

CARBON NANOTUBE ADSORBENTS

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INTRODUCTION

One of the more interesting applications proposed for carbon nanotubes is as storage media for fluids and solids. Of particular interest is their potential for fuel gas storage, especially hydrogen [1]. A full, experimental exploration of their potential in these fields must await developments in the production, purification and ordering of nanotubes. Meanwhile, it is possible to make some assessment of their potential as gas storage media using molecular simulations. The interior of an isolated open carbon nanotube can be viewed as a microporous or mesoporous cylindrical adsorption space (depending upon the nanotube diameter). Also, the interstices between nanotubes may provide additional adsorption space of nanometric dimensions. Therefore, we have been exploring the adsorption of gases in arrays of nanotubes using molecular simulations. In this paper we present some storage capacities for hydrogen at 298 and 77 K and nitrogen at 77 K in carbon nanotube arrays obtained from simulations and compare these to experimental measurements of adsorption in materials containing nanotubes.

MODELS AND SIMULATIONS

The model adsorption space consists of a unidirectional trigonal array of open or closed single wall carbon nanotubes, SWCNT, Figure 1. The diameter D and the nanotube separation G define the geometry of the array.

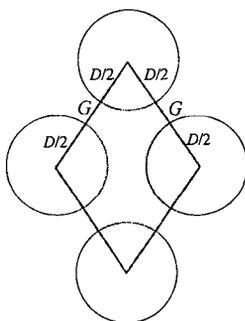


Figure 1. Model trigonal array of single-walled carbon nanotubes of diameter D and separation G . Circles are cross sections of nanotubes. The shaded area is the cross section of the simulation cell.

Table 1. Lennard-Jones potential parameters used for simulations of adsorption of H_2 and N_2 in SWCNT arrays. k_B is Boltzmann's constant.

Gas	LJ Parameter			
	$\sigma_{ff} / \text{\AA}$	$\sigma_{sf} / \text{\AA}$	$(\epsilon_{ff} / k_B) / K$	$(\epsilon_{sf} / k_B) / K$
Hydrogen	2.96	3.19	41.5	35.4
Nitrogen	3.572	3.494	93.98	53.52

We have also studied square arrays of SWCNT [2]. The Grand Canonical Monte Carlo Ensemble method [e.g., 3] was used to simulate equilibrium adsorption of gases in the model array. A single site Lennard-Jones (LJ) 12:6 pair potential was used to represent interactions between gas molecules. The interaction between an adsorbate molecule and a single nanotube was obtained by integration of the LJ potential over the nanotube surface; this potential is applicable to adsorption inside and outside tubes (endohedral and exohedral adsorption [4]). The LJ length (σ) and energy (ϵ) parameters for fluid-fluid (ff) and solid-fluid (sf) potentials are listed in Table 1. The cross section through the simulation cell, perpendicular to the length of the nanotubes, is a parallelogram, Figure 1. The length of the cell parallel to the nanotubes was

normally $10\sigma_m$, although this could be extended to increase the number of molecules in the cell and so reduce errors. The Peng-Robinson equation of state was used to calculate the chemical potentials of bulk gases [5]. The main output from the simulations was the average number of molecules adsorbed in the simulation cell as a function of pressure.

RESULTS AND DISCUSSION

Hydrogen Storage at 298 K and 77 K.

The amount of usable gas in a gas storage system is the delivered capacity, *i.e.*, the amount of gas stored at the higher (storage) pressure less the amount retained in the container at the lower (delivery) pressure. The delivered capacity can be expressed on a gravimetric or volumetric basis; here, a gravimetric basis is considered. For hydrogen, storage and delivery pressures were normally 70 and 1 bar respectively. For studies of the effects of storage pressure on the hydrogen capacity, the storage pressure was varied from 1 to 200 bar. The US DOE hydrogen plan for a fuel cell powered vehicle requires the storage system to have a delivered gravimetric capacity of 6.5 wt% H_2 [1].

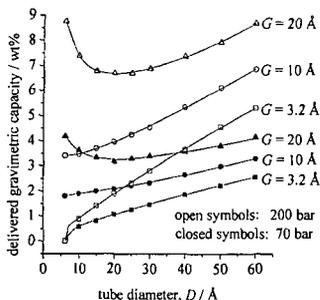


Figure 2. Delivered gravimetric hydrogen capacity at 298 K as a function of tube diameter in trigonal arrays of open single-walled carbon nanotubes with different separations G , for storage pressures of 70 and 200 bar.

Figure 2 shows the delivered gravimetric capacities of trigonal arrays of open SWCNT at 298 K and at storage pressures of 70 and 200 bar. For most of the arrays, capacity increases with increasing nanotube diameter, D , and tube separation, G . The effect of tube diameter on capacity is as expected while the effect of tube separation shows that exohedral adsorption in the interstices between the nanotubes is important. Significant amounts of hydrogen can be stored in the arrays, but none of them achieves the DOE target capacity at 298 K and a storage pressure of 70 bar. The DOE target capacity is achieved at 298 K and 200 bar storage pressure for SWCNT with a wide range of diameters in arrays with a spacing of 20 Å.

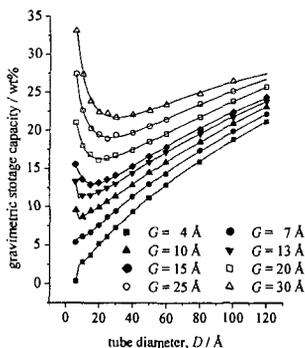


Figure 3. Gravimetric hydrogen storage capacity for trigonal arrays of open single-walled carbon nanotubes at 77 K and 70 bar as a function of tube diameter D and separation G .

The effects of increases in D and G on storage hydrogen capacities at 77 K and 70 bar, Figure 3, are broadly similar to those found at 298 K. The DOE target capacity is reached for arrays with a wide range of D and G values. For arrays with a spacing of 30 Å, the DOE target is exceeded by a considerable margin. The maximum delivered hydrogen capacity of ~33 wt% is reached with an array consisting of widely spaced narrow nanotubes ($D = 6$ Å, $G = 30$ Å) where exohedral adsorption dominates. The non-linear variations in capacity for arrays with $D < 30$ Å and $G > 7$ Å, Figure 3, are the result of complex geometrical factors affecting the space available for adsorption in the simulation cell. The volume of the simulation cell is proportional to $(D + G)^2$, while the mass of carbon in the cell is proportional to D . Thus, when $G \ll D$, the volume available per unit mass is $\sim D$, i.e., the capacities increase with D nearly linearly as in Figure 3. When $G \gg D$, the volume available per unit mass is $\sim 1/D$, i.e., the capacities decrease with increasing D .

Nitrogen Adsorption at 77 K. Figure 4 shows the gravimetric saturation capacity for nitrogen at 77 K and relative pressure $P/P_0 = 1$ for trigonal arrays of open SWCNT as a function of D and G . Qualitatively, the effects of increases in D and G on capacity are broadly similar to those found for hydrogen at 77 K, Figure 3. However, the gravimetric capacities for nitrogen at $P/P_0 = 1$ are more than 10 times higher than that for hydrogen at 70 bar in arrays of the same geometry. This is because (1) the critical temperature for nitrogen is much higher than for hydrogen, and (2) the molecular mass of nitrogen is 14 times that of hydrogen.

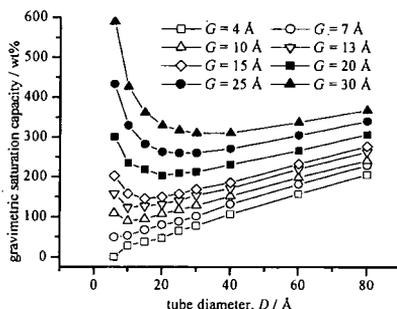


Figure 4. Gravimetric nitrogen saturation capacity for trigonal arrays of open single-walled carbon nanotubes at 77 K and relative pressure $P/P_0 = 1$ as a function of tube diameter D and separation G .

Comparisons of simulations with experiment.

In the case of nanotubes, comparisons between experimental and simulated gravimetric adsorption capacities are complicated because experimental amounts adsorbed have been measured on nanotube samples that have different purities and that have not been ordered into arrays. Also, as the foregoing shows, simulated gravimetric capacities depend upon the geometry of the array.

Comparison of hydrogen capacities at 298 and 77 K.

Table 2. Comparisons of gravimetric hydrogen storage capacities from experiments and molecular simulations.

System	T / K	P / bar	H ₂ capacity / wt%	Ref
SWCNT, 50% purity (E)	300	101	4.2	[6]
Trigonal array of open SWCNT (S)	298	100	4.7 max ^a	d
SWCNT, high purity (E)	80	72	8.25	[7]
Trigonal array of open SWCNT (S)	77	70	0-33 ^b	d

(E) - Experiment; (S) Simulation. a. $D = 60$ Å, $G = 10$ Å; b. $D = 6$ Å, $G = 30$ Å. d. this work

An experimental measurement of hydrogen capacity for 50% pure SWCNT at ambient temperatures and ~101 bar of 4.2 wt% [6], see Table 2, is in reasonable agreement with the hydrogen capacity at similar temperatures and pressures (4.7 wt%) obtained from simulations for trigonal arrays of open SWCNT with $D = 60$ Å, $G = 10$ Å. Molecular simulations of hydrogen storage at 77 K and 70 bar on trigonal arrays of open SWCNT with $D = 7$ Å, $G = 30$ Å, produce a

very high capacity (33 wt%, Table 2). This may be compared with an experimental measurement made on high purity SWCNT at similar temperatures and pressures [7] (8.25 wt%, Table 2). This simple comparison suggests that the experimental hydrogen capacities of nanotubes at 77 K can be increased substantially by developing ordered arrays.

Comparison of nitrogen capacities at 77 K. Some experimental measurements of adsorption of nitrogen on SWCNT have been reported by Alain *et al.* [8]. Here, a more precise comparison between simulation and experiment can be made because the dimensions of the nanotubes ($D \sim 13.8 \text{ \AA}$) are known from high-resolution transmission electron microscopy images. HRTEM also showed that the SWCNT were present in closed packed bundles with $G \sim 3.2 \text{ \AA}$. A comparison of the isotherm for these nanotubes measured using a volumetric apparatus with the results from simulations in trigonal arrays of open and closed SWCNT ($D = 13.8 \text{ \AA}$, $G = 3.2 \text{ \AA}$) is in Figure 5.

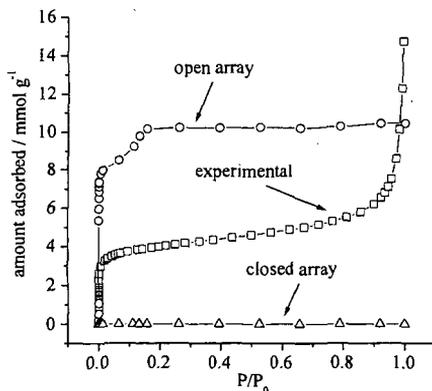


Figure 5. Comparison of experimental isotherms of nitrogen adsorbed at 77 K in single-walled carbon nanotubes to simulated isotherms for the same array geometry ($D = 13.8 \text{ \AA}$, $G = 3.2 \text{ \AA}$) with both open and closed nanotubes.

The simulations show that there is no adsorption in the array of closed SWCNT because the interstitial space is too small to admit nitrogen molecules. The simulated isotherm for the array of open SWCNT is close to Type 1 in the BDDT classification, indicating, as expected, that the nanotubes are behaving as microporous adsorbents. In the case of the experimental isotherm the steep rise at low relative pressures also indicates the presence of micropores. From the average bundle size and tube diameter [8], it is estimated that an average bundle contains about 50 nanotubes. Therefore, the specific surface area of the bundles is $\sim 235 \text{ m}^2 \text{ g}^{-1}$. The measured BET surface area of the nanotube sample is $302 \text{ m}^2 \text{ g}^{-1}$ [8], larger than the estimated bundle surface area. It is believed that the majority of the SWCNT are closed, but it is possible that a small proportion are open so that they may make a contribution to the adsorption at low relative pressures. In addition, the impurities in the sample may also contribute to the BET surface area. The steep rise in adsorption at high relative pressures probably reflects condensation in the sample, possibly between the nanotube bundles. We are carrying out further simulations and experimental measurements of adsorption in carbon nanotubes to clarify these points.

CONCLUSIONS

Molecular simulations of adsorption of hydrogen at 298 K and 70 bar in ordered arrays of SWCNT show that significant storage occurs. However, this is $\sim 70\%$ of the DOE target capacity of 6.5 wt%. Experimental measurements of gravimetric hydrogen capacity at ambient temperatures and ~ 100 bar for carbon nanotube samples are similar to those predicted from simulations. The simulations also show that the target gravimetric hydrogen capacity can be achieved with ordered arrays of nanotubes at 77 K and 70 bar with a wide range of diameters and spacings. Experimental measurements of hydrogen capacity under similar conditions lie within the range predicted from simulations, but at $\sim 25\%$ of the predicted maximum capacity. Simulated and experimental measurements of nitrogen adsorption at 77 K on SWCNT both show some evidence for microporous adsorption. Also, the experimental isotherms show evidence for

capillary condensation at high relative pressures, possibly occurring between bundles of nanotubes.

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