

# Physisorption of Hydrogen on Microporous Carbon and Carbon Nanotubes

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We have investigated the storage capability of microporous carbon materials for gaseous hydrogen both theoretically and experimentally. In the grand canonical Monte Carlo calculation the hydrogen molecules are physisorbed by van der Waals interactions with the surface atoms of carbon slitpores and carbon nanotubes. At room temperature the optimum pore geometry is a slitpore consisting of two graphite platelets separated by a distance that corresponds approximately to two times the diameter of a hydrogen molecule. In this case for a storage pressure of 10 MPa a maximum adsorbed hydrogen density of 14 kg/m<sup>3</sup> can be reached, which corresponds to a gravimetric storage capacity of 1.3 wt %. Only for low gas pressure a cylindrical geometry like that in carbon nanotubes can exceed the storage density of carbon slitpores owing to capillary forces.

## 1. Introduction

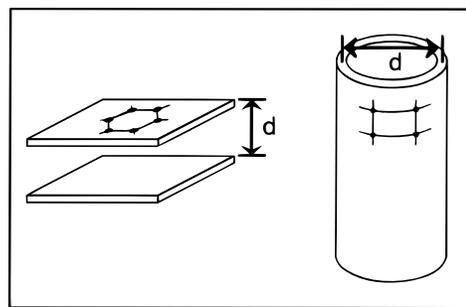
A safe, effective, and cheap storage system is crucial for the future utilization of hydrogen as a pollution-free energy carrier. Besides the established techniques (liquid hydrogen, compressed gas), the storage in a solid-state matrix (e.g., metal hydride) has the advantage of being safe, but fails for most materials with respect to the total weight of the tank system. Therefore carbon with its low atomic weight could help to overcome these disadvantages.

In contrast to the chemisorption in metal hydrides, microporous carbon adsorbs the undissociated hydrogen molecules by van der Waals forces at its surface. But as these binding forces are weak, the physisorption process at room temperature is almost impeded by thermal motion. To store large amounts of hydrogen the carbon samples therefore have to be cooled. However, a cryogenic hydrogen storage system is in most cases economically unprofitable.<sup>1,2</sup>

In recent years, the storage of hydrogen in carbon has attracted new attention owing to the availability of novel carbon nanomaterials, e.g., fullerenes, nanotubes, and nanofibers. The cylindrical structure of carbon nanotubes increases the adsorption potential in the tube core leading to capillary forces and to enhanced storage capability. In a first experiment A. C. Dillon et al.<sup>3</sup> have shown experimentally that carbon nanotubes can store considerable amounts of hydrogen even at room temperature.

Carbon nanofibers consist of stacked nanosized graphene layers forming an ordered structure of slitlike pores with many open edges. Therefore this material also looks promising for gas storage purposes. Recently A. Chambers et al.<sup>4</sup> have shown that 1 g of carbon nanofibers can store at least 2 g of hydrogen gas, which is more than 2 orders of magnitude above the storage capacity of the best activated carbon (AC) samples.

The total amount of adsorbed hydrogen strongly depends on the pore geometry and size as well as on the storage pressure and temperature. To study the influence of all these parameters and to get a better understanding of the adsorption process, we have simulated the hydrogen uptake of carbon slitpores and



**Figure 1.** Pore geometries studied in this work: slitpore with pore size  $d$  and cylindrical pore (nanotube) with diameter  $d$ . The arrangement of individual carbon atoms inside the pore walls is as indicated.

nanotubes with a grand canonical ensemble Monte Carlo program (GCEMC). The simulation results can be used to optimize the pore geometry for hydrogen storage at a given pressure and temperature. For comparison with the calculation results, we have measured the hydrogen uptake of various activated carbon fibers with different specific surfaces. The storage capability of these samples has been determined at room temperature by measuring the pressure drop inside a vessel due to the hydrogen adsorption on the carbon surface.

## 2. Monte Carlo Calculation

The hydrogen uptake is calculated by a grand canonical ensemble Monte Carlo program (GCEMC). The details of the simulation are described elsewhere (see e.g., ref 5), so we give here only a brief summary. In a simulation loop, the motion of hydrogen molecules in a given pore volume for a fixed temperature  $T$  and a chemical potential  $\mu$  is calculated. The carbon pore is built up by  $M$  carbon atoms ( $\approx 2000$ ) being located at the surface of any desired pore geometry. In this work we have studied the two geometries shown in Figure 1, i.e., slitpores and nanotubes. As indicated, the carbon atoms are arranged in a hexagonal pattern inside the walls of the slitpore. To allow a continuous variation of the tube diameter  $d$ , we have chosen a rectangular pattern at the circumference of the nanotubes. (A test of the influence of the arrangement of atoms inside the pore walls for a carbon slitpore shows no significant

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difference between a hexagonal and rectangular pattern.) The particle density in the pore walls is  $A_c = 0.382 \text{ \AA}^{-2}$  for both geometries.

The pairwise interaction energy between two particles separated by a distance  $s$  is calculated by the Lennard-Jones potential

$$U(s) = 4\epsilon \left[ \left( \frac{\sigma}{s} \right)^{12} - \left( \frac{\sigma}{s} \right)^6 \right] \quad (1)$$

For the potential parameters we have used  $\sigma_1 = 2.97 \text{ \AA}$  and  $\epsilon_1/k_B = 33.3 \text{ K}$  (hydrogen–hydrogen) and  $\sigma_2 = 3.19 \text{ \AA}$ ,  $\epsilon_2/k_B = 30.5 \text{ K}$  (hydrogen–carbon) as given in the literature<sup>6,7</sup> and by the Lorentz–Berthelot combining rules. The total potential energy of a particular hydrogen molecule is finally given by summing up all interaction energies (1) between neighboring hydrogen molecules and pore wall carbon atoms.

During the simulation the particle number  $N$  within the pore fluctuates owing to particle displacement, creation, and destruction steps, which are executed with equal frequency. In a creation step, the position of the new particle is chosen randomly within pore volume  $V$  and its potential energy  $U$  is calculated. Finally this creation step is accepted with the probability  $\min(1; P)$  with

$$P = \exp\left(-\frac{U - \mu}{k_B T}\right) \frac{V}{N + 1} \quad (\text{creation})$$

Analogous destruction and displacement steps are accepted with

$$P = \exp\left(+\frac{U - \mu}{k_B T}\right) \frac{N}{V} \quad (\text{destruction})$$

$$P = \exp\left(-\frac{U_1 - U_2}{k_B T}\right) \quad (\text{displacement})$$

To obtain thermal equilibrium,  $10^6$  iterations were performed. Then an additional  $10^5$  iterations are made to get a simulation result for the mean particle number  $\langle N \rangle$  in the pore (which is in the range between 0 and 500 for the parameters used in our calculation). Furthermore values for the following commonly used parameters are calculated:

$$\text{volumetric storage capacity} = \frac{m_{\text{H}_2}}{V}$$

$$\text{gravimetric storage capacity} = \frac{m_{\text{H}_2}}{m_{\text{H}_2} + m_{\text{C}}}$$

$$\text{excess adsorption} = \frac{m_{\text{H}_2} - m_{\text{H}_2}^0}{(m_{\text{H}_2} - m_{\text{H}_2}^0) + m_{\text{C}}}$$

with

$$m_{\text{C}} = \frac{M}{L} \cdot 0.5 \cdot 12.011 \text{ g/mol}$$

$$m_{\text{H}_2} = \frac{\langle N \rangle}{L} \cdot 2.016 \text{ g/mol}$$

$$m_{\text{H}_2}^0 = \frac{N_0}{L} \cdot 2.016 \text{ g/mol}$$

The factor 0.5 in the carbon mass considers a periodic arrangement of the single pores in the whole sample in which each pore wall joins two micropores on both wall sides.  $N_0$  gives the number of hydrogen molecules corresponding to the density of compressed gas inside the accessible pore volume. As this quantity is also subtracted in the experimental result (see below), excess adsorption rather than the total gravimetric storage capacity has to be used for comparison with the experiment.

The relation between the chemical potential  $\mu$  and the pressure  $p$  at a given temperature is calculated by a similar GCEMC simulation of bulk hydrogen gas.

### 3. Experiment

The hydrogen adsorption was measured on a commercial pitch-based carbon fiber (supplied by Kureha Company) activated to different burnoff at 1160 K with  $\text{CO}_2$  and a steam/ $\text{N}_2$  mixture in a horizontal furnace.<sup>8,9</sup>

An activated carbon obtained by chemical activation of a Spanish coal was also used. The preparation procedure is as follows. One gram of coal is mixed with a solution that contains 2 g of the activating agent and dried for 2 h at 383 K. Subsequently, the material was submitted to a pyrolysis process in a horizontal furnace in  $\text{N}_2$  atmosphere with a heating rate of 5 K/min, to the pyrolysis temperature (973 K), which was maintained for 1 h. The pyrolyzed sample is washed repeatedly with a solution of HCl and later with distilled water until free of chloride ions. Once the activating agent is removed, the sample is dried at 383 K for 12 h.

The porous texture of all these samples (Table 1) was obtained by  $\text{N}_2$  and  $\text{CO}_2$  adsorption at 77 and 273 K, respectively, mercury porosimetry and scanning electron microscopy. The study of the porous texture shows that these samples are essentially microporous and that they do not contain meso- and macroporosity.<sup>8,9</sup>

Hydrogen adsorption capacities of the carbon samples were measured volumetrically at about 298 K by the pressure drop of hydrogen gas in contact with the sample. The high-pressure apparatus (Figure 2) consists of two volumes  $V_1$  and  $V_2$  separated by a valve. Volume  $V_2$  is filled with the carbon sample, and the whole apparatus is evacuated. After closing the valve, volume  $V_1$  is filled with hydrogen gas to a pressure of about  $p_1 = 10 \text{ MPa}$ . Then the valve is opened, and the pressure drop to  $p_2$  is recorded. For given volumes  $V_1$  and  $V_2$  the particle numbers in the gas-phase  $n_1$  and  $n_2$  (before and after opening the valve, respectively) are calculated by the real gas law:

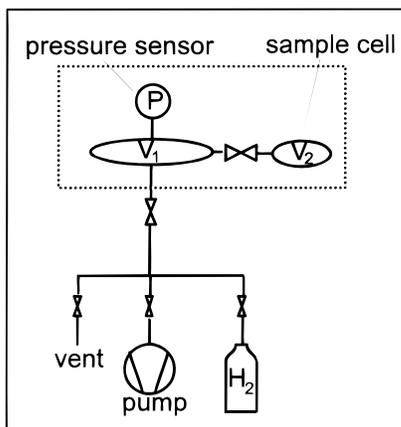
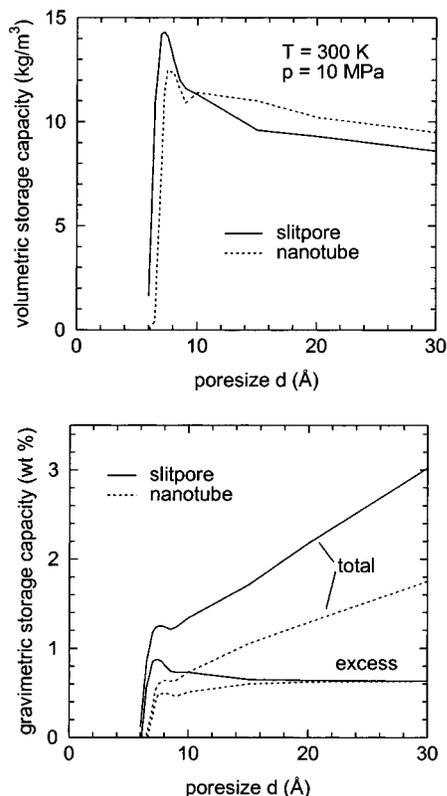
$$\left(p_1 + n_1^2 \frac{a}{V_1^2}\right)(V_1 - n_1 b) = n_1 R T_1 \quad (2)$$

$$\left(p_2 + n_2^2 \frac{a}{(V_1 + V_2)^2}\right)(V_1 + V_2 - n_2 b) = n_2 R T_2 \quad (3)$$

Volume  $V_2$  is given by the void volume of the sample cell reduced by the volume of the carbon sample itself, which is calculated by the carbon mass assuming a bulk skeleton density of  $2260 \text{ kg/m}^3$ . Thus the open pore volume is part of the volume  $V_2$ , and a normal compressed gas density inside the accessible pore volume gives no contribution to the measured adsorption as  $n_2$  will equal  $n_1$ . Only if adsorption takes place, i.e., the  $\text{H}_2$  density surpasses vapor density at least locally,  $n_2$  will be less than  $n_1$ . Then  $n_1 - n_2$  equals the excess adsorption described in section 2.

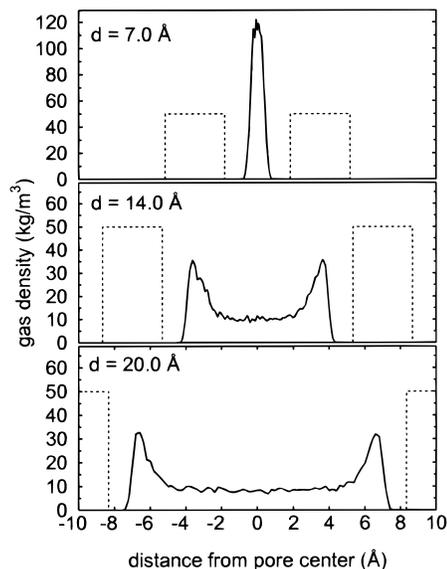
**TABLE 1: Textural Characteristics of Carbon Fiber, Activated Carbon Fibers and Activated Carbon (AC, Obtained by Chemical Activation of a Spanish Coal)**

sample	description	volume CO <sub>2</sub> (cm <sup>3</sup> /g)	volume N <sub>2</sub> (cm <sup>3</sup> /g)	BET area (m <sup>2</sup> /g)
1	nonactivated carbon fiber (CF)	0.17	0.00	300
2	CF activated to 34% with CO <sub>2</sub>	0.49	0.42	1110
3	CF activated to 58% with CO <sub>2</sub>	0.71	0.92	2290
4	CF activated to 34% with steam	0.38	0.39	810
5	CF activated to 62% with steam	0.59	0.76	1895
6	CF activated to 74% with steam	0.54	0.91	2260
7	AC	0.72	0.68	1675

**Figure 2.** Schematic view of the apparatus to measure the hydrogen uptake of carbon samples filled into the sample cell.**Figure 3.** Calculated amount of adsorbed hydrogen as function of the pore size  $d$  for  $T = 300$  K and  $p = 10$  MPa for both pore geometries: (a, top) volumetric storage capacity, (b, bottom) gravimetric storage capacity.

#### 4. Results

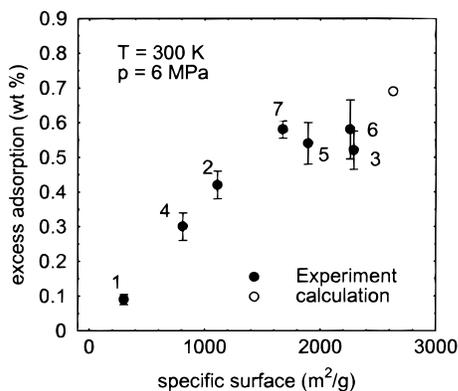
Figure 3 shows the results of calculations of the dependence of the hydrogen storage capacity on the pore size  $d$  of a carbon slitpore and a nanotube at room temperature and  $p = 10$  MPa. There is a sharp maximum in the volumetric storage capacity

**Figure 4.** Variation of the particle density inside a carbon slitpore for  $T = 300$  K and  $p = 10$  MPa. The dashed boxes indicate the position of the pore walls (width 3.35 Å) for three different pore sizes  $d$  as given in the figure.

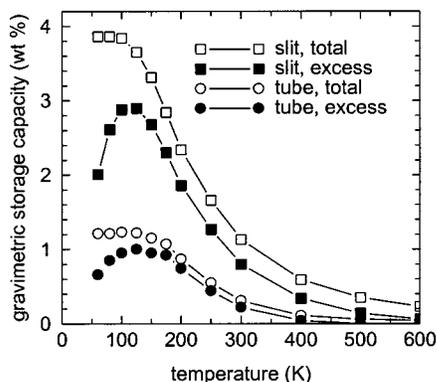
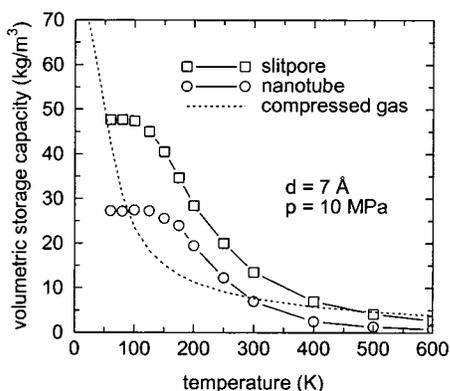
for a pore size of about  $d = 7$  Å for both pore geometries. In this particular case, one hydrogen molecule fits exactly between the slitpore layers or in the tube core, respectively, leading to strong capillary adsorption forces. The peak value for the volumetric storage capacity is 14.3 kg/m<sup>3</sup> for the slitpore geometry in contrast to only 12.5 kg/m<sup>3</sup> for the tube geometry, corresponding to gravimetric excess adsorption values of 0.9 and 0.5 wt %, respectively. The total gravimetric storage capacity of a carbon slitpore with  $d = 7$  Å is 1.3 wt %.

For larger pore sizes  $d$  the volumetric storage capacity decreases asymptotically to the density of the pure compressed gas (7.6 kg/m<sup>3</sup>) while the gravimetric storage capacity, i.e., the total amount of stored hydrogen compared to the pore mass, increases almost linearly with  $d$  for both geometries. At large  $d$ , the excess storage capacity is nearly independent of the pore size and pore geometry and amounts to about 0.6 wt %.

Figure 4 shows the gas density inside a slitpore at three different pore sizes. For large  $d$ , there are two adsorption layers on each side of the slitpore (corresponding to an excess adsorption of 0.6 wt %) separated by a region with the density of pure compressed gas. If the pore size is decreased to  $d = 7$  Å, only one adsorption layer can form between the walls of the pore but the adsorption forces are increased by a factor of 2 owing to the contact with both pore walls. These two effects nearly annihilate at room temperature and  $p = 10$  MPa to give an only slightly increased excess adsorption of 0.9 wt %. Therefore, the gravimetric excess adsorption at room temperature is approximately independent of the pore size and geometry but only depends on the specific surface area of the sample.



**Figure 5.** Measured dependence of the excess storage capacity of various activated carbon samples on the specific surface area. The carbon samples are numbered according to Table 1. For comparison the Monte Carlo result is given at the specific surface area of an ideal graphite plane (2600 m<sup>2</sup>/g).

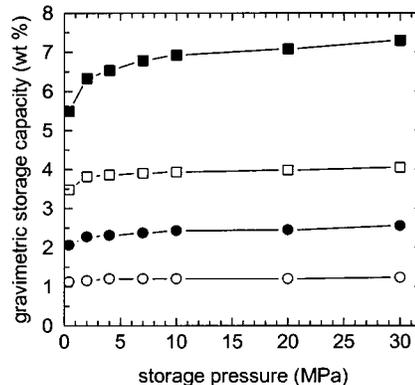
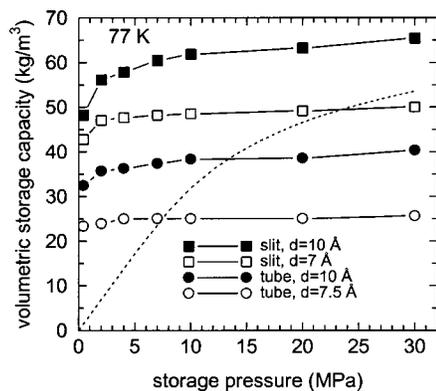


**Figure 6.** Temperature dependence of the amount of adsorbed hydrogen at a storage pressure of 10 MPa for both studied geometries (pore width  $d = 7 \text{ \AA}$ ): (a, top) volumetric storage capacity, (b, bottom) gravimetric storage capacity.

This finding is confirmed by our experimental results (Figure 5), which have been measured on the carbon samples described in section 3. The stored amount of hydrogen is proportional to the specific surface area of the samples. The best sample has a specific surface of 2290 m<sup>2</sup>/g, close to the value for an ideal graphite plane of 2600 m<sup>2</sup>/g. Moreover, the best experimental results are close to the calculated excess adsorption value of 0.69 wt % for a slitpore with  $d = 7.0 \text{ \AA}$ . This behavior encourages us to consider the theoretical model to be valid and to conduct some parameter variations, which we show in the next section.

### 5. Influence of Temperature and Pressure

Figure 6 shows the simulation result of the influence of the temperature on the amount of adsorbed hydrogen. At low



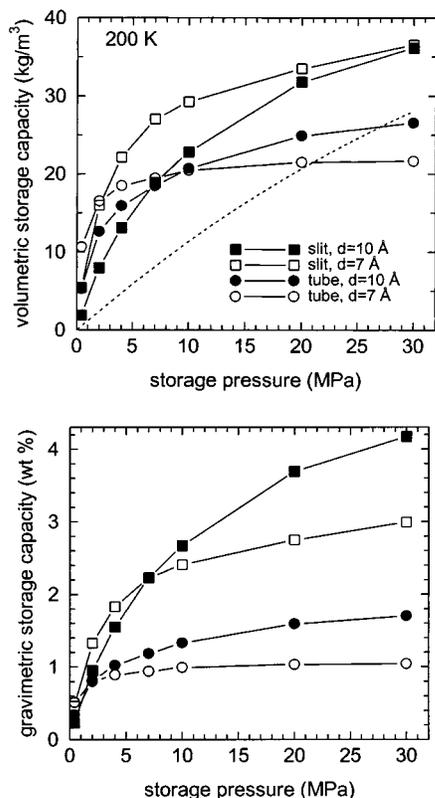
**Figure 7.** Volumetric (a, top) and gravimetric (b, bottom) storage capacity at  $T = 77 \text{ K}$  as function of the storage pressure for both geometries and two different pore widths  $d$ . The dashed line gives the density of compressed hydrogen gas for comparison.

temperatures the total amount of gas inside the pores saturates at a value corresponding to a particle density inside the accessible pore volume exceeding the density of liquid hydrogen by about 20%. A comparison of the volumetric storage capacity with the density of pure compressed hydrogen gas shows that storage by adsorption is most effective in the medium-temperature range with a maximum at about 150–200 K.

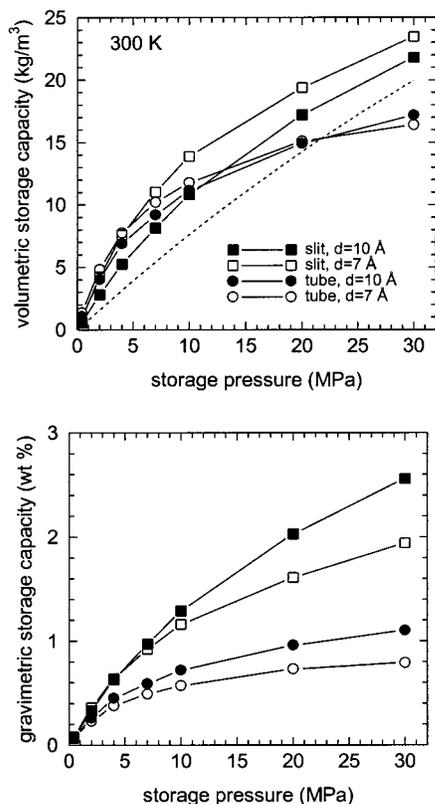
Excess adsorption is maximum at about 130 K for both geometries. At lower temperatures the effect of adsorption is decreased as the compressed gas density is already very high. In general, a carbon nanotube stores 30–60% less hydrogen than a slitpore at  $p = 10 \text{ MPa}$  and  $d = 7 \text{ \AA}$ .

Figures 7–9 show the calculated storage capacity as function of the gas pressure at three different temperatures both for a slitpore and nanotube geometry. For the pore size  $d$  we have chosen the values that give the maximum storage capacity at room temperature and  $p = 10 \text{ MPa}$  ( $d = 7.0$  and  $7.5 \text{ \AA}$  for slitpore and nanotube, respectively). In addition, we have calculated the storage capacity for pores with  $d = 10 \text{ \AA}$  which can hold two layers of hydrogen.

The comparison with the compressed gas density shows that at any temperature the positive effect of the adsorbent is maximum for low storage pressures. At 77 K the storage capacity saturates already at  $p = 5 \text{ MPa}$  while the compressed gas density at this pressure is lower up to a factor of 4. Comparing both studied geometries shows that the cylindrical nanotube geometry has no advantage compared to the slitpore geometry at nearly all storage conditions. Only in the medium-temperature range and at gas pressures below 3 MPa does the volumetric storage capacity of carbon nanotubes exceed the value of the slitpore geometry. As the binding force is weaker in larger pores, the storage density for  $d = 10 \text{ \AA}$  is in general



**Figure 8.** Volumetric (a, top) and gravimetric (b, bottom) storage capacity at  $T = 200$  K.



**Figure 9.** Volumetric (a, top) and gravimetric (b, bottom) storage capacity at  $T = 300$  K.

below the value for the pores with  $d = 7.0$  or  $7.5$  Å, respectively. Only at low temperatures can two adsorption layers form inside the larger pores leading to an increased volumetric storage density.

## 6. Summary and Discussion

We have calculated gaseous hydrogen adsorption capacity of two kind of carbon pores at different temperatures and storage pressures. The results are compared with measurements on activated carbon samples at  $T = 300$  K and  $p = 6$  MPa. The measurements show a linear dependence of the excess adsorption capacity on the specific surface of the activated carbons. Our best samples have a specific surface of  $2290$  m<sup>2</sup>/g and a maximum gravimetric storage capacity of  $0.6$  wt %. This is in good agreement with the calculated value of  $0.7$  wt % for an ideal slitpore with a specific surface of  $2600$  m<sup>2</sup>/g at  $T = 300$  K and  $p = 6$  MPa.

According to our calculations at room temperature and  $p = 10$  MPa, the best achievable volumetric storage density is  $14$  kg H<sub>2</sub>/m<sup>3</sup> for a slitpore of height  $7.0$  Å. This would correspond to  $20\%$  of the density of liquid hydrogen.

At nearly all temperatures and pressures the storage capacity of slitpores is better than the capacity of carbon nanotubes. At  $77$  K even at low pressures two layers of hydrogen gas are adsorbed in the pore volume of micropores with  $d = 10.0$  Å. This corresponds to a gravimetric storage capacity of the nanotubes of about  $2$  wt % while that of slitpores can be up to  $5.5$  wt %. The high hydrogen uptake of  $5$ – $10$  wt % for single-walled nanotube materials measured by A. C. Dillon et al.<sup>3</sup> under their conditions cannot be explained by pure physisorption owing to strong capillary forces in the tube core.

For carbon nanofibers A. Chambers et al.<sup>4</sup> have measured a maximum hydrogen storage capacity of  $68$  wt % at room temperature and at an initial storage pressure of about  $11$  MPa. For comparison we have calculated the amount of physical adsorbed hydrogen in carbon slitpores for these parameters. For  $d = 3.4$  Å (which corresponds to the interplanar distance of the graphene layers in the nanofibers) no hydrogen can be adsorbed at all (see Figure 3). Even if one assumes that the interplanar distance is expanded during the adsorption process, the maximum calculated excess adsorption is  $1$  wt % for  $d = 7$  Å. Therefore the experimental result cannot be attributed to “capillary condensation at abnormally high temperatures” as stated by the authors of ref 4. Further work is needed both experimentally and theoretically to try to reproduce and clarify the various experiments.

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