Hydrogen storage in carbon nanotubes is a recent topic of research and may be an important step towards making mobile hydrogen storage feasible.

Background

Significance of Mobile Hydrogen Storage

It is well-established that pure hydrogen has a much larger energy density (per unit mass) than typical hydrocarbon fuels – 2.6 times more than gasoline, in fact[7]. For a 500 km range, a vehicle would require only 3.1 kg of H2 [5]. The problem is the energy density per unit volume. For the same amount of energy, about four times the volume of hydrogen would be required compared with gasoline[7]. This is fine for stationary applications, but the large space occupied is problematic for mobile applications. It follows that for hydrogen fuel cell vehicles to become prominent, the priority must be in compact and safe on-board hydrogen storage.

Existing Methods of Storage & Associated Problems

Currently, five primary technologies exist that hold promise for mobile hydrogen storage [1]:

1. Compressed H2 gas is the simplest. It can be done at ambient temperature, and in- and out-flow are simple. The density, however, is low compared to other methods.
2. Metal hydride storage involves powdered metals that absorb hydrogen under high pressures (~1000 psia). Heat is produced upon insertion. With pressure release and applied heat, the process is reversed. A major problem is the weight of the absorbing material – a tank’s mass would be 592 kg compared to the 80 kg of a comparable compressed H2 gas tank.

3. Liquid H2 storage is just what it sounds like. The hydrogen storage itself has very high density, but hydrogen boils at about -253°C. From 25% to 45% of the stored energy is required to liquefy the H2 and maintain this low temperature (else the hydrogen will boil away), and bulky insulation is needed.

4. Sponge iron can be treated with steam to cause rapid oxidation, which gives off hydrogen as a byproduct. The iron itself can be considered a consumable fuel – once the entire mass of it has rusted, it is replaced with fresh iron. The steam itself, of course, requires energy to produce (the process occurs at 250°C).

5. Carbon absorption is the newest field of hydrogen storage. Under pressure, hydrogen will bond with porous carbon materials such as nanotubes.

The inherency of the problem is clear: mobile hydrogen storage is currently not competitive with hydrocarbon fuels, and it must become so in order for this potential environmentally life-saving technology to be realized on a great scale. A significant standard of measuring the quality of a hydrogen storage scheme is what percent of the entire system’s weight is recoverable hydrogen:

(1) \[
\text{wt}\% \text{H}_2 = \frac{\text{wt H}_2}{\text{wt H}_2 + \text{wt matrix} + \text{wt equipment}}
\]

The US Department of Energy has issued goals for mobile hydrogen storage research, the most characteristic of which are 6.5 weight percent H2 \[^5\] and 62 kg of H2 per m3 (18.7 molecules per nm3) \[^4\]. Carbon nanotubes may well be a way of efficiently meeting this goal.

**Carbon Nanotubes**

Carbon nanotubes (CNTs) essentially consist of sheets of graphite rolled into seamless tubes and capped at the ends. There are two forms CNTs take: single-walled and multi-walled. As the name implies, single-walled nanotubes (SWNT) are composed of a single sheet of graphite; a diameter range of 0.4 to > 3nm is common\[^2\]. Multiwalled nanotubes (MWNT) are composed of several sheets, arranged concentrically in increasingly larger diameters with diameters in the range of 1.4 to 100 nm. Due to their diminutive dimensions, CNTs have unique physical and electrical properties. These include ultra high thermal conductivities (>3000 W/m-K), a Young’s modulus of \( \approx 0.64 \) TPa, and the elastic ability to extend \( \approx 5.8\% \) of its original length before breaking\[^2\]. More appealing still is the disproportionately large surface area to volume that these materials possess, for this allows for a greater potential of interactions, whether they be physical or chemical in
nature. Also, consider that their dimensions are relative to those of atoms and molecules. This increases the strength that these interactions have between one another, particularly from Van der Waals forces.

**Production**

In order for CNTs to be a viable solution to the problem of mobile hydrogen storage, they must be both easy and cost-effective to produce. Currently CNTs are not inexpensive to produce, especially when the need for specific control over dimensions and purity of the samples is necessary.

The production of CNTs is achieved in three distinct methods:

1. Arc discharge
2. Laser ablation
3. Chemical vapor deposition.

Arc discharge is the most basic of these and involves the use of two graphite electrodes between which a high current is passed. This produces a carbon vapor, in which CNTs form. While arc discharge is fairly inexpensive, it tends to produce samples of low purity. Also it requires special precautions due to the high amperage (100 A) and high temperatures (2000-3000°C)[9].

Laser ablation, utilizes a laser directed at a graphite target which is then heated to roughly 1200°C. The vapor is sent down stream to condense on a cooled collector. This method has the benefit of producing high quality CNTs, but this is offset by the high initial costs and low output[9].
Chemical vapor deposition (CVD), the last method to be discussed here, probably has the greatest potential for use in industry of those mentioned. In CVD, a heated chamber is injected with some carbon based gas, carbon monoxide for instance. Located inside the chamber is a substrate, on top of which a matrix of metal catalysts particles is distributed, when the gas is flows through the chamber the carbon disassociates and begins forming vertical structures on the aforementioned metal particles. This takes place at a relatively low temperature of 700-800°C, as opposed to the first two methods. Also, it is far easier to implement this method in terms of large scale production, though the quality of this method leaves something to be desired[9].

The image above shows the growth of CNT in which the catalyst is elevated by the tube growth[7].

Impurity

Though impurities are often a problem, they can be removed. This plays an important role in hydrogen absorption as NTs consisting of uniform carbon are shown to have higher rates of absorption [6]. These impurities are often generated by the catalysts used in the synthesis of the CNTs, but can be removed by means such as pretreatment of the sample in an acidic bath or by heating in a vacuum at high temperature for short durations. Though any additional processes the nanotubes must undergo only accrues further expenses and thus puts the ultimate goal of affordable nanotubes further from reach[9].