

A REVIEW ON CARBON NANOTUBES FOR HYDROGEN STORAGE

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ABSTRACT

Hydrogen is considered as renewable, and a clean energy carrier and a clean fuel without toxic emission and can easily fuel cells for electricity generation. Hydrogen is highly required for advanced energy conversion systems. One of the potential uses of hydrogen lies in zero emission vehicles powered by a proton exchange membrane fuel cell stack. However, the storage of this substance is considered one of the most important points, therefore this research is focused on the usage of carbon nanotubes. The discovery of high hydrogen storage capacity of carbon nanotubes makes an onboard hydrogen storage system based on carbon nanotubes very promising. In this research, the basic and unique properties of carbon nanotubes are introduced, and the development of synthesis technologies of this novel material is summarized. As well as the unique pore and surface structures of carbon nanotubes are evaluated. Based on the experimental results and theoretical predictions that hydrogen can be effectively adsorbed in carbon nanotubes and after suitable pretreatment, carbon nanotubes may achieve a hydrogen storage capacity higher than 6.5 wt% and 63 kgH₂/m³.

Nevertheless, efforts have to be made to reproduce and verify the hydrogen storage capacity of carbon nanotubes both theoretically and experimentally, to investigate their volumetric capacity and cycling characteristics, to elucidate their adsorption/desorption dynamics, kinetics and mechanism, and finally to clarify the feasibility of carbon nanotubes as a practical onboard hydrogen storage material.

Keywords: Hydrogen, nanomaterials, carbon nanotubes, energy, storage capacity and pollution

INTRODUCTION

The ever fast progress of science and technology accelerates the development of world economy and culture (Noh J. S, et al, 1987). On one hand the start of a new millennium presents human beings with countless opportunities and challenges and as a result, rapidly brings many of us a higher living standard (Veziroglu T. N and Barbir K, 1992).

On the other hand, our world is facing a rapid depletion of natural resources and serious global environmental pollution, mostly due to the overuse of fossil fuels. Nowadays, public concern about the global environmental problems caused by the utilization of fossil fuels and the over dependence of economy on fossil fuels is increasing, and many countries including USA, European Union, Japan, China, etc., are funding in an increasing budget year by year for the searches of possible alternative energy sources to replace fossil fuel. Carbon nanotubes have garnered significant interest due to their promising applications and facile synthesis (Iijima S,1991). This study highlights the applications of CNTs in the field of hydrogen production and storage. Hydrogen energy attracted researchers because of its clean, renewable and sustainable energy with low impact on the environment around the globe (Schwarz J. A,1994). It is expected hydrogen energy systems replace the prevailed fossil fuel in the coming years.

Hydrogen systems exhibit many disadvantages such as production cost and storage aspects (Fan Y. Y,et al,1999). CNTs have the greater capability as support for the manufacture of effectual contrasting in hydrogen production systems (Agarwal R. K,et al,1987). The main focus of this article is their different manufacturing methods along with their models and the purification techniques to obtain the best quality CNTs and then use them in different applications (Veziroglu T. N and Barbir K,1992).

Recently some scientist turned their eyes to hydrogen adsorption in carbonaceous materials with high surface area hoping that the inclusion of porous carbon materials in a hydrogen storage tank can enhance the overall hydrogen storage density by physisorption under certain pressure and temperature condition. In the past ten years, great advances have been made and 3-6 wt% hydrogen adsorption capacities can be obtained for high surface area activated carbons at cryogenic temperatures of liquid nitrogen or lower (Liu C,et al ,1999), but at ambient temperature, activated carbons have very low hydrogen adsorption capacity. More recently, tremendous interest have been aroused by the discovery (Carpentis C,et al,1980)and reproduction of the high hydrogen storage capacity of a novel nonporous carbon material carbon nanotubes.

Hydrogen uptake in Carbon Nanotubes

Activated carbons and activated carbon fibers are considered as good adsorbents, it is due to their high surface area and abundant pore volume, conventional porous (Chambers A,et al ,1998). For the conventional porous carbons, their hydrogen uptake capacity is found to be proportional to their specific surface area and pore



volume, while, regretfully, a high hydrogen adsorption capacity can only be obtained at very low temperatures such as liquid nitrogen temperature, consistent with theoretical calculations. In contrast, in spite of their relatively low specific surface area and small pore volume compared in activated carbons, carbon nanotubes and carbon nanofibers show a surprisingly high hydrogen storage capacity, in the search of reasonable interpretations for this phenomenon, scientists employed different theoretical calculations and simulations. The intentions of the theoretical work are to answer the following important questions.) How do structural characteristics of CNTs influence their physical/chemical hydrogen storage process? (Veziroglu T. N and Barbir K,1992). Where does the adsorption occur, in inner hollow cavities and/or other pore spaces (e.g. inter-tube space and aggregated pores) of CNTs? (Dillon A. C,et al,1997). During the adsorption of hydrogen onto carbon nanotubes, what interaction, chemical or physical, occurs between hydrogen and carbon? (Carpentis C,et al,1980)What is the hydrogen adsorption mechanism of CNTs? (Agarwal R. K,et al,1987)How high can the maximum hydrogen adsorption capacity of CNTs be reached? Simplistic geometric estimate and qualitative discussion since hydrogen molecules at elevated pressure on a solid surface are expected to form a close packed configuration, obtained a simple geometric estimate for close packing capacity of hydrogen molecules above a plane of graphite using purely geometric agreement, which yielded 2.8wt% or 4.1 wt% hydrogen uptake for one layer of hydrogen adsorbed on a single graphene layer.

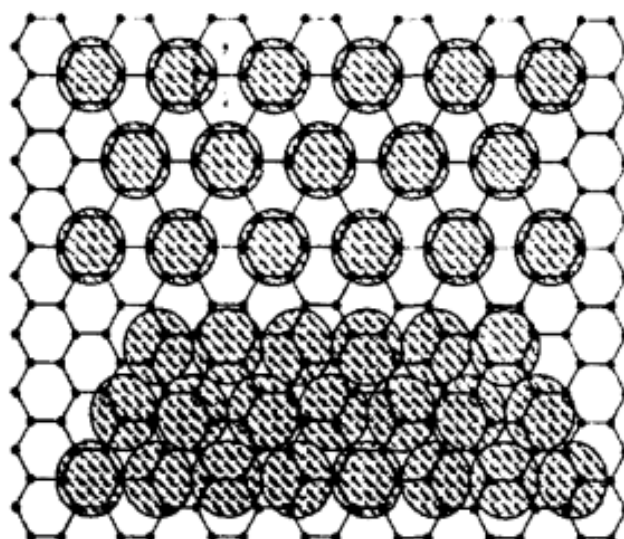


Figure 1. related density of a commensurate and an incommensurate monolayer of H₂ on a graphite surface (Schwarz J. A,1994).

As for carbon nanotube, one important issue currently being debated is whether hydrogen adsorption also occurs in the interstitial channels between adjacent nanotube channels in a rope of SWNTs (Schwarz J. A,1993).

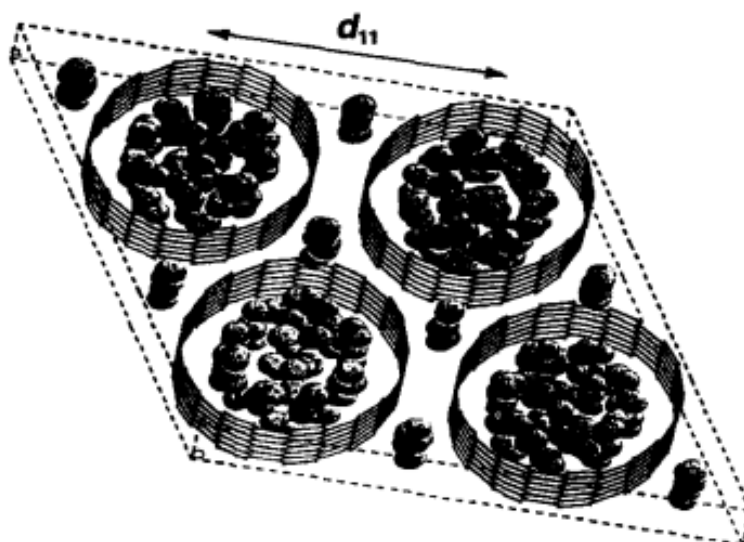


Figure 2. a typical configuration of H₂ molecules adsorbed on a triangular array of CNTs with a lattice constant of d_{11} (Schwarz J. A,1994)

Based on this, the hydrogen adsorption amount under high pressures would be higher than the simplistic geometric estimation. Moreover, it is considered that a hydrogen molecule adsorbed in the interstitial space undergoes much stronger surface attraction than on a single planar graphene surface, since it is in close proximity to three graphene surfaces. Therefore, the hydrogen adsorbed in the interstitial space would be expected to be denser than on a single graphene surface.

Possible Hydrogen Adsorption Sites in Carbon Nanotubes There are many types of pores in carbon nanotubes as discussed above. It can be preliminarily concluded from the theoretical calculations and experimental results that inner cavities, interstices in SWNT bundles, small, aggregated pores of several nanometers among CNTs and carbon islands on the surface of MWNTs are possible sites for hydrogen adsorption (Chambers A, et al, 1998).

The inner cavities of CNTs are primary hydrogen adsorption sites. Many simulations reveal that nano-sized inner cavities in SWNTs and MWNTs (with small diameter) have strong adsorption potentials for hydrogen adsorption and the inner cavities of SWNTs with larger diameter will hold more hydrogen molecules. Experimental results also have proved that cutting and

tips-removing process [(Liu C,et al ,1999), (Iijima S,1991), (Ye Y,et al1999), (Veziroglu T. N and Barbir K,1992)] improves the hydrogen storage capacity of CNTs. Figure 3 shows that a tip-removing process leads to the great increase of small mesopore volume that can be attributed to inner cavities, consistent with the improved hydrogen storage capacity of the MWNTs (Schwarz J. A,1993).

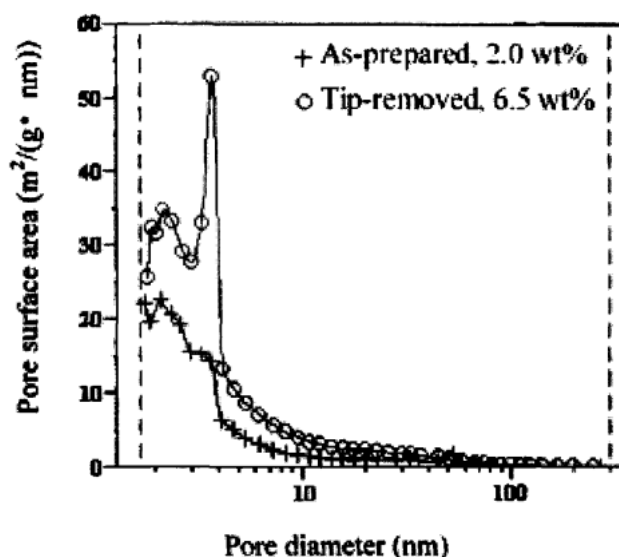


Figure 3. pore size distribution and hydrogen storage capacity of the MWNTs in the as prepared state and after trip removing process (Fan Y. Y,et al,1999).

Table 1. summary of experimental results of electrochemical hydrogen storage in CNTs.

| Material | Synthesis method | Discharge capacity (mAh/g) | Weight hydrogen storage capacity (wt.%) | Reference |
|--------------------|------------------|----------------------------|---|-----------------------|
| SWNTs (low purity) | Arc discharge | 110 | 0.41 | (Veziroglu T. N,1999) |
| SWNTs (purity 90%) | Laser-ablation | 440 | 1.6 | (Fan Y. Y,et al,1999) |
| Li-MWNTs+SWNTs | CVD | 160 | 0.59 | (Noh J. S,et al,1987) |
| SWNTs (purity 80%) | Arc discharge | 800 | 2 | (Chen P,1999) |
| SWNTs (purity 95%) | H2 arc discharge | 316 | 1.2 | (Iijima S,1991) |

CONCLUSIONS

As the conclusion of this research, hydrogen fuel is clean, versatile, efficient and safe, and is the best fuel for transportation, hydrogen energy will play an important role in the energy structure of the future world. As the first experimental result and some of the theoretical prediction indicate that carbon nanotubes can be a promising candidate for efficient hydrogen storage, which may accelerate the development of hydrogen fuel cell driven vehicles. Nevertheless, many efforts have been made to reproduce and verify the hydrogen storage capacity of carbon nanotubes both theoretically and experimentally, to investigate their volumetric capacity, cycling characteristics and release behavior, to correlate the surface and pore structure with hydrogen adsorption behavior, to elucidate the adsorption mechanism. and finally, to clarify the feasibility of carbon nanotubes as a practical onboard hydrogen storage material.

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