# Carbon Nanotubes–A Successful Hydrogen Storage Medium

Vijaya Ilango and Avika Gupta

Abstract—Hydrogen fuel is a zero-emission fuel which uses electrochemical cells or combustion in internal engines, to power vehicles and electric devices. Methods of hydrogen storage for subsequent use span many approaches, including high pressures, cryogenics and chemical compounds that reversibly release H_2 upon heating. Most research into hydrogen storage is focused on storing hydrogen as a lightweight, compact energy carrier for mobile applications. With the accelerating demand for cleaner and more efficient energy sources, hydrogen research has attracted more attention in the scientific community. Until now, full implementation of a hydrogen-based energy system has been hindered in part by the challenge of storing hydrogen gas, especially onboard an automobile. New techniques being researched may soon make hydrogen storage more compact, safe and efficient. In this overview, few hydrogen storage methods and mechanism of hydrogen uptake in carbon nanotubes are summarized.

Keywords—Carbon nanotubes, Chemisorption, Hydrogen storage, Physisorption.

I. INTRODUCTION

HYDROGEN is a convenient, safe, versatile fuel source that can be easily converted to a desired form of energy without releasing harmful emissions [1]. Hydrogen is the ideal fuel for the future since it significantly reduces the greenhouse gas emissions, reduces the global dependence on fossil fuels and increases the efficiency of the energy conversion process for both internal combustion engines and proton exchange membrane fuel cells [2], [3]. Hydrogen used in the fuel cell directly converts the chemical energy of hydrogen into water, electricity and heat [4] as represented by

$$H_2+ ½ O_2 \rightarrow water + electricity + heat$$
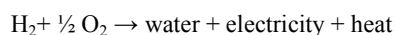
Hydrogen storage cuts across both hydrogen production and hydrogen applications and thus assumes a critical role in initiating a hydrogen economy [5]-[8]. It is expected that any large-scale hydrogen distribution system should address the problem of bulk storage, to provide a buffer between production facilities and fluctuations in demand. Low-cost and efficient bulk storage techniques are a major research goal. One can store hydrogen as either a gas or a liquid.

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II. HYDROGEN STORAGE METHODS

The most widely studied options for storing gaseous hydrogen are underground caverns and depleted underground natural gas formations. Although hydrogen is more prone to leak than most other gases, leakage is shown not to be a problem for these techniques. For example, town gas mixture containing hydrogen has been stored successfully in a cavern in France and helium, which is even more leak-prone than hydrogen, has been stored in a depleted natural gas field near Amarillo, Texas [9].

A. Liquid Hydrogen

Hydrogen becomes liquid at about -253°C at atmospheric pressure and can be stored and transported in this state. A major part of the technical hydrogen is in fact delivered in liquefied form by trailers carrying more than three tons of liquefied hydrogen [10].

B. Compressed Hydrogen Gas

Hydrogen gas can be compressed and stored in storage tanks that can hold it at the required pressure. The tanks can either be made with steel, aluminum or copper alloys that may be encased in fibreglass The steel tanks are most often used for static applications where weight is not a hindrance as the steel tanks tend to be heavy [11]. High pressure tanks also appear in some test automobiles but safety and space remain significant concerns. The tanks tend to be big and bulky with the ongoing concern regarding a leak.

C. Metal Hydride

Metal hydrides, such as MgH_2, $NaAlH_4$, $LiAlH_4$, LiH, $LaNi_5H_6$, $TiFeH_2$ and palladium hydride, with varying degrees of efficiency, can be used as a storage medium for hydrogen, often reversibly [12], [13]. Some are easy-to-fuel liquids at ambient temperature and pressure; others are solids which could be turned into pellets. These materials have good energy density by volume, although their energy density by weight is often worse than the leading hydrocarbon fuels.

D. Carbohydrates

Carbohydrates (polymeric $C_6H_{10}O_5$) release H_2 in a bio reformer mediated by the enzyme cocktail—cell-free synthetic pathway biotransformation [14]. Carbohydrate provides high hydrogen storage densities as a liquid with mild pressurization and cryogenic constraints: It can also be stored as a solid power. Carbohydrate is the most abundant renewable bioresource in the world.

E. Activated Carbon

The hydrogen storage properties of high surface area "activated" carbons have been extensively studied [15]. However, activated carbons are ineffective in storing hydrogen because only a small fraction of the pores in the typically wide pore-size distribution are small enough to interact strongly with hydrogen molecules at room temperatures and moderate pressures. Recently, many new carbon nanostructured absorbents have been produced including graphite nanofibers and carbon multi-wall and single-wall nanotubes. The United States Department of energy (DOE) has fixed two targets for hydrogen storage solutions applied to automotive transportation [16]. The first target requires a ratio of *hydrogen weight / tank weight* that is superior to 0.065 (6.5% weight). This target limits the weight of the tank. The second target requires a hydrogen volumetric density higher than 62 kg/m^3 in order to limit the volume of the tank. Fig. 1 shows the commercially available solutions. Each one is compared to the DOE targets. To satisfy both targets, a solution must be located in the grey region of the graph.
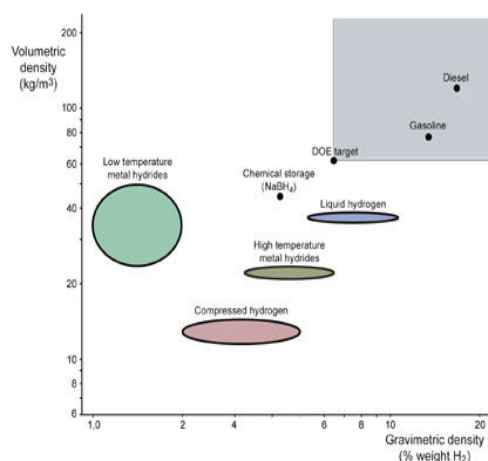

Fig. 1 Status of hydrogen storage systems [16]

III. History of Carbon Nanotubes

In 1985 [17] Kroto and Smalley discovered Fullerene, one of carbon allotropes (a cluster of 60 carbon atoms: C$_{60}$. Later on in 1991, Dr. Iijima discovered this thin and long straw-shaped carbon Nanotubes during a TEM analysis of carbon clusters. This discovery was published in Nature for the first time. The Nanotubes range in length from a few tens of nanometers to several microns and outer diameter from about 2.5nm to 30 nm. A carbon atom in Nanotubes forms a hexagonal honeycomb lattice of sp2 bond with 3 other carbon atoms. As the inner diameters of the tubes extremely thin down to about several nanometers, the tubes are called Nanotubes. Carbon nanotubes occur as two types: multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes [18] (SWNTs), as illustrated in Fig. 2. MWNTs consist of several coaxial cylinders, each made of a single graphene sheet surrounding a hollow core. The most common

techniques for their production are electric arc [19] and chemical vapor deposition (CVD) [20], [21]. The growth of MWNTs may require a catalyst. The outer diameter of MWNTs ranges from 2 to 100nm, while the inner diameter is in the range of 1–3nm, and their length is 1 to several μm [22].
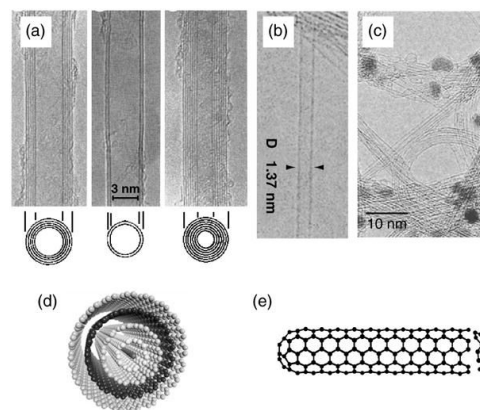

Fig. 2 TEM micrographs of (a) MWNTs and (b) SWNTs [18], [19] (c) TEM micrograph showing bundles of SWNTs, The dark spots are catalyst particles used for nanotube growth. (d) Schematics of MWNT (e) Schematics of SWNT

IV. Mechanism of Hydrogen Storage in Carbon Nanotubes

Hydrogen storage in carbon nanotubes occurs by two mechanisms: physisorption and chemisorptions [23]. The former is characterized by condensation of H$_2$ 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. Early research into potential means of hydrogen storage in CNTs focused on physisorption as the primary storage mechanism. The initial studies were done on H$_2$ 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% H$_2$ 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 [24].

Following up on these findings, others performed similar research into various conditions 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 H$_2$, through physisorption, was performed by C. Lui et al. [25]. Here the viability of CNTs was examined at room temperature and only modest pressures $\approx$10-12MPa. Through the use of hydrogen arc-discharge, three samples of carbon nanotubes were fabricated. Sample 1 was used as synthesized. Samples 2 and 3 underwent a pre-treatment process, which involved soaking in a solution of HCl. Following this, sample 3 was then heat treated in a vacuum [25].

The purpose of the acid bath was to remove all traces of the catalysts. This had little overall effect in increase H_2 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.

A. Chemisorption

S. P. Chan et al. [26] based on first principles calculations, proposed a mechanism for the dissociative chemisorption of H_2 on carbon nanotubes. The breaking of the H--H bond is concerted with the formation of two C--H bonds on two adjacent carbon nanotubes in solid phase, facilitated by the application of high pressure which shortens the interstitial distance between nanotubes. The process is reversible upon the release of external pressure and could make an important contribution to the observed hydrogen storage capacity of carbon nanotubes. The previously unexplained experimental observations of the direct hydrogenation of fullerenes under high pressure lend further support for such a mechanism. Density function modeling indicates that chemisorption holds more promise than physisorption for percent weight hydrogen. 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. [27] predicted 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% H_2 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 [28]. Lithium doping at 650 K reached a storage capacity of 20 wt% H_2. Potassium doping at much lower temperatures (about room temperature) can yield 14 wt% H_2, 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 [28].

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 [27].

Multi-walled carbon nanotubes (MWNTs) [29] with different mean outer diameters in the range of 13–53nm, synthesized by the catalytic decomposition of hydrocarbons using a floating catalyst method, were purified and pretreated with the same procedure for volumetric hydrogen adsorption / desorption measurements. It was found that the hydrogen storage capacity of the purified and pretreated MWNTs was proportional to their diameter, and that hydrogen in all types of MWNTs measured could not be completely desorbed at room temperature and ambient pressure. A possible mechanism for the above behavior was proposed based on the results of cryogenic nitrogen adsorption analysis and high-resolution transmission electron microscopy observations.

V. CONCLUSION

The mechanism of hydrogen storage in CNTs is not clear yet. Since CNTs possess nanoscaled pore structures and a relatively high specific surface area, it is generally accepted that the physisorbed hydrogen accounts for the major part of the stored hydrogen. Some researchers have reported from experimental investigations that a small amount of chemisorption also took place, the evidence for which was the desorption of hydrogen at higher temperatures [30]. Carbon materials are being heavily investigated because of their promise to offer an economical solution to the challenge of safe storage of large hydrogen quantities. Hydrogen is important as a new source of energy for automotive applications. It is clear that the key challenge in developing this technology is hydrogen storage. Hydrogenation of carbon nanotubes holds promise for the future of mobile hydrogen storage. Moreover, it holds some advantages over other existing methods of hydrogen storage, which have their own impracticalities. Though there are setbacks, research suggests that sufficient storage is theoretically possible. Carbon based systems have received research interest due to their light weight, high surface area and chemical stability. The effect of surface area, pore volume and heat of adsorption on hydrogen uptake can be studied using the low cost montmorillonite and vermiculite clays/incorporated pillared clays and a comparative study can be done with the carbon nanotubes With the talent and unrelenting efforts of today's innovators, hydrogenated carbon nanotubes may someday make hydrogen vehicles more viable and competitive than at present. Hydrogen energy system is expected to progressively replace fossil fuels in future. Hydrogen production, storage and conversion have reached a technological level although plenty of improvements and new discoveries are still possible. The hydrogen storage is often considered as the bottleneck of the renewable energy economy based on the synthetic fuel hydrogen.

and support in facilitating this research.

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