

HYDROGEN CRYOSORPTION ON MULTI WALLED CARBON NANOTUBES

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Abstract

We present a Temperature Programmed Desorption (TPD) study on H₂ adsorption on multiwalled carbon nanotubes (MWNT) at very low pressure (<10⁻⁶ Torr) and temperature (12-30 K). Our results show a hydrogen take up limit in the range of 10⁻⁸ mol per gram depending on the adsorption temperature. We compare the MWNT cryosorption capacity with that of commonly used activated carbon and discuss the possibility of employing MWNT as cryosorber in large particle accelerators.

INTRODUCTION

In the synchrotrons and colliders beams of charged particles circulate in a storage ring in circumference in cold bore vacuum chambers. The relativistic particles emit synchrotron radiations which deteriorate the vacuum by desorbing gases such as H₂, CO₂, CO, H₂O and CH₄ [1-2] from the walls. A solution of this problem is the installation of cryosorbers in the collider on cryogenic elements operating at very low temperatures. Several types of cryosorbers have been studied since a few years.

Due to its high specific surface area and large pore volume, porous carbon is considered as a good adsorbent [3]. A wide variety of commercial and speciality carbons has been tested so far as possible candidates for hydrogen sorption [4-6]. In particular, carbon nanotubes (CNTs) and carbon nanofibers show surprisingly high hydrogen storage capacity at either room temperature or liquid nitrogen temperature. Recently, a number of experimental studies of hydrogen adsorption on single walled carbon nanotubes (SWNT) has appeared in literature [4,7-11].

Usually, three different techniques are widely applied to study the hydrogen adsorption and storage in solids: the volumetric method, which measures the pressure drop owing to hydrogen absorption after loading the specimen contained in a constant volume [12]; the gravimetric method, which measures the sample weight changes due to absorption or desorption [13]; and the TPD technique. This latest measures the hydrogen signal during desorption in high vacuum using mass spectrometry, it is highly sensitive allowing to study samples with masses even below 1 mg and is especially suited for loading at low pressures. [3-10].

In an initial work, Dillon et al. [11] estimated the hydrogen uptake to be 5-10 wt.% for adsorption conditions of about 0.5 bar and 273 K, followed by

cooling and pumping to 133 K and 10⁻⁶ Torr. The heat of adsorption determined from the temperature programmed desorption (TPD) measurements was close to 20 kJ/mol. This value should be compared to 4 kJ/mol for H₂ on graphite and with the theoretical 6.3 kJ/mol obtained for SWNT. [14-15] More recent work by the same group indicates that uptake of about 7-8 wt% is achievable on SWNT samples of high purity.[14-15]

Ye et al. [14] reported hydrogen adsorption on purified SWNT samples at 80 K over a pressure range from 0.5 to 160 bar. They observed very little adsorption at the lowest pressure. Similarly, Wilson et al. [15] measured isotherms of H₂ and D₂ deposited on single walled, closed end carbon nanotube bundles and observed two well distinct steps corresponding to adsorption on at least two different sites, grooves/interstitials and the graphene surface.

In this work we present some primary results of a TPD study on H₂ adsorption on multi walled carbon nanotubes (MWNT) and on activated graphite at very low pressure and temperatures as a function of coverage. We show that the hydrogen pumping efficiency can be greatly improved if carbon NTs are employed as cryosorbers.

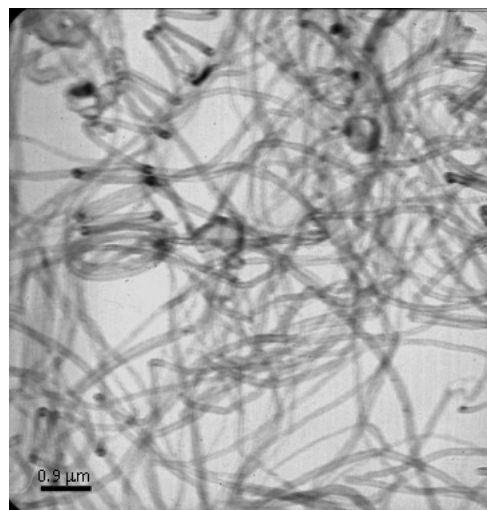


Figure 1: TEM image of the MWNT sample used in this study.

EXPERIMENTAL

The experiments were conducted in an ultra high vacuum chamber evacuated with a turbo pump. The chamber base pressure was in the mid 10⁻⁹ Torr. Purified MWNT powder grown with CVD technique was dispersed in ortho dichlorobenzene, sonicated, and

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directly deposited on the head of a close cycled He cold finger. Sample temperature was monitored with a Au-0.7%Fe/Chromel thermo couple. H₂ gas (99.99% purity) was admitted to the chamber through a precision leak valve and the loading pressure was typically 10⁻⁶ Torr. During heating, the desorbed gases were analyzed by a quadrupole mass spectrometer (QMS), and the sample temperature was simultaneously recorded.

RESULTS AND DISCUSSION

In Fig. 1 we show a Transmission Electron Microscopy (TEM) image of our MWNT sample. It can be clearly seen that these purified nanotubes are capped and do not contain large amorphous carbonaceous particles and have quite similar diameters of 15 nm.

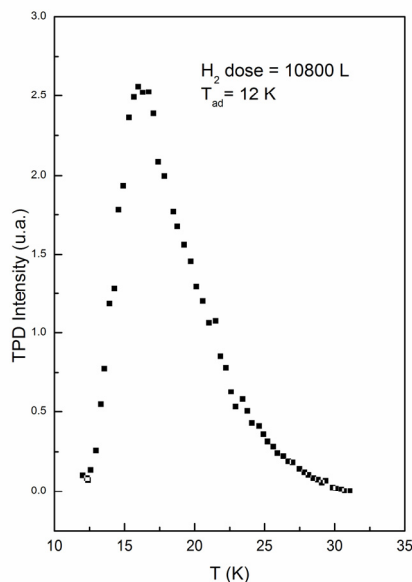


Figure 2: TPD spectrum for H₂ dose of $\Phi=10800$ L on MWNT at an adsorption temperature of 12 K.

In Fig 2 we illustrate a typical TPD spectrum for H₂ dose of $\Phi=10800$ L (1L=10⁻⁶ Torr s) on MWNT at an adsorption temperature of 12 K. Each data point in the figure actually is an integral QMS intensity at atomic mass units 2 and is proportional to the desorption rate. We mention that no water or other contamination signals were detected during either adsorption or desorption.

The total desorption intensity I_{tot} , area of the TPD curve as that shown in Fig.2, is directly proportional to the hydrogen uptake. In Fig. 3 we plot I_{tot} as a function of H₂ dose for 10 mg MWNTs at 16 K. It is interesting to note that I_{tot} increases linearly with Φ at low doses and saturates at about $\Phi=1000$ L indicating that hydrogen adsorption does not go beyond one monolayer and the desorption kinetics is of the first order. We point out that the sorption process is completely reversible and the I_{tot} value remains unchanged within the experimental errors even after many sorption cycles.

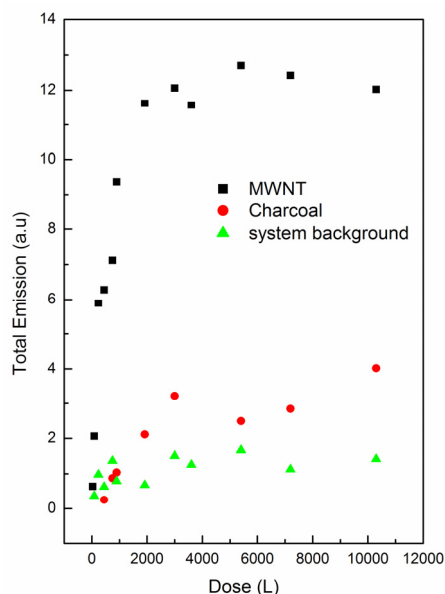


Figure 3: H₂ uptake as a function of adsorption dose at a constant condensation temperature of $T=16$ K. The data are obtained by integrating the total area of TPD spectra as those shown in Fig.2. Also shown are the results for the same amount of charcoal and for the system background without any cryosorber.

In Fig. 3 we also show the results for the system background adsorption without nanotube cryosorbers which clearly confirms that the H₂ uptake is entirely due to MWNTs. For comparison, the behaviour of 10 mg charcoal powders under exactly the same experimental conditions is also depicted. We see that it exhibits very similar characteristics as that of MWNTs but with a total hydrogen adsorbed amount about four fold smaller.

Finally, in Fig. 4 is plotted the saturated I_{tot} as a function of adsorption temperature T_{ad} . As expected, the total hydrogen pumping efficiency decreases with the cryosorber temperature. For $T_{ad}>27$ K, no H₂ adsorption is observed.

Our results contrast sharply with those reported for hydrogen storage measurements at higher temperatures and pressures and strongly indicate that under high vacuum conditions, hydrogen do not adsorb on the nanotube surface beyond the sublimation temperature and the diffusion is essentially inhibited, as already suggested by some theoretical calculations. Unfortunately, to our knowledge, so far there is no work reported in literature concerning the molecular hydrogen adsorption on carbon nanotubes for T_{ad} below the liquid nitrogen temperature (77K). More quantitative works are currently being undertaken to determine the realistic possibility of using nanotubes as cryosorbers in UHV systems.

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REFERENCES

- [1] V. Baglin, Vacuum Performances Estimation of the cryosorbers to be installed in the LHC LSS, Vacuum technical Note 04-06 EDMS N0: 478338, CERN – AT division (2004).
- [2] B. Angerth, F. Bertinelli, J.-C. Brunet, R. Calder, J. Gomez-Goni, O. Grobner, A. Mathewson, A. Poncet, C. Reymermier and E. Wallen, the Cold vacuum System of the Large Hadron Collider, CERN, AT Division 1211 Geneva 23, 2467.
- [3] Takefumi Horiuchi and Tsutomu Ooi, Cryogenic properties of composite materials, *Cryogenics* 35, 677 (1995).
- [4] V.V. Simonyan, J. K. Johnson, Hydrogen storage in carbon nanotubes and graphitic nanofibers, *Journal of Alloys and Compounds* 330, 659 (2002).
- [5] S. Hynek, W. Fuller, J. Bentley, *Int. J. Hydrogen Energy* 22, 601 (1997).
- [6] J.S. Noh, R.K. Agarwal, J.A. Schwarz, *Int. J. Hydrogen Energy* 12 693 (1987).
- [7] Peng-Xiang Hou, Shi-Tao Xu, Zhe Ying, Quan-Hong Yang, C. Liu, Hui-Ming Cheng, *Carbon* 41 (2003) 2471.
- [8] Hui-Ming Cheng, Quan-Hong Yang, Chang Liu, *Carbon* 39 (2001) 1447.
- [9] C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, M. S. Dresslhaus, *Science* 286 (1999) 1127.
- [10] K. Tada, S. Furuya, K. Watanabe, *Physical Review B*, 63 (2001)155405.
- [11] A. C. Dillon, K. M. Jones, T.A. Bekkedahl, C. H. Klang, D. S. Bethune, M. J. Heben, *Nature* 386 (1997), 377.
- [12] Y.-Y. Fan, B. Liao, Y.-L. Wei, M.-Q. Lu, H.M. Cheng, *Carbon* 37 (1999) 1649.
- [13] R. Strobel, L. Jorissen, T. Schliermann, V. Trapp, W. Schultz, K. Bohmamm, G. Wolf, J. Garche, *J. Power Sources* 84 (1999) 25.
- [14] Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Kiu, A.G. Rinzler, D. Colbert, K.A. Smith, R.E. Smalley, *Appl. Phys. Lett.* 74 (1999) 2307.
- [15] T. Wilson, A. Tyburski, M. R. DePies, O.E. Vilches, D. Becquet, M. Bienfait, *Journal of Low temperature Physics*, 126 (2002) 403.