HYDROGEN STORAGE IN CARBON NANOTUBE ARRAYS

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Introduction

Recently, there has been a resurgence of interest in the potential of carbon materials as hydrogen storage media following claims that single wall carbon nanotubes, SWCNT [1], and certain types of vapour grown carbon fibres [2] may have high hydrogen storage capacities at room temperature. Selective oxidation of carbon nanotubes can remove end caps to reveal their hollow centres that are cylindrical, microporous or mesoporous adsorption spaces. The interstitial spaces in arrays of nanotubes, bounded by external tube surfaces, are of nanometric dimensions and therefore may also contribute to adsorptive capacity. Accordingly, both adsorption inside and between nanotubes (endohedral and exhohedral adsorption) should be considered in arrays of nanotubes. Although a few papers have been published on simulation studies of hydrogen storage in carbon nanotubes [3-4], no systematic work has been presented. Here, we report some results from our systematic grand canonical Monte Carlo, GCEMC, molecular simulations of hydrogen adsorption in arrays of SWCNT.

Models and Simulations

Adsorption potentials for gas-solid interactions for endohedral and exohedral adsorption in isolated SWCNT were derived from Lennard-Jones (LJ) 12:6 pair potentials and a model of SWCNT in which the carbon atoms are considered to be uniformly distributed over the whole nanotube wall. Values used for LJ energy and distance parameters, ε and σ, for gas-gas (gg) and gas-solid (gs) interactions are $\varepsilon_{gg} / k_B = 41.5$ K, $\sigma_{gg} = 2.96$ Å, and $\varepsilon_{gs} / k_B = 35.4$ K, $\sigma_{gs} = 3.19$ Å, where k_B is Boltzmann's constant. In the model array, either open or closed ended SWCNT of diameter D are placed at the corners of squares (square array) or triangles (hexagonal array) with sides of D + G, where G is the separation between adjacent nanotubes. We employed a GCEMC molecular simulation method modified to account for adsorption in large arrays of cylindrical rather than slit-shaped spaces, using the potential described above. The volumetric capacities at different pressures p, V(p) (volume of gas at STP / volume of solid), were calculated from equilibrium amounts adsorbed derived from the simulations; delivered capacities were calculated using the equation $V_{del} = V(70 \text{ bar}) - V(1 \text{ bar})$.

Results and Discussion

A hydrogen-fuelled vehicle with a 500 km range requires a recoverable storage density of 62 kg (H_2) m^{-3} [1], equivalent to a delivered volumetric capacity, V_{del}, of 695 (STP) v/v. Simulations of endohedral adsorption of hydrogen in SWCNT at ambient temperatures yield low values of delivered capacity. For example, values of V_{del} in the range 63-64 v/v were obtained for adsorption of hydrogen at 298 K in SWCNT with D in the range 11-15 Å. This is about 10% of the target capacity and similar to the volumetric delivered capacity for hydrogen gas compressed to 70 bar at 298 K. Thus, only the results at 77 K are presented here.

The delivered hydrogen capacity as a function of D and G for square arrays of closed SWCNT is shown in Figure 1. The capacities are all lower than the target, except in arrays consisting of the smallest tubes with sufficiently large tube separations, which are very close to the target. Generally, V_{del} decreases with D at large G and increases with G at all D. This is because in closed tube arrays only interstitial space is available to hydrogen molecules and this space increases with G. The minimum of delivered capacity was found at D=10Å and G=4Å. In this configuration, the interstitial space is just wide enough to hold one row of hydrogen molecules. The potential inside this space is so strong that even at 1 bar it is almost full of molecules and the number of molecules adsorbed will not change very much by increasing pressure, resulting in the lowest capacity. The optimal configuration is D=6Å, G=20Å with V_{del} = 689 (STP) v/v.

Opening tubes can improve the delivered capacity of square arrays, especially for arrays with small G and large D, where the increase in delivered capacity can be as high as five times (cf. Figures 1, 2). This is because endohedral adsorption in such systems is more important. However, the maximum does not change much and the

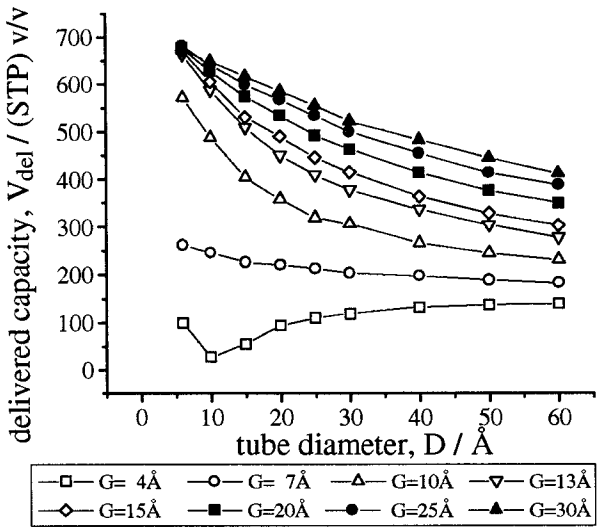

Figure 1. Delivered hydrogen capacities of closed SWCNT square arrays at 77 K.

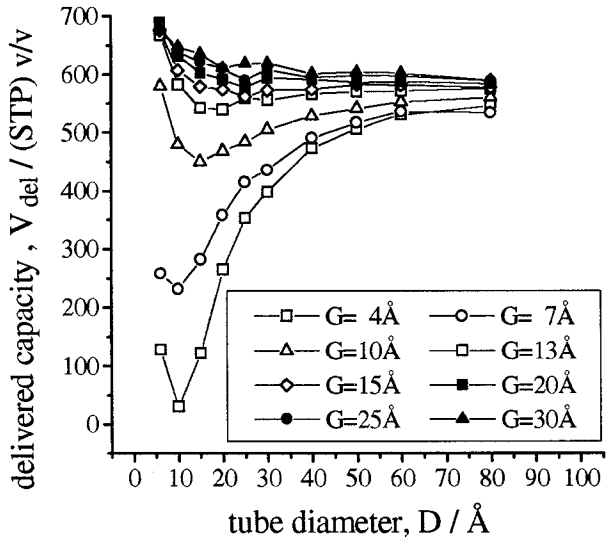

Figure 2. Delivered hydrogen capacities of open SWCNT square arrays at 77 K.

optimal configuration remains the same. It is interesting that in the optimal configuration, endohedral adsorption makes no contribution to the capacity. The maximum delivered capacity is solely due to the contribution of interstitial adsorption. Another feature is that when the tube diameters are sufficiently large, all delivered capacities are between 500~600 (STP) v/v and hardly change with either D or G.

In hexagonal arrays, the delivered capacities as functions of D and G are similar to square arrays, cf. Figures 2, 3. There is no significant difference between

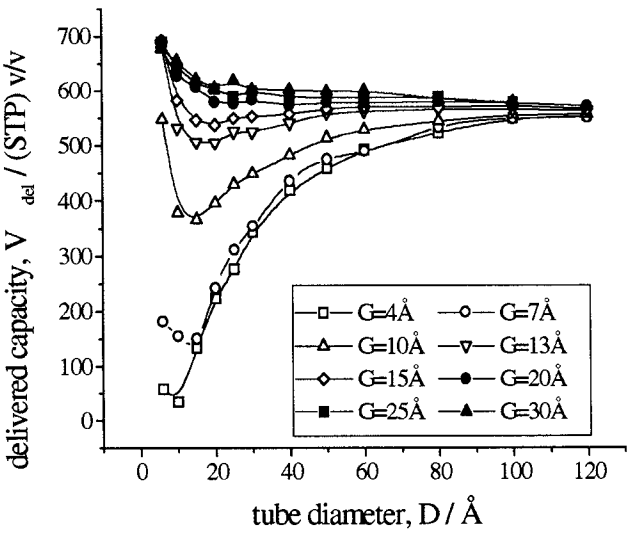

Figure 3. Delivered hydrogen capacity of open SWCNT hexagonal arrays at 77 K.

the two systems. However, the optimal configuration is D=6 Å and G=15 Å with the maximum capacity of 692 (STP) v/v. This maximum is a little higher than that of square arrays and is very close to the target.

Conclusions

Molecular simulations of adsorption of H_2 at 77 K in square and hexagonal arrays of single wall carbon nanotubes show that delivered capacities close to the target of 695 (STP) v/v may be achievable for arrays of small tubes with sufficiently large separations. The highest capacities are similar for closed or open tubes and square or hexagonal arrays. Opening tubes only improves hydrogen capacities of large tubes and/or arrays with small separations. A delivered capacity between 500~600 (STP) v/v should be achievable with larger SWCNT arrays. However, as quantum effects were not considered in this study, the delivered hydrogen capacity may be a few per cent lower than has been shown here.

References

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