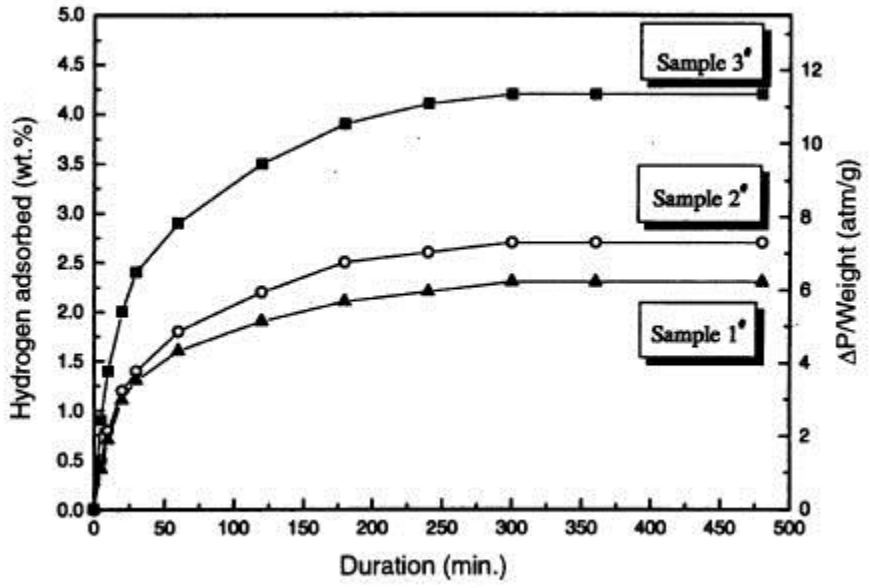
HYDROGENATION OF CARBON NANOTUBES

Hydrogen storage in carbon nanotubes occurs by two mechanisms: physisorption and chemisorption[8]. The former is characterized by condensation of H2 molecules inside or between CNTs. Chemisorption, in contrast, uses a catalyst to dissociate the molecular hydrogen and allow it to bond with some of the unsaturated carbon bonds along the tube.

Physisorption

Early research into potential means of hydrogen storage in CNTs focused on physisorption as the primary storage mechanism. The initial studies were done on H2 adsorption of untreated carbon soot, which contained only 0.1-0.2 weight % SWNTs, it was found that this amorphous carbon was able to absorb 0.01 % H2 by weight. From these results it was extrapolated that a sample of highly pure SWNTs could reach a 5 to 10 % weight adsorptivity and thus the overall goal of 6.5 weight % put forth by the DOE[5].

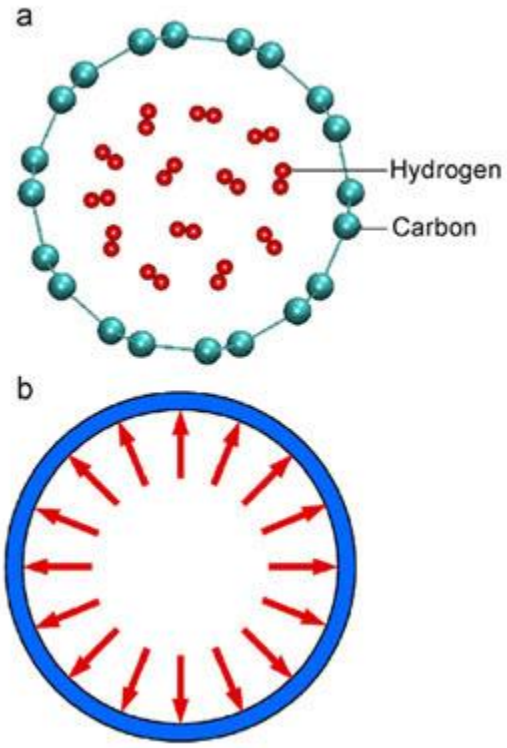


Following up on these findings, others performed similar research into various conditions under which to improve the percent of hydrogen uptake, and while insightful these were done under unrealistic conditions; such as near cryogenic temperatures or extremely high pressures.

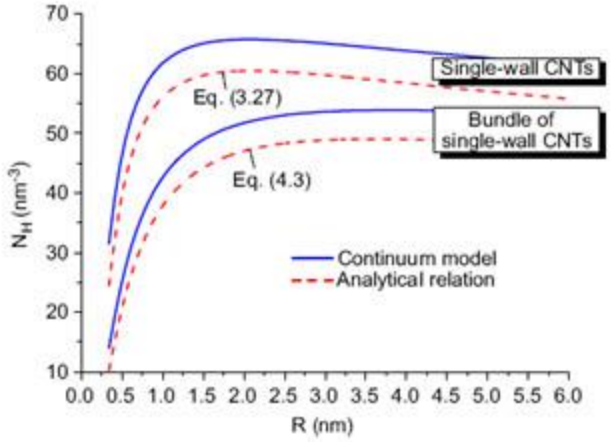
The most realistic take on the ability of CNTs to absorb H2, through physisorption, was performed by C. Lui et al. [6]. Here the viability of CNTs was examined at room temperature and only modest pressures ≈10-12MPa. Through the use of hydrogen arc-discharge, three samples of carbon nanotubes were fabricated. Samples 2

and 3 underwent a pre-treatment process, which involved soaking in a solution of HCl acid. Following this, sample 3 was then heat treated in a vacuum. The results of hydrogen absorption can be seen the figure to the right[6].

The purpose of the acid bath was to remove all traces of the catalysts. This had little overall effect in increase H2 storage potential. The greater gain was found by the heating of sample 3 in a vacuum which evaporated any and all organic compounds that had formed of the surfaces of the CNT, thus demonstrating the need for clean and unobstructed surface interactions between hydrogen and the carbon atoms of the nanotubes. Though this showed a potential for hydrogen storage, the results were still far from ideal and made evident the inherent limitation of physisorption.



Attempts to model physisorption have lead to a study comparing analytical atomic modeling (AFEM) with a continuum model, in which the carbon tube is equated to a pressure vessel and the hydrogen stored is equated to an internal pressure. The figure to the left, from Chen et al in 2008[4], shows the analogy between the two methods (where (a) is AEFM, and (b) is the continuum model).



This study showed hope that CNTs could achieve the desired 18.7 molecules per nm3 as mentioned earlier in this article. The figure above, from the same study[4] shows a correlation between nanotube radius and simulated storage capacity.

Chemisorption

Density function modeling indicates that chemisorption holds more promise than physisorption for percent weight hydrogen[8]. C-H bond strength prediction indicates that it is theoretically possible to release the C-H bonds at STP. The specific means by which to do so are still out of our reach technologically, though Nikitin et al [8] predict that an appropriate metal catalyst and a precisely calculated CNT diameter should be able to accomplish this. Under laboratory conditions, this team achieved 5.1 ± 1.2 wt% H2 storage at STP.

Through alkali doping, chemisorption in carbon nanotubes can be increased a good deal under laboratory conditions, though it must be done at higher temperatures [3]. Lithium doping at 650 K reached a storage capacity of 20 wt% H2. Potassium doping at much lower temperatures (about room temperature) can yield 14 wt% H2, though the resulting hydrogen-rich tubes are unstable and prone to spontaneous combustion. Both processes involved 2 hours of hydrogen uptake, which is not practical for vehicle use [3].

A method of chemisorption was also proposed by researchers at Penn State, in which clusters of metal nanoparticles are chemically affixed to the surface of carbon nanotubes. These metal clusters, in this case platinum, act as doorways into the surface of the tubes. Some of the hydrogen is absorbed by the metal, converting them to metal hydrides, while the bulk is absorbed into the CNT where it adheres to the walls. Conveniently this increases the temperature at which the nanotubes can absorb hydrogen from near cryogenic temperatures to those temperatures more convenient for implementation. The temperature is dependent exclusively on the selection of metal used, thus there are possibilities to provide a range of functionality. Nickel and magnesium were other alternatives which were considered due to the heavy weight of platinum. Still a

major concern with this method is the cost of the nanotubes themselves, which were roughly $25,000 per pound[8].

Source : http://me1065.wikidot.com/hydrogen-storage-in-carbon-nanotubes