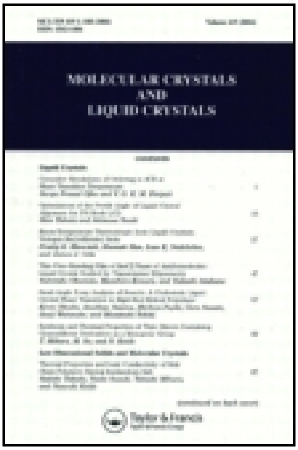

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Occlusion of Hydrogen in Alkali Metal-Intercalated Cup-Stacked Carbon Nanofibers

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Hydrogen storage in alkali metal-graphite intercalation compounds (AGICs) prepared from cup-stacked carbon nanofibers (A-CNFs, A=K, Rb and Cs) was studied by means of thermal desorption of hydrogen. The hydrogen sorbed to stage-1 K-CNFs amounts to 0.067 dm^3 (STP) per gram of carbon, most of which is fixed to KGIC as a chemical component.

Keywords: carbon nanofiber; graphite intercalation compound; hydrogen storage

INTRODUCTION

Hydrogen is a clean energy resource, and therefore an effective storage system is required for utilization of hydrogen energy. We have

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studied sorption of hydrogen to alkali metal-graphite intercalation compounds (AGICs, A=K, Rb and Cs) prepared from an exfoliated and recompressed sheet of graphite flakes (Grafoil GTA, Union Carbide, USA). The hydrogen sorbed to stage-1 KGIC amounts to 0.076 dm^3 (STP) per gram of carbon at room temperature and 20 kPa hydrogen pressure. Most of the hydrogen is accommodated in the bulk as hydride ions [1].

Here we have extended our study to AGICs prepared from fibrous graphite: cup-stacked carbon nanofibers (CNFs). A single CNF, typically *ca.* 50 nm in outer diameter and 25 μm in length, is comprised of stacked cups made of 9–12 truncated conical graphene sheets with the interlayer distance of 0.34 nm and the inclination of *ca.* 20° with respect to the fiber axis, and a long hollow core along the axis, *ca.* 15 nm in diameter. Zigzag outer- as well as inner-surfaces consist of graphene sheet-planes and edges. Therefore, CNFs would be easily intercalated with alkali metal and hydrogen due to their crystalline structure, for edges of graphene-sheets are found on the surface and slipping of truncated conical sheets in parallel with each other would expand their interlayer spacing.

EXPERIMENTAL

Alkali metal-intercalated cup-stacked carbon nanofibers (A-CNFs, A=K, Rb and Cs) were prepared from CNFs (Curbere 24HT, GSI Creos Co., Japan) by the two-zone vapor transport method, the same as used for the preparation of AGICs from carbon filaments grown in argon plasma [2]. CNFs had been preheated at 623 K *in vacuo* for a few days. The composition x in AC_x for A-CNFs was determined by the gravimetric analysis of the components separated on thermal desorption of alkali metal at 1070 K *in vacuo*. It was 11.2–11.7, 8.2–9.7, and 7.6 for K-CNFs, Rb-CNFs, and Cs-CNFs, respectively. Hydrogen-doped A-CNFs, denoted as A-CNFs(H_2), were prepared by exposing A-CNFs to hydrogen (Takachiho Chemicals, 99.9999% purity) of *ca.* 60 kPa for more than a week at room temperature.

A-CNFs and A-CNFs(H_2) easily decomposed in the atmosphere, so that they were transferred from a reaction ampoule through a breakable glass seal to pre-evacuated sample cells. The powder x-ray diffraction of A-CNFs showed a very broad pattern in the 2θ region corresponding to the interlayer distance of 0.5–0.6 nm. Their stage structure was confirmed by Raman microscope spectroscopy with Nd^{3+}-YAG laser excitation at 532 nm. Thermal desorption of hydrogen from A-CNFs(H_2) was observed by counting hydrogen desorbed upon raising temperature of a sample at a constant rate of 5 K min^{-1} from

300 to 1100 K with the aid of a quadrupole mass-analyzer. The total amount of hydrogen sorbed to A-CNFs was estimated from their thermal desorption spectrum in the same way as described in the previous paper [1].

RESULTS AND DISCUSSION

Raman scattering from A-CNFs (A=K, Rb and Cs) exhibited a peak consisting of two components in the vicinity of 560 cm^{-1} and a broad asymmetric band around 1500 cm^{-1}. The feature of the band is quite similar to that of stage-1 AGICs (A=K, Rb and Cs), in contrast with a sharp peak observed at 1577 cm^{-1} for pristine CNFs, which is assigned to the E_{2g2} in-plane mode of stacked graphene sheets. These spectral features indicate that CNFs have been intercalated with alkali metal to form stage-1 A-CNFs, where their local structure of approximate D_{6h} symmetry has been preserved.

Upon exposure of stage-1 K-CNFs to hydrogen, they turned from dark brown to bluish black and their Raman spectrum changed from an asymmetric band to a sharp peak observed at 1601 cm^{-1}, which was identical with the peak observed for stage-2 K-CNFs, as shown in Figure 1. These changes demonstrate that K-CNFs were hydrogenated

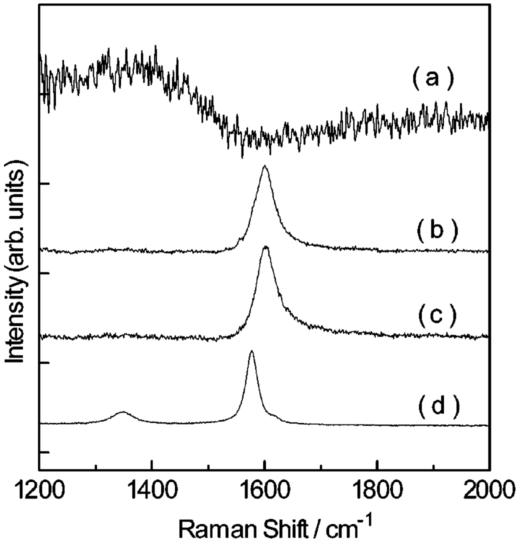

FIGURE 1 Raman spectra of (a) stage-1 K-CNFs, (b) K-CNFs (H_2), (c) stage-2 K-CNFs, and (d) pristine CNFs.

to K-CNFs(H_2) and their structure changed to stage-2. On the other hand, exposure of stage-1 Rb-CNFs and Cs-CNFs to hydrogen did not make a change in color or in their asymmetric Raman band, which indicates that their structure remained unchanged.

A thermal desorption spectrum of K-CNFs(H_2) exhibits a prominent peak at 500 K accompanied with small shoulders around 420 and 450 K, as shown in Figure 2. The spectral feature is quite similar to that observed for grafoil-based KGIC(H_2). Plots of ln P *vs.* $1/T$ give a straight line in the region from 465 to 495 K, indicating that the rate of the desorption in the region is determined by diffusion of hydrogen species in the bulk with the activation energy of 42 kJ mol^{-1}. Rb-CNFs(H_2) showed a thermal desorption spectrum consisting of a sharp peak at 480 K, a small peak at 425 K and a shoulder around 400 K. A straight line obtained by plotting of ln P *vs.* $1/T$ indicates that the hydrogen desorbed in the region from 450 to 480 K derives from hydrogen species in the bulk. The activation energy for desorption is estimated at 41 kJ mol^{-1}.

AGICs (A=K, Rb and Cs) are active in the dissociation of hydrogen molecules into atoms in the H_2-D_2 equilibration reaction [3], and hydrogen is accommodated as hydride ions in KGIC(H_2) and as hydrogen atoms in RbGIC(H_2) [4,5]. Thus, in the same manner, K-CNFs are

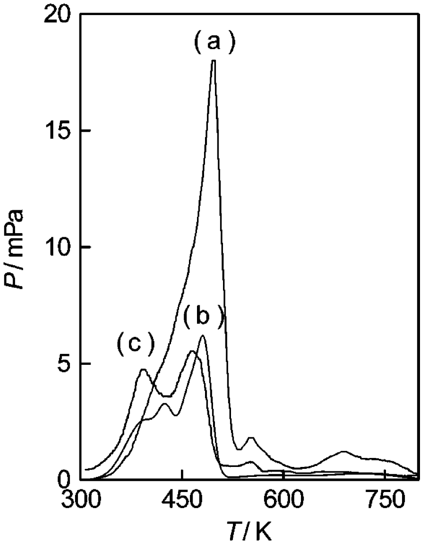

FIGURE 2 Thermal desorption spectra of (a) K-CNFs(H_2), (b) Rb-CNFs(H_2), and (c) Cs-CNFs(H_2).

considered to occlude hydrogen as hydride ions in the bulk and Rb-CNFs as hydrogen atoms. The hydrogen desorption observed in the region lower than 450 K seems to originate from hydrogen molecules and atoms adsorbed on the surface. Cs-CNFs(H_2) showed two broad desorption bands in the temperature region lower than the region where K-CNFs(H_2) and Rb-CNFs(H_2) showed the desorption originating from hydrogen species in the bulk. These bands appearing in the low temperature region seem to be attributable to hydrogen adsorbed on the surface. The total amount of the hydrogen sorbed to K-CNFs and that to Rb-CNFs are estimated at 0.067 and 0.027 dm^3 (STP) per gram of carbon, respectively.

In conclusion, most of the hydrogen sorbed to K-CNFs is fixed to KGIC as a chemical component.

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