

# Hydrogen Storage Capacity Characterization of Carbon Nanotubes by a Microgravimetric Approach

Aidong Lan and Alexander Mukasyan\*

Center for Molecularly Engineered Materials, Department of Chemical and Biomolecular Engineering,  
University of Notre Dame, Notre Dame, Indiana 46556

Received: April 19, 2005; In Final Form: June 30, 2005

An accurate gravimetric apparatus based on a contactless magnetic suspension microbalance was developed. This unit was used to measure the hydrogen storage capacity for a variety of carbon nanotubes (CNTs) at room temperature and hydrogen pressures up to 11.5 MPa. The results show that regardless of their synthesis methods, purities, and nanostructures all investigated CNT products possess relatively low hydrogen storage capacities (<0.2 wt %). For comparison, the adsorption characteristics of these samples were also measured at a pressure of 0.1 MPa and liquid nitrogen temperature (~77 K) by a conventional volumetric approach. The methodological aspects related to the accuracy of the hydrogen uptake measurements are also discussed.

## Introduction

Utilization of hydrogen as a fuel is important because of the current shortage in mineral energy sources and increasing problems with environmental pollution. One major obstacle to the development of the hydrogen economy, where H<sub>2</sub> will be effectively used in advanced fuel cells to produce clean and efficient energy, is the lack of safe and cost-effective gas storage devices. Thus, the development of novel materials with high hydrogen storage capacities and stable properties is of critical importance.

For conventional physical sorption, the gas-adsorption performance of a porous solid media is maximal when its pore size is on the order of a few molecule diameters.<sup>1</sup> Thus, carbon nanotubes (CNTs), having nanosized tubular microstructure, generated intense interest owing to its potential ability to adsorb hydrogen.<sup>2–7</sup> The earliest data of hydrogen adsorption on single-walled carbon nanotubes (SWCNTs) was reported in 1997.<sup>2</sup> Since that time, a large number of papers have been published. Analysis of the literature showed that the hydrogen storage capacities of such materials varied over a wide range, from 0.1 to 10 wt %. We believe that such a discrepancy in the experimental data is due to the lack of reliable methods for measurements of hydrogen uptake properties at high gas pressures.

Three main approaches were used to determine the hydrogen storage capacity of carbon materials: volumetric,<sup>4–10</sup> gravimetric,<sup>11–14</sup> and temperature-programmed desorption.<sup>2</sup> However, analysis of relevant publications showed that the majority of results on CNT hydrogen uptake were obtained by volumetric methods and, as it was noted above, the reported data are extremely dispersed.<sup>4–10</sup> The latter can be explained by several pitfalls of the volumetric method. For example, the results can be adversely affected by the unavoidable hydrogen leakage under high-pressure conditions. In addition, the temperature variations caused by the adiabatic gas expansion that occurs

during the measurement procedure may lead to errors in the hydrogen uptake evaluation.<sup>4</sup>

It is important to note that among the approaches mentioned above the gravimetric method is the only direct gas uptake measurement technique. However, the major concern in using the conventional gravimetric apparatus, where the sample cell and balance are in direct contact, is to avoid the influence of experimental conditions (temperature, pressure, gas flows, etc.) on the accuracy of the weight measurements. Thus, to date only a few reliable experimental data on CNT hydrogen uptake obtained by this method were reported.<sup>11–14</sup>

We developed a new so-called “contactless” apparatus for hydrogen storage capacity measurement, which was built based on a magnetic suspension microbalance (Rubotherm, Germany). This technique prevents the influence of any disturbance taking place in the sample cell on the balance and allows measurement of the sample weight with high precision under extreme conditions (hydrogen pressures up to 14 MPa and temperatures up to 800 K). Through the use of this apparatus, detailed investigations on the hydrogen storage capacity of a wide variety of CNT materials synthesized in our laboratory and commercially available were conducted.

## Experimental Setup

A gravimetric unit was designed and built, as schematically shown in Figure 1, to perform studies on hydrogen storage properties of CNT materials. It can be seen that instead of hanging directly on the balance the sample cell is linked to a so-called suspension system. This system consists of a permanent magnet, a sensor core, and a device for decoupling the sample cell from the balance. Through the use of magnetic coupling, the measuring force is transmitted contactlessly from the cell to the microbalance that is located outside the sample chamber under normal conditions. Such a design eliminates almost all restrictions that are inherent to conventional gravimetric measuring instruments.

This technique has several advantages as compared to conventional ones. First, it allows sample pretreatment con-

\* Author to whom correspondence should be addressed. Phone: (574) 631-9825. Fax: (574) 631-8366. E-mail: amoukasi@nd.edu.

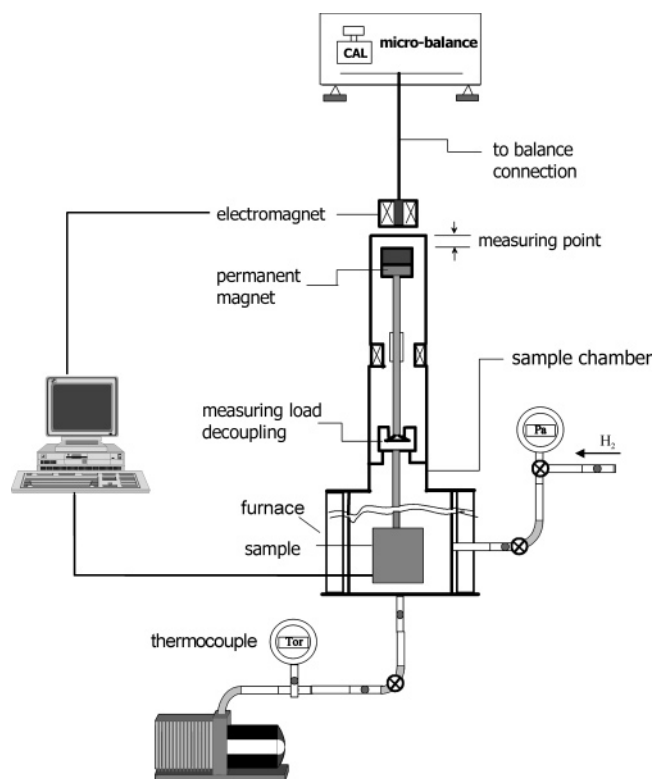


Figure 1. Schematic diagram of the gravimetric measurement unit.

ducted under precisely controllable conditions, e.g., vacuum  $\leq 10^{-3}$  Torr and temperatures up to 800 K. Second, it permits hydrogen uptake measurements to be conducted at gas pressures up to 15 MPa with a sample load of 0–25 g. In addition, the data acquisition system and automation software were developed to monitor gas pressures and sample temperatures. These parameters were recorded every 15 s, with an accuracy of 0.007 bar and 0.1 K, respectively. Before each experiment, self-calibration of the microbalance was performed. The buoyancy test with a blank sample bucket at various hydrogen pressures was also carried out.

To verify the performance of the system, benchmark measurements at room temperature were conducted on a LaNi<sub>5</sub> sample (purity of 99.9%, Testbourne Ltd., U.K.), which has well-known hydrogen adsorption properties. The obtained hydrogen uptake value of 1.496 wt % at room temperature (RT) is in an excellent agreement with the data reported.<sup>14</sup> It is worth noting that these trials showed exceptionally good reproducibility and were consistent with the expected system accuracy.

CNT material (typical weight  $\approx 0.2$  g) was loaded into a Teflon or stainless steel bucket, which was suspended in the sample chamber. The typical time used for the system stabilization under 0.1 MPa of air at RT was 1 h. Then the sample chamber was pumped down to a vacuum less than  $10^{-2}$  Torr and was kept under this condition for 1 h. Thereafter, hydrogen (ultra-high-purity, 99.999%) was admitted into the chamber in a controlled manner. The continuous monitoring of the sample temperature and weight was conducted through all these stages. The typical duration of the hydrogen uptake measurement at the desired gas pressure was 24 h.

To obtain additional insights on the hydrogen storage properties of these CNTs, the hydrogen adsorption measurements were also performed by using a commercial volumetric system Quantachrome Autosorb 1C (Quantachrome Instruments,

USA) at 77 K and 0.1 MPa. Prior to the measurements, the samples were degassed under a vacuum of  $10^{-5}$  Torr at 600 K for 5–24 h.

### Methodological Remarks

The microgravimetric apparatus used in this work has a resolution limit of 10  $\mu$ g, a reproducibility (standard deviation) of 20  $\mu$ g, and a relative error less than 0.002% of the measured value. According to this, for a sample with a weight of 200 mg, a resolution 0.01 wt % can be achieved. To reach such a high accuracy, every measured weight value ( $W_i$ ) has to be corrected by a so-called zero-point adjustment. The zero point is a weight obtained under such conditions that the permanent magnet is decoupled from the sample cell and is in a freely suspended state. In these studies, the zero points are acquired between every four measurements of the sample weight. The corrected weight values ( $W_i^{\text{cr}}$ ) are calculated by data interpolation between two adjacent zero points as follows

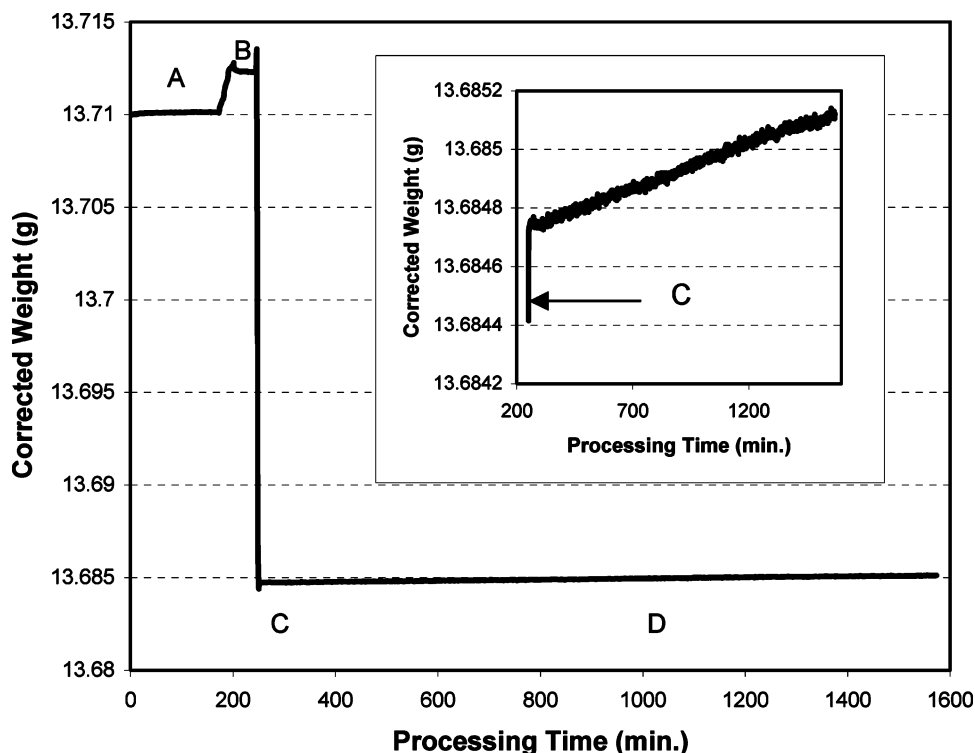
$$W_i^{\text{cr}} = W_i - \left[ (t_i^{\text{w}} - t_1^0) \frac{M_2^0 - M_1^0}{t_2^0 - t_1^0} + M_1^0 \right] \quad (1)$$

where  $M_2^0$  and  $M_1^0$  are two adjacent zero-point values,  $t_1^0$  and  $t_2^0$  are time points at which these two values were measured,  $t_i^{\text{w}}$  ( $i = 1, 2, 3, 4$ ) are the time points for four consecutive sample weight measurements, and  $W_i$  ( $i = 1, 2, 3, 4$ ) and  $W_i^{\text{cr}}$  ( $i = 1, 2, 3, 4$ ) are the corresponding measured and corrected sample weights.

The hydrogen storage capacities for various CNT materials (see below) were obtained based on the analysis of the corrected weight versus time profiles (see example in Figure 2). Several distinct process stages (noted A, B, C, and D) with different conditions can be outlined. The first stage (A) involves sample stabilization (conditions, air,  $P = 0.1$  MPa at RT, duration 1 h). The sample degassing takes place during stage B (vacuum  $P < 10^{-2}$  Torr, temperatures up to 500 K, durations up to 24 h). The third stage (C) is a transition stage (with a duration of 1–5 min) where hydrogen gas is admitted to the system up to the desired pressure at RT. It is assumed that the hydrogen uptake primarily occurs during stage D (gas pressures up to 15 MPa, RT, and typical duration of 24 h).

In the inset of Figure 2, a distinguished positive slope in the  $W^{\text{cr}}(t)$  profile (stage D) can be seen, which indicates that the sample weight increases with time. However, one should be cautious in the data interpretation of such weight gains. For example, the buoyancy effect may also contribute to the observed weight gain owing to the unavoidable small system leak (24 h processing time at  $P_{\text{H}_2} > 10$  MPa). In addition, the temperature change during the long-term measurements can also affect the measured weight values. Nevertheless, these effects can be taken into account with the available accurate pressure and temperature data.

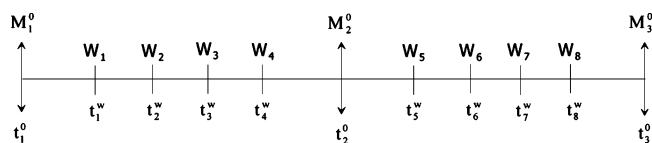
Other important methodological aspects are related to stage C, where significant changes of environmental condition take place. At this stage, the hydrogen gas is filling the sample chamber, and a considerable “spike” in the  $W^{\text{cr}}(t)$  profiles is frequently observed (Figure 2). Analysis shows that this spike has primarily an artificial origin and thus is not related to the gas-adsorption process. The variations in sample weight, temperature, and zero-point values during this transition period are presented in Figure 3. By comparison of profiles in Figures 3a and 3b, it can be seen that under this nonsteady condition the absolute value of the corrected weight depends on “randomly”



**Figure 2.** Typical profile of sample corrected weight versus time. A, B, C, and D denote the four different stages of the measurement procedure: (A) initial stabilization (RT, 1 atm, air); (B) degassing (RT,  $P = 10^{-2}$  Torr); (C) pressurizing by hydrogen; (D) steady pressure conditions.

measured zero-point values. This effect occurs owing to unsynchronized onsets for the pressure change in the system and the time for zero-point measurements.

More specifically, let us consider three consecutive zero points and eight weight points measured during stage C, as illustrated below



Assume that  $W_4 = W_5$  (i.e., no hydrogen uptake occurred) and  $M_2^0 = M_3^0$  (i.e., identical pressure–temperature conditions during the time interval between  $t_2^0$  and  $t_3^0$ ). Substituting this into eq 1 yields

$$W_5^{\text{cr}} - W_4^{\text{cr}} = (M_1^0 - M_2^0) \left( 1 - \frac{t_4^w - t_1^w}{t_2^0 - t_1^0} \right)$$

If the difference  $(M_1^0 - M_2^0)$  is large (e.g., owing to the significant gas pressure change during the time interval between  $t_1^0$  and  $t_2^0$ ), then a considerable artifact  $(W_5^{\text{cr}} - W_4^{\text{cr}})$  will be observed on the corrected weight profile, as is evident in Figure 2a.

The calculation method to obtain the final hydrogen uptake values is based on two assumptions: (1) the sample volume remains constant during stage D; (2) hydrogen is considered as an ideal gas. Note that the experimental conditions are well above the critical point (33.2 K and 1.3 MPa) for hydrogen. Under these assumptions, the buoyancy contribution,  $\Delta m^b$ , for the sample weight can be calculated as follows

$$\Delta m^b = (V_0 + V_s) \frac{P_i M_{\text{gas}}}{RT_i} \quad (2)$$

where  $P_i$  and  $T_i$  are the pressure and temperature in the system,  $V_0$  is the volume of the whole suspended device, while  $V_s$  is the volume of the sample,  $M_{\text{gas}}$  is the molecular mass of gas, and  $R$  is the gas constant.

The hydrogen uptake  $W_H$  is calculated as follows

$$W_H = (W_f^{\text{cr}} - W_{\text{in}}^{\text{cr}}) + (\Delta m_{\text{in}}^b - \Delta m_f^b) \quad (3)$$

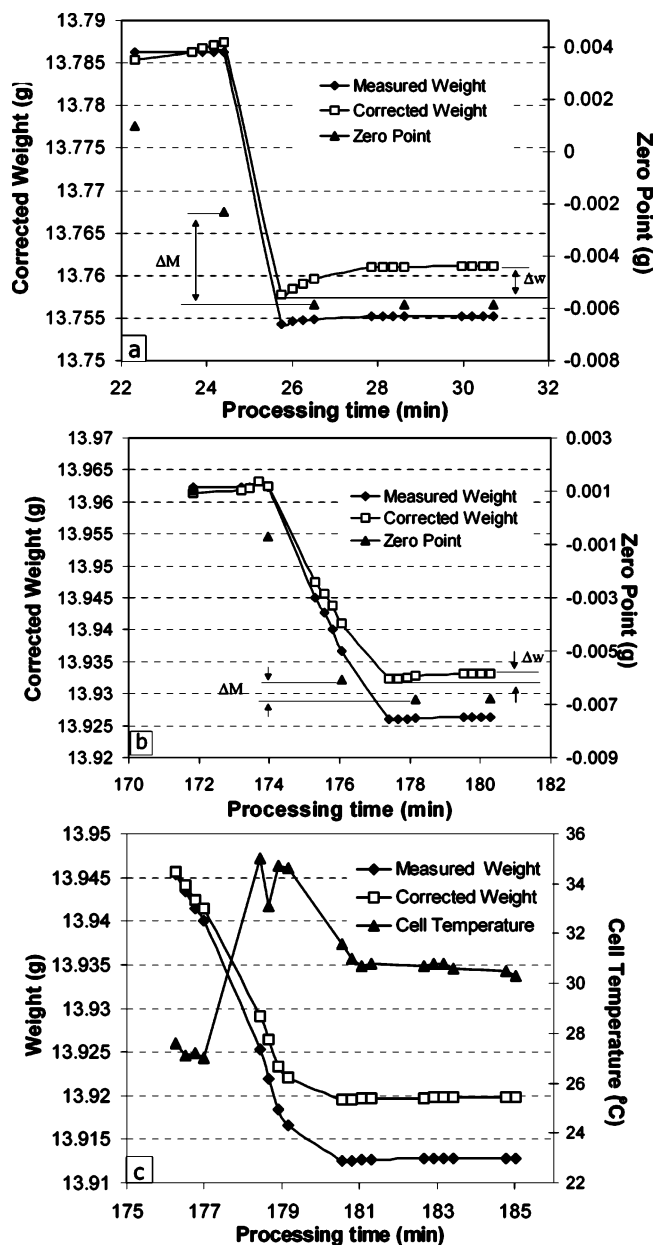
where  $W_{\text{in}}^{\text{cr}}$  and  $W_f^{\text{cr}}$  are the initial and final corrected weights at stage D and  $\Delta m_{\text{in}}^b$  and  $\Delta m_f^b$  are the corresponding buoyancy corrections.

From this simple equation, one can conclude that if during stage D the gas pressure and ambient temperature remains constant, then there is no buoyancy contribution to the hydrogen uptake value. However, the buoyancy can be accurately accounted for by eq 3 if the pressure and temperature in the chamber changes during long-term experiments. Also note that in this study  $V_0$  is about 2 orders of magnitude higher than  $V_s$ ; thus the effect of possible sample density variation on the calculation of hydrogen storage capacities is negligible.

## Results and Discussion

A variety of CNT materials were evaluated in this work. They included multiwalled carbon nanotubes (MWCNTs) synthesized in our laboratory by the so-called floating catalyst method,<sup>16</sup> high-purity MWCNTs and SWCNTs commercially obtained from the MER Corporation (Tucson, AZ), as well as two other SWCNTs produced by the CarboLex Company (Lexington, KY) and Carbon Nanotechnologies, Inc. (CNI; Houston, TX).

The synthesis methods and some material properties are listed in Table 1. The specific surface areas (SSAs) of all samples were measured by using the Brunauer–Emmett–Teller (BET)<sup>17</sup> method. As expected, the SWCNT samples show much higher SSAs as compared to the MWCNT samples. The CNI product possesses the highest specific surface area of 910 m<sup>2</sup>/g. This value is close to the theoretically predicted maximum (1315



**Figure 3.** Sample weight change during a transition period (C), when H<sub>2</sub> gas is filling the sample chamber.

m<sup>2</sup>/g) for SWCNT structures<sup>18</sup> but is lower than the measured value for AX-21 activated carbon (~2800 m<sup>2</sup>/g).<sup>19</sup> The other two SWCNT products (i.e., MER\_1 and CarboLex), have smaller (by a factor of 4) specific surface areas. These results can be explained by the relatively low SWCNT content (Table 1) in these materials. Additional details on the characterization of the materials under investigation can be found elsewhere.<sup>4,9,20–22</sup>

**TABLE 1: Characteristics of Used CNT Materials**

sample materials	synthesis method	purity	sample description	surface area (m <sup>2</sup> /g)
CNI	HiPCO CVD	85+ wt % SWCNTs	bundled microstructure, ~10–100 nanotubes/bundle; individual nanotube is ~1.2 nm in diameter	910
CarboLex	arc discharge	50–70 wt % SWCNTs	single-walled closed-ended tubes with average diameters of ~1.4 nm	230
MER_1	arc discharge	12+ wt % SWCNTs	1.2–1.4 nm diameter, 10–50 μm length and up to 20 nanotubes in bundle.	200
MER_2	catalytic CVD	90+ wt % MWCNTs	average diameter ~35 nm and length ~30 μm	13
ND	floating catalytic CVD	90+ wt % MWCNTs	diameter varied between 10 and 40 nm and average lengths up to tens of micrometers	62

**TABLE 2: Hydrogen Storage Capacities for Pristine CNT Samples Obtained by Both Gravimetric and Volumetric Approaches**

sample materials	H <sub>2</sub> content (wt %) <sup>a</sup>	
	gravimetric method (RT, P <sub>H<sub>2</sub></sub> = 11.5 MPa)	volumetric method (T = 77 K, P <sub>H<sub>2</sub></sub> = 0.1 MPa)
CNI	0.19 (0.21)	1.19 (1.31)
CarboLex	0.12 (0.53)	0.47 (2.08)
MER_1	0.18 (0.90)	0.52 (2.60)
ND	0.01	0.08
MER_2	0.01	0.06

<sup>a</sup> The values shown in brackets are the hydrogen storage capacities per 1000 m<sup>2</sup>/g specific surface area.

The hydrogen uptake data obtained at room temperature and a storage pressure of 11.5 MPa for different CNT materials are listed in Table 2. For comparison, the hydrogen adsorption data for the same products measured under normal gas pressure and a low temperature of 77 K by using volumetric methods are also presented. It can be seen that the hydrogen storage capacities obtained by the gravimetric approach for all investigated CNTs do not exceed 0.2 wt %. It is worth noting that the hydrogen uptake for the CNI product (0.19 wt %; Table 2) is 3–4 times smaller than those previously reported values for the same material by using volumetric methods at lower gas pressures (0.43 wt % at 7 MPa<sup>9</sup> and 0.60 wt % at 10 MPa<sup>10</sup>). Also note that under a much lower pressure of 0.1 MPa and at liquid nitrogen temperature (77 K) much higher hydrogen adsorption capacities for CNT products (up to 1.2 wt %) were observed.

No simple correlation between CNT specific surface area and its hydrogen sorption characteristics was found. On one hand, the CNI product with the highest SSA possesses the maximum storage capacity, while the MWCNTs, with the lowest specific surface area, show negligible uptakes. On the other hand, the MER\_1 sample with a specific surface area lower than that for the CarboLex sample exhibits a higher hydrogen uptake. Also the estimations show that in terms of hydrogen storage capacity per unit of surface at room temperature (values in brackets in Table 2) MER\_1 sample has the highest value.

The dependence of CNT hydrogen storage capacity as a function of hydrogen pressure and its reproducibility were also investigated. Figure 4 presents the example of such data obtained for MER\_1 carbon nanotubes. It can be seen that initially the increase in hydrogen pressure enhances the gas uptake, and a plateau was observed at pressures larger than 10 MPa (Figure 4a). Additional experiments at higher gas pressures are required to confirm that hydrogen adsorption saturation was reached. From Figure 4b, one can also conclude that the sample shows good reproducibility for its hydrogen uptake property.

Finally, attempts were made to change the sorption capacity of the materials by different types of “activation” treatments. These treatments include (a) annealing in air to remove



**TABLE 3: Hydrogen Storage Capacities of CNT Samples after Different Pretreatments**

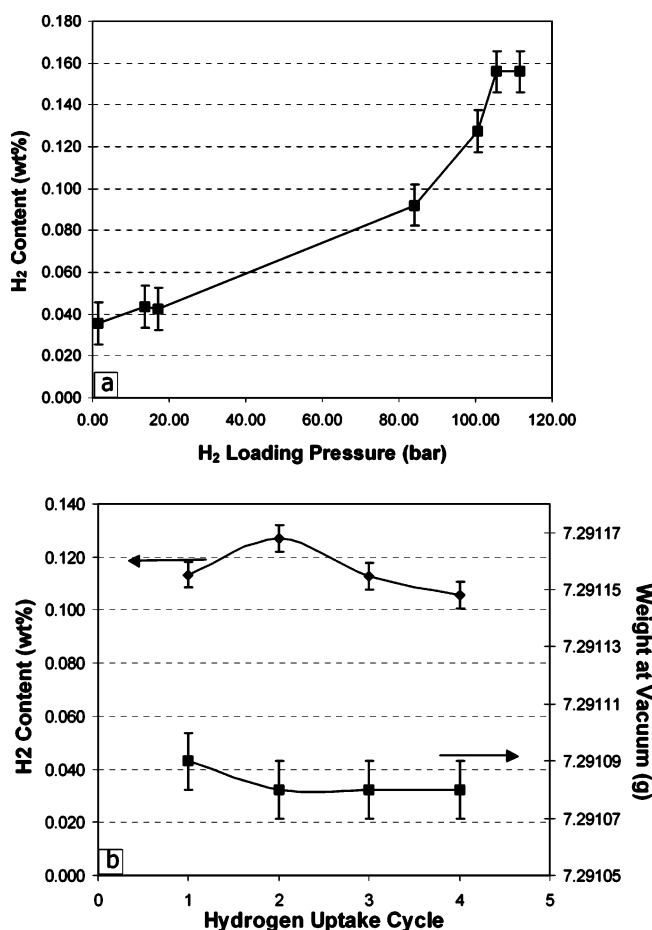
material	treatment type	H <sub>2</sub> content (wt %)		BET surface area (m <sup>2</sup> /g)
		gravimetric (RT, P <sub>H<sub>2</sub></sub> = 110 bar)	volumetric (T = 77 K, P <sub>H<sub>2</sub></sub> = 1 bar)	
MER_1	as prepared	0.18	0.52	200
	high vacuum 100 °C	0.20	0.55	200
	high vacuum 200 °C	0.20	0.58	200
	high vacuum 300 °C	0.26	0.68	200
	air, 300 °C	0.04	0.03	48
	HNO <sub>3</sub>	0.01	0.50	260
CarboLex	as prepared	0.12	0.47	230
	vacuum 300 °C	0.10	0.52	230
	air, 300 °C	0.04	0.18	100
	HNO <sub>3</sub>	0.01	0.84	428

amorphous carbons,<sup>8</sup> (b) leaching in HNO<sub>3</sub> solution (1:1 acid-to-water ratio) to eliminate metal particles present in samples and to form defects in the nanotube structure,<sup>13</sup> and (c) high-vacuum (10<sup>-5</sup> Torr) and high-temperature (up to 600 K) degassing.<sup>4</sup> Results of both gravimetric and volumetric measurements on treated MER\_1 and CarboLex samples are summarized in Table 3.

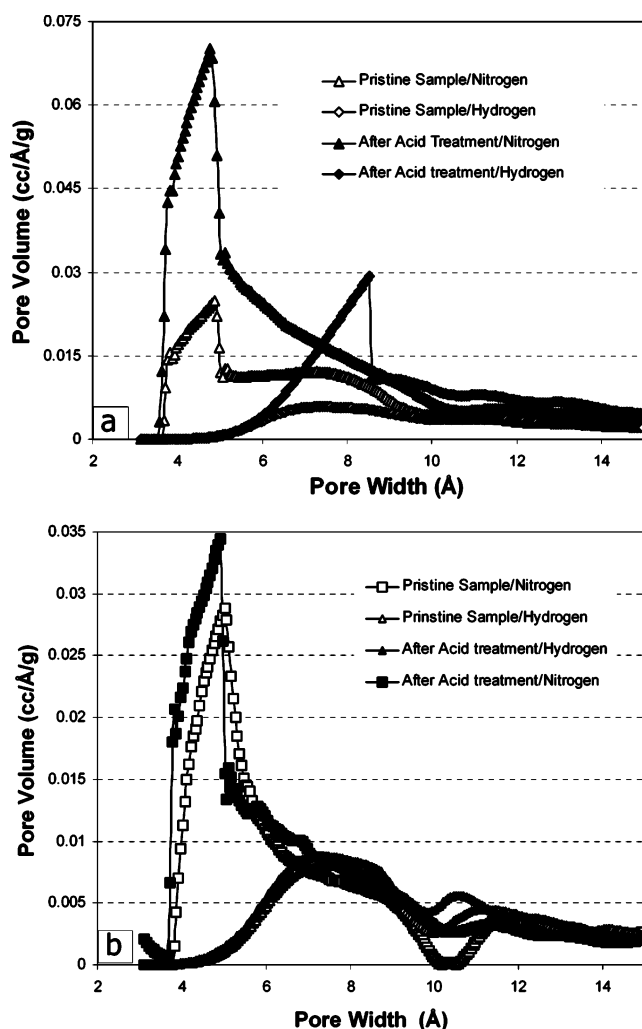
Among these treatments, high-vacuum outgassing for MER\_1, while it does not influence SSA, leads to a slight increase in the room-temperature hydrogen uptake. This change can be attributed to the well-known effect of sample surface “cleaning” achieved by high-vacuum (10<sup>-3</sup> Pa), high-temperature (600 K) degassing.<sup>23</sup> Also after the samples were annealed in air, a significant decrease in SSA as well as hydrogen storage capacities of both samples were observed. Additional thermo-

gravimetric analysis (TGA) of these samples conducted in air showed that onset-burning temperatures of both CNTs are close to 600 K. This suggests that the employed heat treatment procedure in air leads to partial destruction of the materials’ nanostructure, resulting in the observed decrease in all sorption characteristics.

Further, an inspection of Table 3 reveals nontrivial changes in sample properties after treatment in acid at RT. On one hand, for both samples SSA increases. In particular, the large change was observed for CarboLex material (from 230 to 430 m<sup>2</sup>/g). Also note that changes in hydrogen adsorption at 77 K follow the same trend. On the other hand, the hydrogen uptake at RT



**Figure 4.** Dependence of hydrogen uptake for the MER\_1 SWCNT product as a function of (a) gas pressure and (b) number of cycles with a pressure up to 11.5 MPa.



**Figure 5.** Pore size distribution of micropores (Horvath-Kawazoe method) of the (a) MER\_1 and (b) CarboLex samples. (Hydrogen and nitrogen are used as adsorbates.)

decreases. The measured micropore size distributions of the pristine and treated samples showed a significant increase in small size (4–8 Å) pore volume after treatment in acid (Figure 5). In addition, a substantial decrease (e.g., by a factor of 2 for CarboLex) in metal particle content was observed by TGA analysis. These data suggest that acid treatment leads to a twofold effect, i.e., the formation of the defects on the walls of CNTs and the etching of the catalyst particles. It is believed that the formation of defects leads to the increase in sample specific surface area, while the elimination of catalyst particles may explain the decrease in hydrogen uptake at RT. Indeed it was reported in the literature<sup>24</sup> that the contribution of metal catalytic particles to the hydrogen storage capacities of CNTs can be significant.

## Conclusions

An accurate gravimetric apparatus based on a contactless magnetic suspension microbalance was developed. Through the use of this unit, the hydrogen storage uptakes for a variety of CNT materials over a wide range of gas pressures were measured. It was found that all investigated CNT products show relatively small hydrogen storage capacities. In view of a significant discrepancy between some previously reported data and our results, we believe that all claims of high hydrogen storage capacity (>1 wt %) at room temperature are doubtful and may be due to the consequence of experimental errors.

**Acknowledgment.** This work was supported by the U. S. Army CECOM RDEC through Agreement No. DAAB07-03-3-K414. Such support does not constitute endorsement by the U. S. Army of the views expressed in this publication.

## References and Notes

(1) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic Press: London, 1982.

- (2) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune D. S.; Heben, M. J. *Nature* **1997**, *386*, 377.
- (3) Ritschel, M.; Uhlemann, M.; Gutfleisch, O.; Leonhardt, A.; Graff, A.; Taschner, Ch.; Fink, J. *Appl. Phys. Lett.* **2002**, *80*, 2985.
- (4) Tibbetts, G. G.; Meisner, G. P.; Olk, C. H. *Carbon* **2001**, *39*, 2291.
- (5) Rzepka, M.; Lamp, P.; de la Casa-Lillo M. A. *J. Phys. Chem. B* **1998**, *102*, 10894.
- (6) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, *286*, 1127.
- (7) Ye, Y.; Ahn, C. C.; Witham, C.; Fultz, B.; Liu, J.; Rinzler, A. G.; Colbert, D.; Smith, K. A.; Smalley, R. E. *Appl. Phys. Lett.* **1999**, *74*, 2307.
- (8) Anson, A.; Callejas, M. A.; Benito, A. M.; Maser, W. K.; Izquierdo, M. T.; Rubio, B.; Jagiello, J.; Thommes, M.; Parra, J. B.; Martinez, M. T. *Carbon* **2004**, *42*, 1242.
- (9) Kajiura, H.; Tsutsui, S.; Kadono, K.; Kakuta, M.; Ata, M.; Murakami, Y. *Appl. Phys. Lett.* **2003**, *82*, 1105.
- (10) Lawrence, J.; Gu, X. *Appl. Phys. Lett.* **2004**, *84*, 918.
- (11) Quinn, D. F. *Carbon* **2002**, *40*, 2767.
- (12) Li, X. S.; Xu, H. W.; Xu, C. L.; Mao, Z. Q.; Wu, D. H. *Int. J. Hydrogen Energy* **2003**, *28*, 1251.
- (13) Poirier, E.; Chahine, R.; Benard, P.; Cossement, D.; Lafi, L.; Melancon, E.; Rose, T. K.; Desilets, S. *Appl. Phys. A* **2004**, *78*, 961.
- (14) Henneberg, E.; Bernhardt, B.; Bohmhammel, K. *Thermochim. Acta* **2004**, *415*, 43.
- (15) *Handbook on the Physics and Chemistry of Rare Earths, Hydrogen Absorption in Inter-Metallic Compounds*; Buschow, K. H. J., Gschneidner, K. A., Eyring, L., Eds.; North-Holland: New York, 1984; Vol. 6.
- (16) Cheng, H. M.; Li, F.; Su, G.; Pan, H. Y.; He, L.; Sun, X.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1998**, *72*, 3282.
- (17) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.
- (18) Züttel, A.; Sudan, P.; Mauron, Ph.; Kiyobayashi T.; Emmenegger, Ch.; Schlapbach, L. *Int. J. Hydrogen Energy* **2002**, *27*, 203.
- (19) Chahine, R.; Bose, T. K. *Int. J. Hydrogen Energy* **1994**, *19*, 161.
- (20) Bougrine, A.; Dupont-Pavlovsky, N.; Naji, A.; Ghanbaja, J.; Maréché, J. F.; Billaud, D. *Carbon* **2001**, *39*, 685.
- (21) Bronikowski, M. J.; Willis, P. A.; Colbert, D. T.; Smith, K. A.; Smalley R. E. *J. Vac. Sci. Technol., A* **2001**, *19*, 1800.
- (22) Fan, Y.; Kaufmann, A.; Mukasyan, A.; Varma A. *Carbon*, manuscript submitted for publication.
- (23) Rouquerol, F. *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*; Academic Press: San Diego, CA, 1999.
- (24) Yildirim T.; Ciraci, S. *Phys. Rev. Lett.* **2005**, *94*, 175501.