydrogen storage capacity on milling pot volume. The hydrogen storage capacity of AC-1 milled for up to 10 h remained almost the same regardless of pot volume. However, the capacity of AC-1 milled for more than 20 h using a 30 ml pot tended to be larger than that obtained when using a 45 ml pot and the difference was about 0.5 wt.%. This difference may depend on the milling process.

Fig. 2 shows XRD patterns of milled AC along with the milling times. The intensities at around 24 °C of AC milled for more than 20 h using a 30 ml pot were weaker than those obtained when using a 45 ml pot [3]. This indicates that AC milled for more than 20 h using a 30 ml pot made more progress in terms of nanostructure than when using a 45 ml pot; that is there was an increase in the number of trapping sites for hydrogen storage.

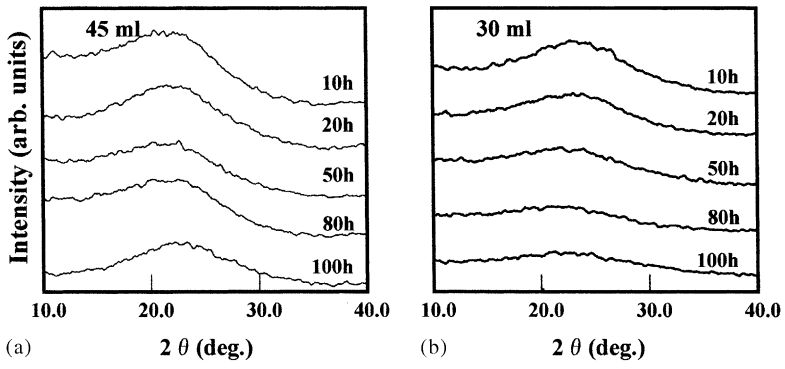

Fig. 2. Comparison of XRD patterns of AC milled using 30 and 45 ml pots.