

HYDROGEN DESORPTION AND ADSORPTION MEASUREMENTS ON GRAPHITE NANOFIBERS

C. C. Ahn, Y. Ye, B. V. Ratnakumar*, C. K. Witham, R. C. Bowman, Jr.* and B. Fultz

Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125.

Graphite nanofibers were synthesized and their hydrogen desorption and adsorption properties are reported for 77 and 300 K. Catalysts were made by several different methods including chemical routes, mechanical alloying and gas condensation. The nanofibers were grown by passing ethylene and H₂ gases over the catalysts at 600°C. Hydrogen desorption and adsorption were measured using a volumetric analysis Sieverts' apparatus, and the graphite nanofibers were characterized by transmission electron microscopy (TEM) and BET surface area analysis. The absolute level of hydrogen desorption measured from these materials was typically less than 0.01 H/C atom, comparable to other forms of carbon.

*and Jet Propulsion Laboratory, Pasadena, CA 91109

INTRODUCTION

The main impediment to the use of hydrogen as a transportation fuel is the lack of a suitable means of storage. Compressed gas storage is bulky and requires the use of high strength containers. Liquid storage of hydrogen requires temperatures of 20K and efficient insulation. Solid state storage offers the advantage of safer and more efficient handling of hydrogen, but promises at most 7% hydrogen by weight and more typically 2%. There has therefore been much interest in recent reports[1] that certain carbon graphite nanofibers[2] can absorb and retain 67 wt% hydrogen gas at ambient temperature and moderate pressures (i.e., up to 23 standard liters or 2 grams of hydrogen per gram of carbon at 50 - 120 bar). The highest hydrogen adsorption reported for any graphite fiber microstructure was 11 wt%[1]. Approximately 90% of the absorbed hydrogen was claimed to be desorbed at ambient temperature by reducing the pressure, while the balance is desorbed upon heating. Such claims are especially noteworthy, given that, up to this point, the typical best value of hydrogen adsorption in carbon materials has been on the order of 4 wt%, or 0.5 H/C (although there is also a recent claim that up to 10 wt% was achieved for H storage in single wall nanotubes[3]). Owing to the potential importance of new materials with high hydrogen storage capacity for the world-wide energy economy, transportation systems and interplanetary propulsion systems, we have synthesized graphitic structures of appropriate morphology to make our own measurements of hydrogen absorption and desorption.

MATERIAL SYNTHESIS AND MORPHOLOGY

Several graphite nanostructured materials were prepared using Fe-Cu catalysts of different compositions, in order to generate a range of fiber sizes and morphologies. We used either chemical methods, mechanical alloying or gas condensation to produce the catalysts. The chemical method consisted of reduction of Fe and Cu nitrate precursors using the generic conditions of Rodriguez and Baker that produce high yields of graphite nanofibers[2, 4, 5]. Mechanically alloyed catalysts were produced using a SPEX 8000 mixer/mill using Fe and Cu powders in appropriate proportions[6]. A variation of the gas condensation method[7] was also used to produce catalyst.

Catalysts were placed in a tube furnace and their surface oxide was reduced using a 7 vol% H₂ in Ar mixture at either 250 or 550 °C for 1 hr. The fibers were then grown by passing a mixture of ethylene and H₂ gases over the catalysts at a temperature of 600 °C. A summary of the ten different materials we prepared is outlined below in Table I.

Sample #5 showed a range of microstructures including corkscrews, tubes and a significant fraction of fibers with the “herringbone” morphology as shown in Fig. 1. Here we see a high resolution TEM micrograph which shows the herringbone structure formed by c-axis graphitic planes, typical of the nanofiber morphology. Before exposure to hydrogen, the samples were vacuum annealed at 900 °C.

HYDROGEN DESORPTION MEASUREMENTS

Our Sieverts’ apparatus (i.e., a volumetric system for quantitative measurement of gas absorption and desorption by solids) used metal seals, an oil-free vacuum pumping system and research purity hydrogen gas[8]. Pneumatic valve operation and pressure and temperature data monitoring were computer controlled, permitting automatic isotherm data collection. The system was thoroughly leak checked at 200 bar and calibrated to ensure reliable determination of the hydrogen storage properties.

Desorption measurements were performed at 77 and 300 K by first placing about 0.3g of sample in the reactor. H₂ gas was admitted into the evacuated reactor to achieve a typical pressure of 4.5 or 80 bar for the 77 K runs or 180 bar for the 300 K runs. This pressure was maintained for 15 hrs. to allow the sample to reach equilibrium. The reactor was valved off from the rest of the system and the system was evacuated again. The desorbed H₂ was then measured by a pressure transducer. Identical runs were also performed on an empty reactor chamber so that the data could be properly corrected for instrument effects. For comparison, we also performed measurements on a “Saran” carbon, a pure, dense, porous material with high surface area, formed by the pyrolysis of polyvinylidene chloride. The microstructure of this material consists of graphite microcrystals in an amorphous carbon matrix[9]. In addition to H₂ desorption measurements, sample surface areas were measured using a Micromeritics ASAP 2000 BET surface analysis apparatus with N₂ gas.

RESULTS AND DISCUSSION

Results from five sets of runs from the “Saran” carbon and Sample #5 and #8 are shown in Fig. 2. For comparison, at the maximum pressure of 3 bar at 77 K, the hydrogen adsorption capacity of the Saran carbon is 2.4 wt%. The desorption of H₂ in the graphite nanofiber samples is small but measurable. For the size of our samples, the sensitivity was better than 1% accuracy on a per atom basis. Table II summarizes the results of BET surface area measurements and hydrogen desorption data. Data from a high performance activated carbon sample denoted AX-21 were obtained from the literature[10] and included for comparison.

As measured on a per atom basis, our graphite nanofibers may seem to show adsorption beyond what one might expect from normal surface adsorption. When comparison is made to the Saran carbon, the ratio of hydrogen coverage to surface area seems high for the graphite nanofibers. We would expect a change in slope of such an isotherm but this was not observed. We believe this results from the presence of surface irregularities in the graphite nanofibers that are not detected by the larger N₂ molecules in our BET measurements. Support for this viewpoint is found in the shapes of the isotherms in Fig. 2. At a given temperature the isotherms for the graphite nanofibers and the Saran carbon have a similar shape, but a vertical offset. This difference by a scaling factor implies the same isosteric heat of adsorption for both types of carbons, but there are more available sites for the Saran carbon.

None of the present hydrogen adsorption or desorption measurements performed on any of the carbon nanofiber materials has indicated a hydrogen storage capacity that exceed the values previously reported for various activated carbons[10, 12]. In light of our results, the results of Chambers, et al[1] are especially surprising. Their claim of 2 gms of H₂ per gm of C storage imply that 16 monolayers of H₂ must be accomodated within each graphitic plane (using a hard sphere model and their value of 0.289 nm kinetic diameter for H₂) in order to account for the reported adsorption. Their data for H₂ adsorption in graphite of 4.5 wt% implies that even this material accomodates H₂ beyond the 2.7 wt% value that one would achieve with the commensurate $\sqrt{3}$ structure. Furthermore, their reported hydrogen capacity for graphite at room temperature is over an order of magnitude greater than the

values determined by others[10, 12] for activated carbons at 298 K. The best of these carbons yielded H₂ adsorption in the range of ~5 wt% only when cooled to below 100 K.

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References

- [1] A. Chambers, C. Park, R. T. K. Baker and N. M. Rodriguez, *J. Phys. Chem. B*, **102** 4253 (1998).
- [2] N. M. Rodriguez and R. T. K. Baker, "Storage of Hydrogen in Layered Nanostructures", U. S. Patent #5,653,951, Issued Aug. 5, 1997.
- [3] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune and M. J. Heben, *Nature* **386**, 377 (1997).
- [4] N. M. Rodriguez, *J. Mater. Res.* **8**, 3233 (1993).
- [5] N. M. Rodriguez, A. Chambers, and R. T. K. Baker, *Langmuir* **11**, 3862 (1995).
- [6] B. Fultz, C. C. Ahn, S. Spooner, L. B. Hong, J. Eckert and W. L. Johnson, *Metall. Trans.* **27A**, 2934 (1996).
- [7] B. Fultz, C. C. Ahn, E. E. Alp, W. Sturhahn and T. S. Toellner, *Phys. Rev. Lett.* **79**, 937 (1997).
- [8] R. C. Bowman, Jr., C. H. Luo, C. C. Ahn, C. K. Witham and B. Fultz, *J. Alloys Comp.*, **217**, 185 (1995).

- [9] R. A. Wessling, Polyvinylidene Chloride, Gordon & Breach, New York, 1977.
- [10] Y. Zhou and L. Zhou, *Sci. in China* **B39**, 598 (1996).
- [11] M. Nielsen, J. P. McTague and W. Ellenson, *J. Phys.* **38** C4/10-C4/18 (1977).
- [12] R. Chahine and T. K. Bose, *Int. J. Hydrogen Energy* **19**, 161 (1994).

TABLE I. Range of catalyst compositions and reactant gases used to produce graphite nanofibers.

Sample	Catalyst composition, Preparation method	Reduction temp. °C	Reactant Gas composition	Nanofiber growth temp. °C/ time
#1	Fe ₇₅ Cu ₂₅ (chemical)	550	H ₂ :C ₂ H ₄ (80:20)	600/1 hr
#2	Fe ₇₀ Cu ₃₀ (chemical)	550	H ₂ :C ₂ H ₄ (80:20)	600/1 hr
#3	Fe ₇₀ Cu ₃₀ (chemical)	550	H ₂ :C ₂ H ₄ (20:80)	600/1 hr
#4	Fe ₈₀ Cu ₂₀ (chemical)	550	H ₂ :C ₂ H ₄ (20:80)	600/1 hr
#5	Fe ₉₀ Cu ₁₀ (mech. alloy)	550	H ₂ :C ₂ H ₄ (20:80)	600/1 hr
#6	Fe ₈₅ Cu ₁₅ (mech. alloy)	550	H ₂ :C ₂ H ₄ (20:80)	600/1 hr
#7	Fe ₉₀ Cu ₁₀ (gas condens.)	550	H ₂ :C ₂ H ₄ (20:80)	600/3 hrs
#8	Fe ₉₀ Cu ₁₀ (gas condens.)	250	H ₂ :C ₂ H ₄ (20:80)	600/3 hrs
#9	Fe ₈₀ Ni ₂₀ (mech. alloy)	250	H ₂ :C ₂ H ₄ (20:80)	600/3 hrs
#10	Fe ₈₀ Ni ₂₀ (gas condens.)	250	H ₂ :C ₂ H ₄ (20:80)	600/3 hrs

TABLE II. Comparison of surface area as measured by BET, desorbed atomic ratio of H to carbon, and total H coverage assuming diameter of solid molecular H of 0.351 nm[11].

Carbon Sample	Specific Area (m ² /g)	H/C at 4.5 bar 77 K	H/C at 160 bar 300 K	H coverage (m ² /g)
AX-21 data from [10]	3000	0.24	0.06(at 70 bar)	150
Saran carbon	1600	0.29 [3 bar]	0.05	130
#5	25	0.02	0.029	73
#8	23	—	0.025	63

FIGURE CAPTIONS

Figure 1. High resolution image from end of graphite nanofiber showing herringbone morphology. Inset at lower left shows lattice planes from boxed region.

Figure 2. Log-Log plot of 77 and 300 K isotherm data showing amount of adsorbed hydrogen/carbon for Sample #5 and #8 as a function of pressure. When multiple runs were taken, error bars are shown, with only the top half of the error bars drawn for clarity. Traces from Saran carbon are also shown for comparison.

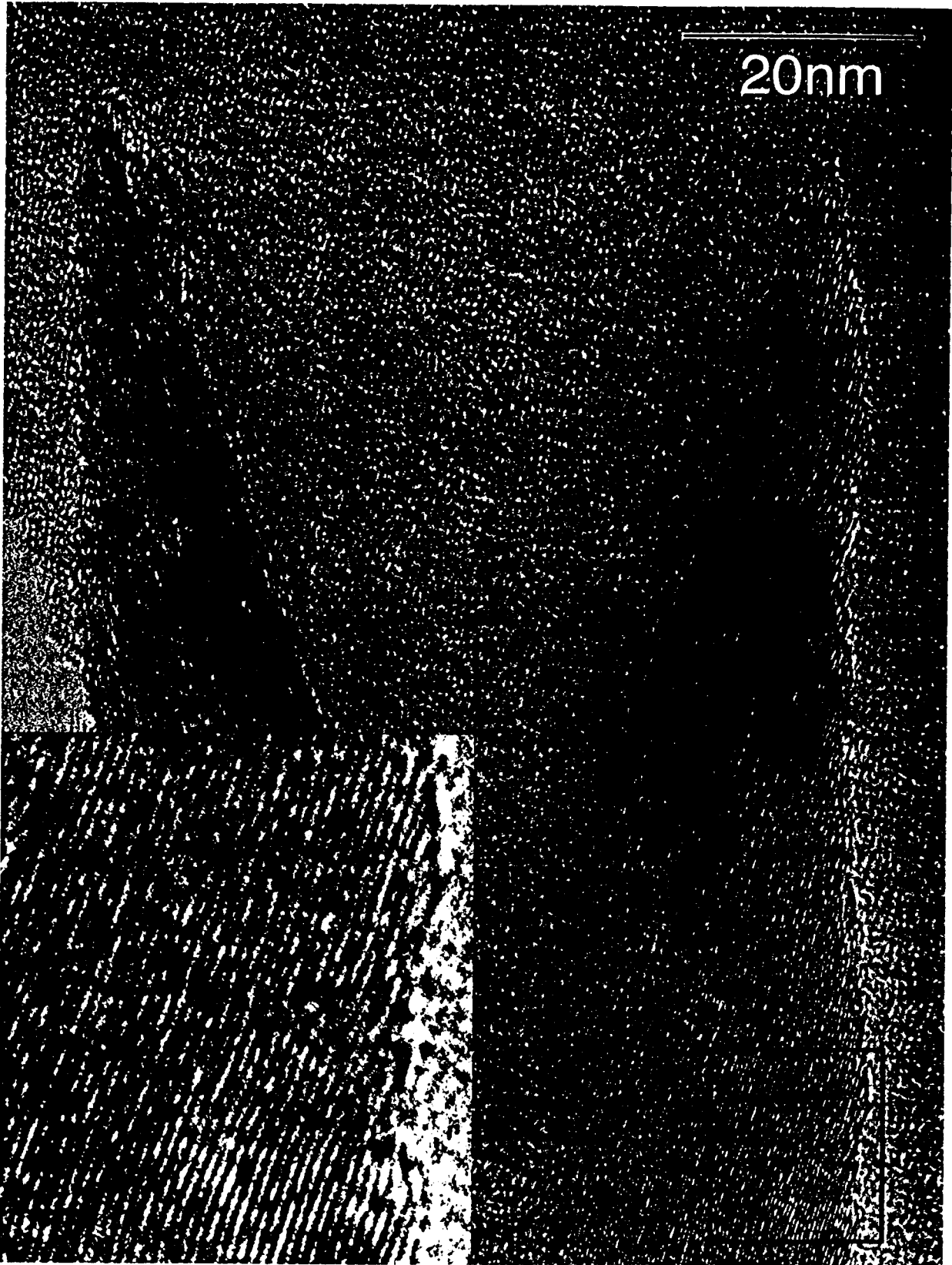


Fig. 2.

