Hydrogen Storage in Carbon Nanotubes
For the purposes of pollution free vehicular fuel cells and secondary batteries

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Abstract:

Herein are discussed briefly the mechanisms theorized and supported by experiments or calculations pertaining the adsorption of hydrogen into carbon nanotubes. Affects of tube size, pressure, and temperature on hydrogen uptake in carbon nanotubes are also discussed. In particular, single-walled carbon nanotubes are discussed because of their promising hydrogen adsorption characteristics. Also, alkali-doping of carbon nanotubes and its benefits are discussed.

Introduction:

Today there is a growing need for alternative and clean fuels that can replace our growing dependence on fossil fuels for vehicular propulsion. One such fuel is hydrogen, the most abundant element in the universe. It also creates no pollutants when burned as a fuel. However, due to its explosiveness, an efficient storage method is needed for hydrogen to become a replacement for gasoline. Four main technologies are being explored for hydrogen storage: compressed gas, liquefaction metal hydrides, and physisorption [4]. It has been claimed that physisorption is the most promising hydrogen storage method for meeting the goals of the DOE Hydrogen Plan for fuel cell powered vehicles [4]. Carbon nanotubes are a possible solution to the storage of hydrogen in fuel cell powered vehicles due to their low density, high strength, and hydrogen adsorption characteristics. Current work surrounding hydrogen storage in carbon nanotubes is aimed at investigating the mechanisms of hydrogen adsorption into carbon nanotubes.

It has been proposed that hydrogen can be adsorbed by carbon nanotubes in two ways, physisorption and chemisorption. Physisorption of hydrogen occurs in carbon nanotubes by trapping hydrogen molecules inside the cylindrical structure of the nanotube or by trapping hydrogen in the interstitial sites between nanotubes. M. Rzepka et al.3 used a grand canonical ensemble Monte Carlo program (GCEMC) to study the influence of geometry, size, storage pressure, and temperature on the hydrogen uptake of carbon nanotubes. The GCEMC is described briefly by M. Rzepka et al.3 and in more detail by one of the references cited in their paper. Rzepka et al.3 found a maximum volumetric storage capacity at 300 K and 10 MPa for a pore size of about d = 7 ≈ [3]. The peak value for the volumetric storage capacity is 12.5 kg/m3 corresponding to a gravimetric storage capacity of 0.5 wt % [3]. In this case, one hydrogen molecule fits exactly in the tube core leading to strong capillary adsorption forces [3]. For larger pore sizes d the volumetric storage capacity decreases asymptotically to the density of the pure compressed gas (7.6 kg/m3) while the gravimetric storage capacity, i.e., the total amount of stored hydrogen compared to the pore mass, increases linearly with d [3]. At d = 7 ≈ and 10 MPa and low temperatures the total amount of gas inside the tube saturates at a value corresponding to a particle density inside the accessible tube volume exceeding the density of liquid hydrogen [3]. 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 [3]. At 77 K and d = 7 ≈ increasing storage pressure was found to increase the hydrogen uptake in carbon nanotubes.

Chemisorption occurs by hydrogen dissociation and reaction with carbon, in the case of carbon nanotubes. Liu et al. noticed that, after treating carbon nanotubes with hydrogen gas under high pressure, there was residual H2 during the desorption cycle that could be released only upon heating to temperatures above 400 K [7]. A recent experiment using high purity single-walled nanotubes found a first order phase transition under high H2 pressure, similar to the hydride phase observed in metal-hydrogen systems [2]. Siu-Pang Chan et al. discuss the interaction between a hydrogen molecule with a single carbon nanotube, as in gas phase conditions, and with a solid of carbon nanotube arrays under high pressure [1]. They found chemical adsorption to be unfeasible under gas phase conditions, but possible in the solid of a carbon nanotube array. The dissociative chemisorption of hydrogen molecules in the interstitial region on the exterior of carbon nanotubes is made possible by the high pressure environment in the storage experiment [1]. Siu-Pang Chan et al. first modeled the interaction between a hydrogen molecule with a single (6,6) armchair carbon nanotube [1]. In the case of an incoming hydrogen molecule, with the HóH bond perpendicular to the carbon nanotube, there is no reaction only deformation of the nanotube [1]. Through calculations, Siu-Pang Chan et al. found that the formation of an HóC bond by this method is not enough to compensate the breaking of the HóH bond [1]. In the case of an incoming hydrogen molecule, with the HóH bond parallel to a CóC bond, there was also no reaction only deformation of the nanotube [1]. This also occurred with other trajectories of the hydrogen molecule [1]. This indicates that a direct reaction between an H2 molecule and a single nanotube would indeed be very difficult [1]. In contrast, the solid phase, composed of bundles of carbon nanotubes, provides a unique environment that is dependent on the external pressure and makes it possible for the H2 dissociative chemisorption on carbon nanotubes [1]. The key difference between the solid phase and the gas phase is the presence of many carbon nanotubes in a tightly packed array in solid [1]. For a concerted dissociative addition process in the gas phase, the H2 is pushed directly towards the wall of a carbon nanotube and the resulting van der Waals repulsion is too strong to overcome [1]. In solid, the incoming H2 is pushed towards the interstitial region between two neighboring nanotubes [1]. The van der Waals repulsion is reduced, whole the two nanotubes and the H2 molecule are lined up optimally for converted H2 dissociation [1]. The need for high pressure comes from the carbon-carbon distance between two nanotubes, which at ambient pressure was calculated to be 3.8 ≈ [1]. However, this is small enough for a H2 molecule to pass through without a reaction [1]. External pressure helps the chemisorption process by compressing the solid and decreasing the carbon-carbon distance between two adjacent nanotubes to 2.6 ≈ [1]. The pressure also decreases the elasticity of the nanotubes and forces the carbon atoms into bonding position with the incoming H2 molecules [1].

Of the various types of carbon nanotubes producible, single-walled nanotubes (SWNT) are the simplest, being but a single graphite plane rolled into a thin tube [2]. SWNTs self-organize into ìropesî that consist of hundreds of aligned SWNTs on a twodimensional triangular lattice, with an intertube spacing (van der Waals gap) of approximately 3.2 ≈ [4]. SWNTs have large theoretical surface areas that are on the order of those for high-surface area activated carbons [4]. Activated carbons have been shown to have very high hydrogen adsorption capabilities, higher than those of carbon nanotubes in many cases (see ref. 1). Hydrogen can be stored in bundles of SWNTs, where H2 molecules are physisorbed at the exterior surfaces of SWNTs of interstitial spaces between SWNTs separating the intertube distances, under high pressure of hydrogen gas [5]. At low pressure adsorption of hydrogen on SWNT material saturates like that of the saran carbon, scaled by the surface area of the ropes [2]. At pressures above 40 bar, however, the isotherms indicate that the SWNT material undergoes a transition to a new state of hydrogen coverage [2]. From the large observed H/C ratio at high pressures, it was deduced, by Y. Ye et al., that the surface area would have to increase by about an order of magnitude [2]. This is consistent with the hydrogen permeating into the ropes, separating them into individual SWNTs with full exposure of their outer and perhaps inner surfaces, and physisorbing onto the carbon surfaces [2]. This high density phase must involve tube decohesion, since the hydrogen coverage is high and the attractive van der Waals and exchange forces are attenuated when the tubes are separated by short distances [2]. The thermodynamic driving force for this tube decohesion is the high chemical potential of the hydrogen gas at high pressure [2]. The hydrogen molecules that adsorb on the surface of the SWNTs undergo a decrease in chemical potential [2]. The equality of chemical potential in two-phase equilibrium requires the reduction of the chemical potential of hydrogen gas in the high capacity phase to be equal to the loss of van der Waals cohesive energy [2].

When hydrogen adsorbs to a SWNT material, there are different geometries possible. During chemisorption the hydrogen ions will exothermically adsorb to the top sites of carbon atoms on the tube wall, forming an arch-type geometry, essentially hydrogen atoms bonded to every carbon atom on the outside of the tube wall [5]. This enhances sp3-like hybridizations in the tube and expands the nanotube diameter to 7.78 ≈, from the initial diameter of 6.88 ≈ [5]. Another geometry, where hydrogen atoms are bonded alternatively at the exterior and interior of the nanotube, is called zigzag-type [5]. This geometry is more stable due to the minimization of the strains on the CóC bonds, resulting in less expansion of the average diameter (7.13 ≈) [5]. Another stable geometry occurs when molecular hydrogen is stored in the empty space inside a carbon nanotube [5]. It is expected that larger tube diameters will increase hydrogen storage capacity in a linear manner [5]. Excessive hydrogen storage will result in large repulsive energies and eventually breakdown the tube wall [6]. S. M. Lee et al. conclude that these repulsive energies determine the maximum storage capacity of hydrogens inside nanotubes and the stability of the tubes [6]. To estimate the maximum storage capacity, they assume the hydrogen density (nH/volume) to be nearly constant inside the tube [6]. The volume and the number of the hydrogen atoms increase square of the radius, whereas the number of carbon atoms increases linearly with the radius [6]. Therefore, they expect hydrogen storage to be linearly proportional to the radius or diameter [6].

Another area under investigation is the doping of carbon nanotubes with alkali-metals. Chen et al.8 has reported high H2 uptake of 20 and 14 % can be achieved for Li-doped and K-doped multi-walled carbon nanotubes (MWNTs) in milligram quantities, respectively, under ambient pressure [7]. The K-doped MWNTs can adsorb H2 at room temperature, but they are chemically unstable, whereas the Li-doped MWNTs are chemically stable, but require elevated temperatures (473 to 673 K) for maximum adsorption and desorption of H2 [7]. Chen et al. observed the formation of LiH species before CóH formation by Fourier transform infrared spectroscopy (FTIR) [8]. This suggests that Li may act as a catalytic active center for the H2 ñ dissociative adsorption [8]. The dissociated hydrogen atoms may spill over from Li sites to the carbon network, and finally become bonded to carbon atoms [8].

Discussion:

Efficient hydrogen storage in carbon nanotubes requires control of tube size, pressure, and temperature. With current technology it is possible to obtain solid carbon nanotubes with small distributions of tube size. Pressure and temperature remain as the two main control factors that need to be addressed. Very good hydrogen adsorption in carbon nanotubes has been obtained at temperatures below 100 K and peaking at temperatures between 150 and 200 K. However, these temperatures are not economically feasible for fuel cells and secondary batteries. On the other hand, at room temperature hydrogen adsorption can be increased by increasing the storage pressure. This method of increasing hydrogen adsorption is feasible and possible at ambient temperature. Volumetric storage capacities can reach approximately 17 % at a pressure of 30 MPa and temperature of 300 K [3]. This storage capacity is well above the goals of the DOE Hydrogen Plan. Single-walled carbon nanotubes offer better adsorption properties than that of other carbon nanotubes because of their maximum in surface area. Because they can now be produced with such a low distribution of tube size, they provide a good foundation for future research into the application of carbon nanotubes for hydrogen fuel storage. Doping with lithium and potassium have been shown to dramatically improve the hydrogen storage capabilities of carbon nanotubes at ambient conditions. Research into this area could lead to very efficient and affordable fuel cells that would be applicable to the automotive industry.

Conclusions:

Carbon nanotubes are a promising material for use in fuel cells and hydrogen storage. However, all mechanisms and condition of hydrogen adsorption onto carbon nanotubes are not yet clearly understood. At this point it is not economically feasible to produce fuel cells utilizing carbon nanotubes, but results indicate that they may not be far away. The main areas of research needed to advance this material into widespread use or the trash can, consist of tube size, doping agents, temperature affects on hydrogen adsorption and desorption, and the affects of pressure on hydrogen adsorption and desorption.

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