

HYDROGEN ADSORPTION ON SINGLE-WALLED CARBON NANOTUBES

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Introduction

Single-walled carbon nanotubes have attracted considerable attention as candidates for hydrogen storage materials [1]. Various reports have been made of considerable amounts of hydrogen taken up at 80 EK [2], room temperature, [3], and even higher temperatures [4]. Adsorption isotherms have been calculated based on simulated tube arrays as a function of the diameter the tubes, the structure of the tube bundles, and the interaction potential between hydrogen and the tube walls [5]. In the work described below, we have used a tapered element oscillating mass analyzer to obtain isotherms for hydrogen adsorption at 25 EC and up to 700 psia for various samples of single-walled carbon nanotubes. Adsorption of excess hydrogen up to nearly 1.2 wt% of the sample has been observed.

Experimental

A block diagram of the apparatus including the TEOM Series 1500 Pulse Mass Analyzer (Rupprecht and Patashnick) is given in Fig. 1.

PULSE MASS ANALYZER BLOCK DIAGRAM

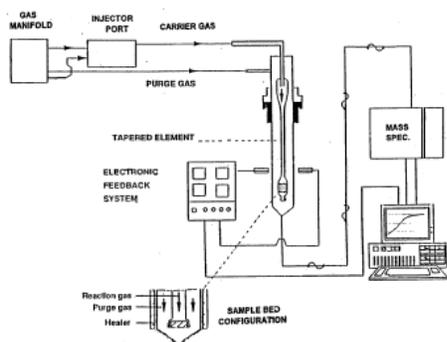


Fig 1. Block Diagram of the Rupprecht and Patashnick PMA 1500 and Associated Hardware

The PMA 1500 is a mass measuring device that employs a tapered glass element that is stimulated to vibrate at its

natural frequency. The element consists of a hollow glass tube with a cylindrical sample bed, diameter 4 mm, height 6 mm, at one end. Samples were packed into the bed between “Astro quartz” wool plugs. Occasionally samples were placed in two parts separated by quartz wool. Samples were retained by a ventilated gold-plated metal cap. The apparatus is capable of operating from ambient temperature to 700EC and from ambient pressure to 700 psia.

Separate gas streams were used to carry gas through the sample (reactive gas) and to sweep the volume outside the sample bed (purge). The same gas was used for both streams in all measurements described here, but flow rates were individually adjusted using mass flow controllers as required. Changes in the mass of the sample bed are related to changes in the frequency of oscillation of the tapered element through equation 1.

$$) m = k/(1/f_1^2 - 1/f_2^2) \quad (1)$$

Mass changes were recorded at 25 EC as the pressure followed a program that increased stepwise to 700 psia and back to ambient. Measurements were made for the empty reactor as well as the packed reactor. In the case of the empty reactor, the mass change was attributed to the change in density of the gas contained in the reactor volume. For the packed reactor the change is attributed to the combination of that for the change in density of the free gas and that for the amount of excess gas adsorbed on the sample. Isotherms were generated by subtracting the value of the mass change found with the empty reactor from the corresponding value found with the packed reactor for each step in pressure.

Nanotubes were purchased from Tubes @ Rice in two grades. “As Prepared Grade” was obtained as a solid, fibrous, ill-defined mat. It was subjected to modest grinding in a ball mill to make it easier to load into the sample cell. “Purified Grade” was purchased as a suspension in toluene. Typically 15 mL of the suspension was withdrawn from the bulk sample and evaporated in a stream of dry nitrogen at ambient temperature. When

toluene was no longer evident, the sample was dried at 140 EC for up to a week.

A modified nanotube sample was prepared by mild oxidation. Nanotube samples (50-75 mg) were placed in a 20 cm long by 12mm ID Vicor tube that was fit with quartz wool plugs to retain the sample. This was placed inside a 15 cm by 20mm ID Vicor tube in a tube furnace. The tube containing the sample was connected with PTFE fittings to 1/4" stainless steel gas lines. The exit gas stream was monitored by mass spectrometry. A stream of Ar or He at 5 cc/min was used to flush out air, then CO₂ was added at 5 cc/min (total flow 10 cc/min). The sample was then heated to ca 600 EC until CO evolution was no longer evident. The samples were cooled under inert gas flow.

Hydrogen, helium, and nitrogen were Matheson UHP grade. In some experiments these were dried by passing the gas through a Matheson Gas Purifier Cartridge Type 452 (4A molecular sieve).

In a typical experiment, a 30 to 50 mg sample was packed into the bed, flushed with dry helium or nitrogen, and heated to 200 C in the inert gas flow for 2 or more hours. After the signal from the mass spectrometer indicated that the release of small amounts of water and oxygen was complete, the sample was cooled to room temperature. Both reactant and purge gas flows were then switched to hydrogen and sufficient time was allowed for complete gas replacement as judged by the mass spectrum of the exit flow. Measurements of pressure vs. mass were made using a program that increased the gas pressure in 7 steps to 700 psia, holding pressure constant for 20 minutes after each increment. The pressure was decreased after 20 minutes at the maximum, usually by the same format of 100 psi steps and 20 minute intervals.

Results

An adsorption isotherm for hydrogen on an activated carbon is given in Fig. 2 in terms of both weight per cent hydrogen and moles H₂/kg carbon. The isotherm is nearly linear up to the limit of pressure for these measurements, reaching a value of 0.66 wt% (3.3 mole/kg) at 700 psia. Isotherms for hydrogen and other gases up to about 280 psi have recently been determined by a manometric technique on this same lot of activated carbon [7]. Comparison of the two sets of data reveals the value measured by manometry at room temperature and 200 psi is 1.2 moles/kg, while the corresponding point from the PMA at 25 EC is 1.04 moles/kg. There is reasonable agreement between the values obtained by the two different techniques.

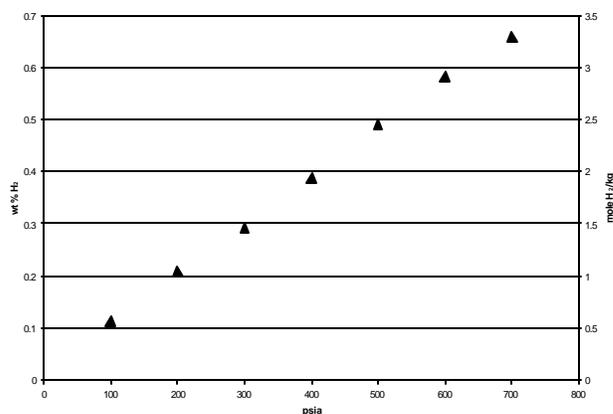


Fig 2. Adsorption Isotherm: Hydrogen on Activated Carbon

Two isotherms for a sample of "as prepared" tubes from Rice are shown in Fig 3. The upper curve (A) was taken

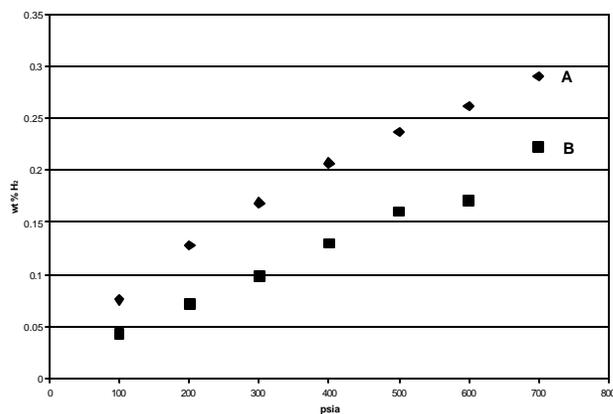


Fig. 3 Adsorption Isotherms: Hydrogen on "As Prepared" Rice Nanotubes.

A. After treatment at 200 ° C; B. After treatment at 700 ° C

after the sample had been heated *in situ* to 200 EC under a flow of helium, then cooled before the isotherm experiment was begun. The lower curve (B) was obtained in a subsequent experiment after the sample had been heated in a similar manner to 700 EC. Pyrolysis at 700 EC reduced the affinity of the sample for hydrogen by a significant amount. The exit gases were monitored by the in-line mass spectrometer throughout the course of heating. Hydrogen, methane, and carbon oxides were detected as the temperature increased. After the sample had returned to 25 EC, the PMA measured a weight loss of 13.2 mg, or 23.2% of the sample weight. (Data in Fig. 3 have been corrected for loss of sample weight to allow direct comparison of the two data sets on the basis of actual sample weight.)

In comparison to the sample of activated carbon used earlier (Fig 2.), the as prepared nanotube sample

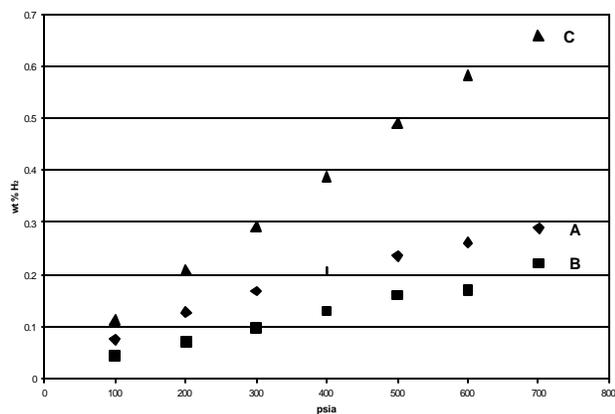


Fig 4 Comparison of Adsorption Isotherms of Hydrogen on: “As Prepared” Rice Nanotubes (A and B) and Activated Carbon. (C).

has at best roughly one half the storage capacity under the same pressure. Again, the ultimate storage capacity of either the fresh or the pyrolyzed sample has not been reached at the highest pressure used here.

“Purified” nanotubes obtained from Tubes @ Rice have undergone oxidation by reflux in 2.6 M nitric acid for 12 hours. The oxidation selectively removes amorphous carbon, leaving behind a greater proportion of nanotubes in the sample. The relative amount of the residual metal catalyst left in the sample increased as well because an overlay of graphitic carbon protects these particles from removal by oxidation. The metal content was determined by complete combustion of the sample using TGA. The isotherms given in Fig 5 were normalized on the basis of carbon content to obtain a more useful comparison. The four isotherms compare the results obtained after different treatments were applied to the same sample.

The four isotherms do not show large differences. Isotherms A and B were taken sequentially after the sample was first packed into the bed. Heating to 700 EC had a modest effect on the total hydrogen stored on the sample as shown when Curve A is compared to B. After isotherm B was completed, the sample was removed, milled by agitation in a small ball mill, and repacked in the bed. Milling the sample in air in this way decreased its capacity slightly (Curve C). This loss was mostly restored when the sample was again pyrolyzed (Curve D).

Perhaps more significant than the differences in the amount of hydrogen adsorbed are the differences in the slopes over the nearly linear region of the isotherms

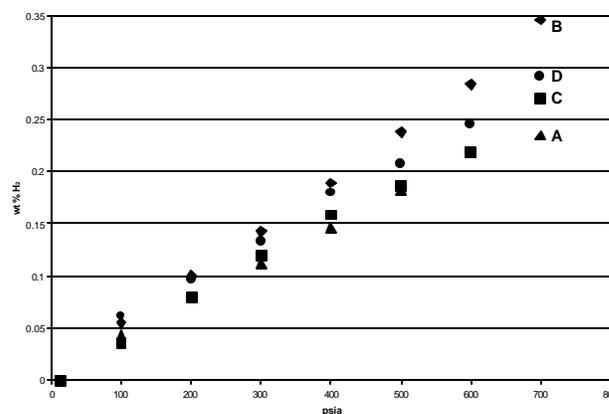


Fig 5. Comparison of Adsorption Isotherms of Hydrogen on Purified Rice Tubes: A. Sample Treated at 200 EC in He atm. B. Sample (A) Treated at 700 EC in He atm. C. Sample (B) after removal and milling in air. D. Sample (C) Treated at 700 EC in H₂ atm.

depending on whether the sample had been heated to 700 EC (Curves B and D) or not (Curves A and C). The mass spectra of the gases that were produced during pyrolysis were consistent with the loss of carboxyl and other oxygen containing functionalities. These could be introduced during either the oxidative purification or the milling procedure. A separate experiment in which another sample was pyrolyzed on five different occasions over several days indicated that repetition beyond the initial pyrolysis had little effect on the storage capacity or the slope of the isotherms. It seems reasonable that functional groups removed in the initial pyrolysis could have blocked access to some storage sites, but because the mean tube diameter is 1.2 nm, it seems unlikely that the mouths of all the tubes would be effectively closed by pendant groups. Theoretical results [8] suggest that another site of nanotube storage capacity lies in the interstitial spaces of the nanotube arrays that make up the ropelike structure. The amount of storage in the interstitial volume is strongly influenced by the spacing between individual tubes, typically only 3-4 angstroms. It seems likely that the pore mouths to the interstitial volumes could be blocked or changed by pendant groups on individual nanotubes. It should be noted that pyrolysis of purified tubes results in a modest increase in hydrogen storage (Fig 5.), but in the case of as prepared tubes it results in a modest decrease (Fig 3.). A speculative rationalization of this difference is that the purified tubes have experienced a strong oxidation that may have left behind a greater number of functional groups to block entry to storage sites.

Oxidation of purified Rice tubes under a stream of CO₂ at about 600 EC produced a sample with significantly increased hydrogen storage capacity. The isotherm shown in Fig. 6 reaches 1.16 wt % hydrogen at 700 psia.

Acknowledgment

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Disclaimer

Reference in this work to any specific commercial product is to facilitate understanding and does not necessarily imply endorsement by the United States Department of Energy.

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The oxidative procedure removes about 37 % of the previously purified sample which was significantly less resistant to oxidation by CO₂ than the remainder. The rope-like structures are left intact. This form of activation indicates that manipulation of the physical/chemical structure of a given sample of nanotubes may significantly improve its hydrogen storage characteristics. Further work along these lines is in progress.

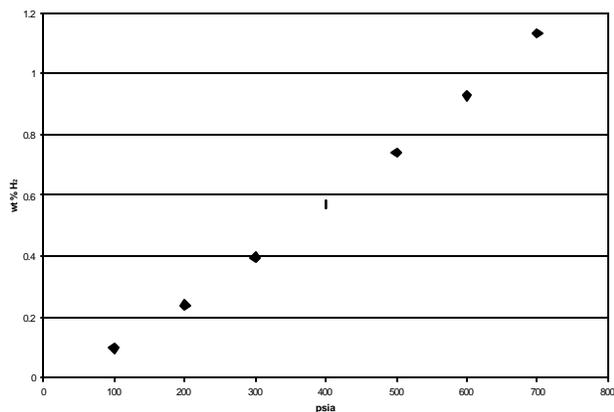


Fig 6. Adsorption Isotherm: Hydrogen on Purified Rice Nanotubes after CO₂ Oxidation

Fig. 7 provides a comparison and summary of the data described above. The hydrogen isotherms for the various samples of tubes bracket that found for a typical activated carbon. The ultimate capacity of the best sample investigated here will certainly exceed 1.2 wt %, and thus tubes represent potentially interesting hydrogen storage media.

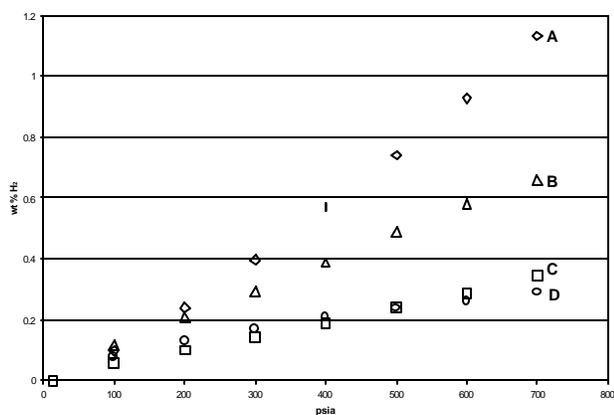


Fig. 7. Comparison of Adsorption Isotherms of Hydrogen on Various Carbons. A. CO₂ Oxidized Purified Rice. B. Activated Carbon. C. Purified Rice After Pyrolysis at 700°C. D. As Prepared Rice