Dual quartz crystal microbalance for hydrogen storage in carbon nanotubes

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Received 25 November 2006; received in revised form 10 February 2007; accepted 10 February 2007

Available online 5 April 2007

Abstract

Hydrogen storage in single-walled carbon nanotubes (SWCNTs) was investigated by using a dual quartz-crystal microbalance (QCM). The chamber pressure can be adjusted from $10^{-9}$ torr up to 1 MPa. The dual QCM decreases the frequency fluctuations that originate from environmental variables such as temperature and pressure. Our moisture-free chamber enables us to measure accurately the hydrogen storage capacity in carbon nanotubes. Highly purified SWCNTs store about 0.2 wt% of hydrogen at room temperature under 0.5 MPa through physical adsorption. Our SWCNTs without baking adsorb up to 1 wt% of water, often obscuring the hydrogen storage capacity. Our results suggest that the hydrogen storage capacity relies strongly on the functional groups remaining on the SWCNTs which may enhance the storage capacity.

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Keywords: Hydrogen storage; Carbon nanotubes; Quartz-crystal microbalance; Water molecules

1. Introduction

Empty inner spaces of individual carbon nanotubes (CNTs) and inter-tube spaces provide mesoscale pores that can retain fuel gases like hydrogen [1,2]. Dillon et al. examined this possibility in 1997 [3] and reported 5–10 wt% of storage capacity from the pristine single-walled CNTs (SWCNTs). Since then, intensive research has been done. In spite of predicted high storage capacity that utilizes inner empty spaces and interstitial sites among tubes [4,5], the measured values of storage capacity range widely from 0.03 to 20 wt% [6–12]. Thus, the poor reproducibility and huge discrepancy in storage amount have been strongly debated.

This inconsistency arises mainly from sample preparation and method of measurement [11]. From a theoretical point of view, the molecular hydrogen physisorbs weakly on an ideal nanotube wall. The available empty inner space of CNTs can also store hydrogen. This implies that the storage capacity is expected to rely on the types of nanotubes, as predicted from theoretical calculations. The presence of defects, other functional groups, and impurities such as catalysts and carbonaceous particles also affect the interaction of molecular hydrogen. Thus the sample preparation condition is a crucial factor in determining the storage capacity. The method of measurement and experimental conditions are also important. For example, electrochemical approach utilizes protons in electrolyte such that protons chemisorb on the nanotube wall and furthermore are stored as a form of molecular hydrogen inside SWCNTs particularly at high coverage of hydrogen [13–15]. One common practice is to use a low-vacuum volumetric techniques similar to those used for metal hydrides [16]. In this approach, the presence of moisture, which is inevitable in its chamber structure, has been a serious issue. Like metal hydrides, CNT are sensitive to ambient moisture. Special care must be taken to remove the effect of moisture, so that the hydrogen storage capacity can be precisely measured. Thus, in addition to well-defined sample conditions, the choice of storage method and the accurate control of the measurement environments are other crucial factors that must be considered when measuring storage capacity.

In this report, a dual quartz-crystal microbalance (QCM) in a high vacuum system was employed to reduce the effect of
water vapor during adsorption and desorption measurements. Furthermore, the dual QCM reduces frequency drift due to temperature and pressure changes by using one of QCM as a reference. Our system operates with pressures from $10^{-9}$ torr up to 1 MPa. Although our system is not capable of testing a large quantity of specimen, a reliable study of adsorption mechanisms, within the practical pressure range, can be conducted.

2. Experimental

Two QCMs were mounted inside a vacuum system, as shown in Fig. 1 (a). This chamber was pumped out using a mechanical pump and a turbo-molecular pump. The base pressure of the system ranged from 1 to $2 \times 10^{-9}$ torr after a bake-out. When hydrogen was introduced, the gate valve was closed to isolate the turbo-molecular pump from the chamber. Thus, no moistures are able to diffuse into the chamber through a turbo-molecular pump. The conventional gate valve was sustainable up to 2 MPa [17]. To minimize the water vapors flowing into the system during hydrogen intake, hydrogen gas with a purity of 99.999% was used through a liquid-nitrogen trap, as shown in Fig. 1(b). In addition to the gas inline, another cryo-trap was used on a venting line to capture water vapors that might be introduced into the chamber during ventilation. After exhausting hydrogen gas through the venting line, the line was closed and the chamber was open to the turbo-molecular pump that has been running since the beginning. While charging and discharging hydrogen gas, we tried to minimize the effect of water vapors. The spectroscopy in Fig. 1(c) presents the partial pressure of the residual gases right after bake-out. The partial pressure of the remaining water is shown in Fig. 1(d). In comparing the concurrent hydrogen partial pressure after hydrogen intake, where the hydrogen pressure reaches up to $5 \times 10^{-5}$ torr, as shown in the inset in Fig. 1(d), the amount of water vapors in the chamber was negligible.

For weighing hydrogen adsorbed onCNTs, AT-cut quartz crystals oscillating at a resonant frequency of 6 MHz was used. In general, the resonant frequency of a QCM is highly susceptible to temperature and pressure variations. To account for the frequency shift caused by such environmental changes, we installed another AT-cut quartz crystal. To minimize the effect of temperature further, the two QCMs were mounted on a water-circulating substrate where the temperature is controlled by a chiller. The temperature was consistently monitored using a thermocouple mounted on the QCM substrate. The sample was heat-treated by a baking process to remove moisture.

Highly purified SWCNTs were purchased from Iljin Co. The quality and crystallinity of these SWCNTs were examined with different characterization tools. For instance, Raman spectroscopy in Fig. 2(a) features the radial breathing modes (RBM) near 165 cm$^{-1}$, corresponding to a diameter of 1.5 nm. The weak D/G peak ratio in the spectroscopy indicates high crystallinity with minimal defects in the sample. In addition, thermogravimetric analysis (TGA) with air shown in Fig. 2(b) indicates a burning temperature near 776 K [18], which is a characteristic of SWCNTs, and relatively low metal residues; below 2 wt%. The purity of the SWCNTs was visually confirmed using transmission electron microscopy (TEM) in Fig. 2(c). Amorphous carbon layers on the SWCNT surface were not visible and the bundle size was found to be 10–30 nm.

To load the SWCNTs on the quartz crystals, SWCNTs were dispersed in dichloroethane (DCE) solution using a sonicator and sprayed onto the quartz crystal. The weight of the loaded SWCNTs on an active area of QCM was between 80 and 120 µg that was derived from a linear approximation of the frequency shift to the mass change; described by Sauerbrey [19,20]. According to his expression, if the sample is within two percent of the crystal weight, the added mass, $m_f$, can be expressed as a function of the quartz crystal mass, $m_q$, as follows:

$$m_f/m_q = -(v_q - v_f)/v_f,$$

where $v_q$ and $v_f$ are the resonant frequencies with and without the added mass, respectively. Therefore, the weight of the loaded SWCNTs was always kept below two percent of total crystal weight during the experiments. The frequency difference was measured in a vacuum at 24°C before and after loading the SWCNTs and was converted to the corresponding weight. After spraying SWCNTs on the quartz crystal, the crystal was heat-treated at 150°C for 20 min to remove the organic solution and then transferred to the vacuum system. The complete removal of DCE solvent (vaporization temperature: 83°C at atm) was confirmed by the Fourier-transformed infrared spectroscopy.

3. Results and discussion

Fig. 3 presents the change of the QCM frequencies with hydrogen intake and release. Once the hydrogen gas was filled in the chamber with a pressure of up to 0.5 MPa, the pressure was held for about 6 h. When hydrogen gas was introduced into the chamber, the two QCMs responded in distinctively different ways. The resonant frequency of the reference QCM abruptly

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal, N/m²</td>
</tr>
<tr>
<td>$m_q$</td>
<td>quartz crystal mass</td>
</tr>
<tr>
<td>$m_l$</td>
<td>film mass</td>
</tr>
<tr>
<td>$v_q$</td>
<td>resonant frequency of quartz crystal</td>
</tr>
<tr>
<td>$v_f$</td>
<td>resonant frequency with added mass</td>
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<tr>
<td>amu</td>
<td>atomic mass unit</td>
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increased, as shown in Fig. 3(a). On the other hand, the resonant frequency of the SWCNT-loaded QCM suddenly dropped, as shown in Fig. 3(b). This behavior was reproducible in response to the pressure. A plateau in the frequency-shift curve from the reference QCM was observed before and interpreted as a pressure-induced effect [21]. However, in good contrast
with the reference QCM, a significant frequency drop in the SWCNT-loaded QCM is ascribed to the hydrogen adsorption. With repetition of this experiment, the frequency change in the SWCNT-loaded QCM became smaller, with an initial downshift from 20 Hz during the first cycle to only a few Hz by the third cycle, as shown in Fig. 3(b). Yet, the reference QCM did not reveal an appreciable change in the frequency, as shown in Fig. 3(a).

The frequency change of the SWCNT-loaded QCM was replotted in Fig. 3(c) after deducting pressure and temperature effects from the reference QCM. One intriguing feature in Fig. 3(c) was that the SWCNT-loaded QCM recovered nearly 70% of the down-shifted frequency less than an hour after the hydrogen release. The temperature was maintained close to 24°C within less than 0.3°C during the entire experiment. The desorption time constant for physisorbed hydrogen should be virtually instantaneous with the release of pressure. The initial frequency change of up to approximately 50% upon pressure release may be due to physisorption. On the other hand, any hydrogen desorbed after the time constant, may be responsible for micropores residing deep inside of CNT bundles. The additional 30% of the frequency change was gradually recovered over the next several hours. This suggests that the adsorption of hydrogen gas is more complicated than simple physisorption. This complexity could be attributed to the structure of SWCNT bundles and/or functional groups on the CNT surface. The general trend of this change was very similar during repeated cycling, although the frequency change was reduced in the second and third cycles. In accordance with smaller frequency shifts from run to run, the recovery time to reach the hydrogen loading frequency was shorter. During first cycle, it took almost 40 h to return to the initial frequency. This recovery time dropped to about 25 h in the following runs. If water molecules were added during the experiment, CNT loaded-QCM would not recover its initial frequency. Using Eq. (1), the storage capacity of the purified SWCNTs in Fig. 3(c) was about 0.2 wt%, which is comparable to the reported results for SWCNTs [22,23].

After running a few cycles, our vacuum system was baked out at 130°C for about 24 h in order to remove moisture in SWCNTs. After the bake-out, the base pressure was 1–2 × 10⁻⁹ torr. Hydrogen gas was then introduced into the chamber through a liquid-nitrogen trap. The SWCNT-loaded QCM displayed a sudden up-shift in frequency, as shown in Fig. 4(a). The frequency change was much smaller than that of the reference QCM, indicating that hydrogen was absorbed, just not as much as before the bake-out. This is demonstrated more clearly by the net frequency change shown in Fig. 4(b). In another experiment, the effect of the bake-out on hydrogen storage capacity was very reproducible. In both runs in Fig. 4(b), the storage capacity was reduced to 0.1 wt%, compared to the measurement without a bake-out process. Such a difference in the hydrogen storage capacity of SWCNTs may be the result of physisorbed chemical species or functional groups that are weakly bonded to the surface of CNTs. After these samples were exposed to air again for a few days, the storage capacity was recovered to nearly 0.2 wt%. Thus the hydrogen adsorption induced by
the presumed functional groups seems to improve the storage capacity in SWCNTs.

In order to clarify the existence of the functional groups in SWCNTs, we carried out temperature-programmed desorption (TPD) in an ultrahigh vacuum (UHV) system. The same sample used in the previous experiments was loaded into the UHV chamber after exposing a few days in air. No appreciable peaks were observable up to 560 K within 50 amu, as shown in Fig. 4(c). The higher molecular species up to 100 amu were not detected as shown in Fig. 4(d). The water or oxygen molecules in air could be adsorbed in the sample preparation, but not as a simple form of molecules but as functional groups such as CO and COOH particularly near the defects on the tube wall or tube edges[24,25]. Desorption of hydrogen and water molecules at around 700 K in Fig. 4(c) may explain a presence of such functional groups.

However, the increase in storage capacity in our works is in contrast with the previous study [26]. The water adsorption on graphite nanofibers (GNF) is known for a quite favorable process because a herringbone stacking of graphene layers exposes numerous edges to the surface. Once the water vapor is adsorbed on the graphite nanofibers, the graphene edges on the surface decompose the water vapors and GNF become more hydrophilic by carboxyl groups. The agglomeration of water molecules at the edge hinders the diffusion of hydrogen into the inter-tube distance in bundles, rather than impeding the migration of hydrogen into the inter-tube space. In addition to this physical phenomenon, a possible chemical process that might go into effect is the functionalization of CNTs surface by the physi-adsorption of water. The adsorption of polar molecules like water may change the interaction nature between hydrogen gas and CNTs. The bake-out simply deprived such intercalants or physisorbed-functional molecules from CNTs.

On the other hand, the adsorption behavior of water vapor on CNTs is different from that of GNF. Since our sample experienced several purification steps, it revealed strong hydrophobicity. As the water vapors adhere to CNTs, water molecules would cluster inside an interstitial space and grow until they obtain an energetically stable structure, 0.5 nm$^3$ [27,28], instead of filling the tube-tube crevice by uniformly coating tubes. Thus, we propose that physisorbed water clusters eventually expand then inter-tube distance in bundles, rather than impeding the migration of hydrogen into the inter-tube space. In addition, the physical phenomenon, a possible chemical process that might go into effect is the functionalization of CNTs surface by the physi-adsorption of water. The adsorption of polar molecules like water may change the interaction nature between hydrogen gas and CNTs. The bake-out simply deprived such intercalants or physisorbed-functional molecules from CNTs.

In the test runs for reproducibility, we observed the frequency fluctuation to be about 5–6 Hz. It is difficult to tell whether this frequency fluctuation is attributed to the loss in CNTs or other materials like water. Although the exact origin for this fluctuation is not clear, the fluctuation magnitude is equivalent to 0.02 wt%, which is negligible in our measurement range. While the buoyancy issues must be considered, the buoyancy effect at our pressure range [29,30], and therefore the effect should not change the measured storage capacity significantly.

4. Summary

In summary, using dual QCMs in a high vacuum system, the storage capacity of CNTs has been examined under the
conditions where environmental effects have been minimized. The hydrogen uptake of air-exposed SWCNTs is about 0.2 wt% at 0.5 MPa and drops to 0.1 wt% after baking out the vacuum system. This abnormal behavior of CNTs for hydrogen storage promoted by the physi-adsorption of moisture may be responsible for intercalated water molecules that expand the interlayer distance and/or functionalization of CNTs surface with polar molecules. In our sample, the amount of physisorbed water molecules in CNTs was estimated to be only 1 wt%. If the water in CNTs increases to 11 wt% [31], the hydrogen storage capacity can grow in parallel near 2–3 wt%. This implies that measuring the storage capacity of CNTs could be erroneous unless environmental gas species are not removed. From another aspect, choosing proper functional groups and abundant adsorption sites could result in a high storage capacity of CNTs only through the physical adsorption. This may be a more desirable approach without invoking precautions to high pressure.

Acknowledgments

This work was financially supported by Korea Energy Management Corporation (2004-N-HY12-P-02-0-000) and in part by the MOST through the CNNC and by the SAINT at SKKU.

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