Carbon nanotubes: state of the art and applications/Les nanotubes de carbone : état de l'art et applications

Hydrogen storage in carbon nanotubes

M. Becher [a], M. Haluska [a], M. Hirscher [a,*], A. Quintel [b], V. Skakalova [b],
U. Dettlaff-Weglikovska [b], X. Chen [b], M. Hulman [b], Y. Choi [b], S. Roth [b],
V. Meregalli [b], M. Parrinello [b], R. Ströbel [c], L. Jörissen [c], M.M. Kappes [d], J. Fink [e],
A. Züttel [f], I. Stepanek [g], P. Bernier [g]

[a] *Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany*
[b] *Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany*
[c] *ZSW Ulm, Helmholtzstr. 8, 89081 Ulm, Germany*
[d] *Universität Karlsruhe, Institut für physikalische Chemie, Kaiserstr. 12, 76128 Karlsruhe, Germany*
[e] *Institut für Festkörper- und Werkstoffforschung, 01171 Dresden, Germany*
[f] *Universite Fribourg, Physique Departement, Perolles, CH-1700 Fribourg, Switzerland*
[g] *GDPC, Universite Montpellier II, 34095 Montpellier cedex 05, France*

Presented by Guy Laval

Abstract

Hydrogen storage in new nano-structured carbonic materials is a topic for lively discussion. The measured storage capacities of these materials, which have been announced in the literature during the last ten years are spread over an enormous range from about 0.1 wt% up to 67 wt%. This paper will give a report on the state of the art of hydrogen storage in carbon nanostructures. We shall critically review the recent 'key publications' on this topic, which claim storage capacities clearly above the technological bench mark set by the US Department of Energy, and we shall report new results which have been obtained in a joint project sponsored by the Federal Ministry for Education and Research in Germany (BMBF). *To cite this article: M. Becher et al., C. R. Physique 4 (2003).*

Résumé

Stockage d'hydrogène dans les nanotubes de carbone. Le stockage d'hydrogène dans les nouvelles nano-structures de carbone est un sujet vivement débattu. Les mesures de la capacité de stockage de ces matériaux effectuées dans les dix dernières années s'échelonnent sur une gamme très large, de 0,1 % jusqu'à 67 % en poids. Cet article présente l'état de l'art en ce qui concerne le stockage d'hydrogène dans les nano-structures de carbone. Nous discutons de façon critique les récentes « publications clés » se rapportant à ce sujet qui annoncent des capacités de stockage largement supérieures aux références imposées par le Département de l'Energie américain et présentons les derniers résultats obtenus dans le cadre d'un projet commun sponsorisé par le Ministère Fédéral de l'Education et de la Recherche allemand. *Pour citer cet article : M. Becher et al., C. R. Physique 4 (2003).*

* Corresponding author.
  E-mail address: hirscher@mf.mpg.de (M. Hirscher).

1. Introduction

Recent publications concerning the hydrogen storage capacity of new nano-structured carbonic materials gave rise to the hope that the energy problem of running out fossil fuels could be solved. An appropriate and safe hydrogen storage device would enormously push the application of hydrogen as the clean alternative fuel. The high energy value and the lack of environmental pollutants make the use of hydrogen very attractive. The end product released by a fuel cell or by a modified combustion engine is harmless water. However, the on-board storage for automotive applications has to be efficient, economical and safe. Physical storage by liquefaction or pressurisation requires high energy input and has to overcome associated safety risks. Hydrides reduce the risk factor but the high temperature of dissolution in metal hydrides, e.g., titanium hydride and magnesium hydride, make them less ideal for automotive applications. Several inter-metallic compounds operate near room temperature and moderate pressures, but the gravimetric storage capacity is less than 2 wt%. For automotive applications the technological bench mark has been set at 6.5 wt% (ratio of stored hydrogen weight to the storage medium) by the US Department of Energy (DOE). This guarantees that a fuel cell driven vehicle can drive about 500 km before refuelling.

Carbon materials seemed to be the ideal candidates as hydrogen storage devices. Carbon is one of the very few light materials which are solid at room temperature. Furthermore, different carbonic structures can be produced with large inner surfaces, e.g., activated carbon, fullerenes, carbon nanotubes, carbon nanofibers. Considering an infinitely wide graphene layer, the specific surface area of both sides is 2622 m^2 per gram. High surface area activated carbon structures are commercially available, with specific surface areas up to 3000 m^2 per gram; however, in spite of this, these materials were found to be ineffective for hydrogen storage. Only a small fraction of the carbon surface interacts with hydrogen molecules at room temperature and moderate pressures. The new available nano-structured carbon materials created speculations that capillary forces could enhance gas or hydrogen adsorption, as well as drawing up liquids by capillarity. The adsorption would be a consequence of the attractive potential of the pore walls. However, the effect of a so-called nano-capillarity could neither be experimentally nor theoretically substantiated.

The present paper gives a critical review of hydrogen storage in carbon nanotubes. The following topics: (i) theoretical calculations; (ii) high pressure hydrogen storage; (iii) alkali metal treated carbonic materials; (iv) low pressure hydrogen storage, are discussed and compared to new results which have been obtained in a joint project sponsored by the Federal Ministry for Education and Research in Germany (BMBF).

2. Theoretical calculations

Many theoretical investigations have been performed to predict the hydrogen uptake in carbonic materials, for an overview see, e.g., [1]. The theoretical calculations can mainly be divided into two categories, proposing either the physisorption of hydrogen molecules or the chemisorption of hydrogen atoms by the carbonic material.

The authors proposed that the hydrogen molecules are adsorbed by the carbon structure due to van der Waals forces and studied the hydrogen adsorption utilizing grand canonical Monte Carlo simulations [2–7]. The results of the calculations based on different classical effective potentials or partly including quantum effects at cryogenic temperatures are essentially compatible which each other. The calculated storage capacities at high pressures are less than 1 wt% at ambient temperatures and can not explain the high storage capacities which have been experimentally obtained. The findings agree that the hydrogen storage capacity of the carbonic material rapidly decreases with increasing temperature. By studying arrays of nanotubes and the influence of the geometry, the simulations predict that the storage capacity could reach the gravimetric DOE target at low temperatures for nanotubes with a wide diameter and very large spacing between the tubes of about 1 nm [8]. These kinds of nanotubes with a high surface area are not yet available. The delamination of a bundle of SWNTs would enhance the surface area and therefore the storage capacity, as shown in [9]. At cryogenic temperatures and high pressure a storage capacity of 9.6 wt% has been calculated for an isolated SWNT.

In order to study the formation of carbon-hydrogen bonds ab initio calculations have been performed by several authors [10–17]. The maximum number of hydrogen atoms covalently bound in carbon nanotubes corresponds to a storage capacity of 14 wt%. However, these optimistic values are obtained at very low temperatures and under idealized conditions. Furthermore, chemisorbed hydrogen may be only released at high temperatures and it is therefore useless for technical applications.

While the adsorption energies connected with physisorption of about 1–100 meV are too low to explain the high hydrogen storage capacities experimentally obtained for carbon nanotubes, chemisorption of hydrogen atoms with adsorption energies of about 2–3 eV cannot explain reversible storage at ambient temperature. Cheng et al. [18] predicted, by quantum-mechanic molecular dynamic simulations performed for hydrogen adsorption in SWNTs, an intermediate state. They calculated adsorption energies which range from about 0.2 eV at 77 K and about 0.3 eV at ambient temperature up to about 0.4 eV at 600 K. The authors suggest that a partial electron-transfer interaction between instantaneously distorted carbon atoms of the curved graphene sheet and hydrogen is responsible for the unique strength of the adsorption energy. However, the hydrogen densities

used in their calculations were rather low (0.47 wt%). Furthermore, a hydrogen adsorption mechanism based on dynamic fluctuations will not yield high storage capacities.

3. High pressure hydrogen storage in carbon nanotubes

Very spectacular hydrogen storage capacities of up to 67 wt% were claimed from the group of Baker and Rodriguez for a certain type of carbon nanofibers [19,20]. They measured high hydrogen adsorption for different carbonic materials applying a hydrogen pressure of about 110 atm at room temperature and monitoring 24 h. The highest value of nearly 67 wt% was obtained for herringbone-type carbon nanofibers but even in graphite a very high storage capacity of 4.5 wt% was measured. The press exulted that a fuel cell driven car with this hydrogen storage medium would be able to drive from Paris to Vladivostok. The extremely high values, however, could not be confirmed in any laboratory up to now. In contrast, e.g., Ahn et al. [21] measured, for comparable carbon nanofibers with the same method and under comparable conditions, a storage capacity less than 0.2 wt%. Promising data have been published by a Chinese group, also measuring with the volumetric method. They observed in multi-walled carbon nanotubes a hydrogen uptake of 10–13 wt% at room temperature and 110 atm [22]. The nanotubes had to be boiled in hydrochloric acid. However, in a further publication the same group reduces the storage capacity of the MWNTs by a factor of two [23]. For SWNTs with large diameters treated with hydrochloric acid this group obtained a storage capacity of 4.2 wt% at room temperature [24]. The purity of the samples was about 50–60%. Furthermore, high hydrogen storage capacities of 10 and later 15 wt% were claimed from Gupta and Srivastava for herringbone-type carbon nanofibers [25]. But none of these high values have survived cross-checking by independent research groups repeating the measurements on the same sample in different laboratories. One reason might be that the exchange of samples is often restricted by industrial contracts. Tibbetts et al. [26] examined different carbon materials at high pressures but they found no hydrogen sorption, appreciably above background, at room temperature.

At cryogenic temperatures Ye et al. [27] found a hydrogen adsorption of more than 8 wt% in purified SWNTs at 120 atm. Their adsorption isotherms at 80 K indicated a phase transition at pressures higher than 40 atm. The authors deduced that the surface increased because of a separation of the individual SWNTs in the bundles.

Within the joint BMBF project, volumetric measurements have been performed on different nano-structured materials at various temperatures [28]. At room temperature and pressures of about 80 atm the hydrogen storage capacity is definitely below 1 wt%. The same result has been obtained by the Dresden group within our project investigating different nano-structured materials in the pressure range up to 45 atm [29]. The measured isotherms show no saturation at room temperature. Fig. 1 reflects the storage capacity of SWNTs and activated carbon at room temperature in comparison to LaNi$_5$. At lower temperatures a slight increase of the hydrogen adsorption can be observed. However, we did not observe at 77 K a phase transition for SWNTs, which could indicate a separation of the tubes as deduced by Ye et al. [27]. At low temperature no saturation of the pressure isotherms can be determined at pressures up to 100 atm. In essence, the measured isotherms are in agreement with theoretical calculations based on physisorption of hydrogen molecules.
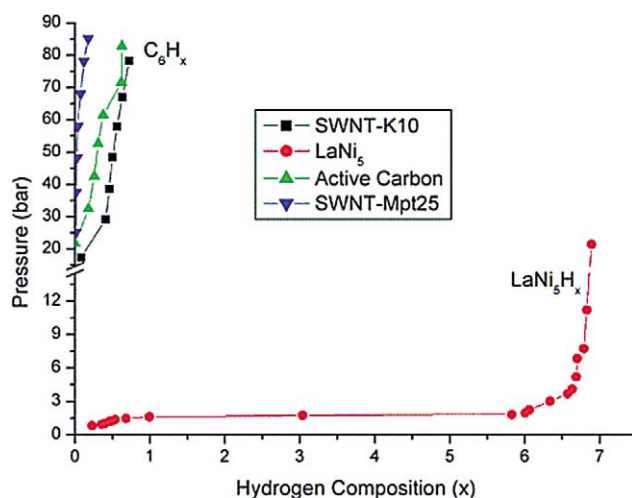

Fig. 1. Hydrogen storage capacity of several nano-structured carbonic materials at room temperature applying hydrogen pressures up to 90 atm in comparison to the hydrogen storage capacity of LaNi$_5$ under hydrogen pressure.
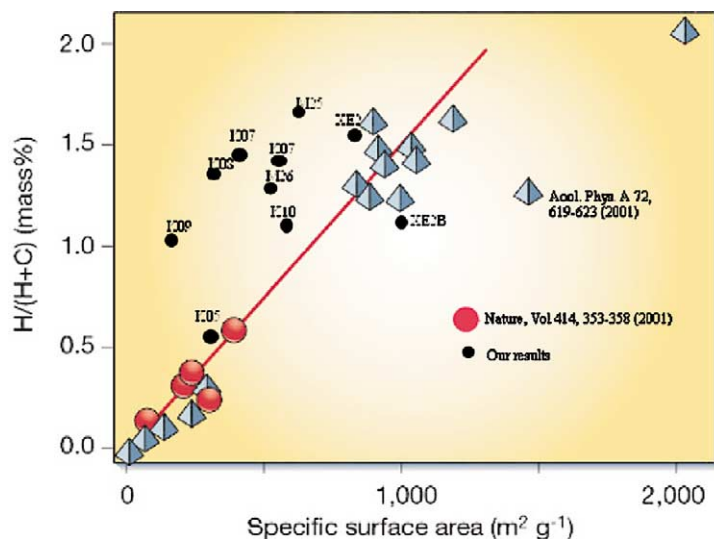
Fig. 2. Hydrogen storage capacity of different carbonic materials is plotted versus the specific surface area [33]. Blue triangles: carbon nano-structures measured at 77 K and 1 atm and best-fit line of these data [30]; red circles: nano-structured carbon samples electrochemically measured [31,32]; black dots: nano-structured carbon samples at 77 K and 80 atm [28].

A correlation between the specific surface area of the carbon samples and the hydrogen adsorption has been examined by Nijkamp et al. [30] and Züttel et al. [31,32], proposing an approximate linearity between the two properties. In essence, our results at 77 K and 50–55 atm show this correlation and are compared with their data in Fig. 2.

The hydrogen storage capacity of the carbonic samples with surface areas between 300 and 1500 m^2 per gram measured at 77 K and high pressure are higher than the values of Nijkamp et al. obtained at 77 K and ambient pressure and that of Schlapbach and Züttel measuring at ambient temperature using the electrochemical method [33].

4. Hydrogen storage in alkali metal treated carbonic materials

The intercalation of graphite with alkali metals has been carefully examined in the 1970s (see, e.g., [34]). However, the intercalation of carbonic materials with hydrogen, up to now, has not been successful. In spite of hydrogen showing in many respects comparable physical properties to alkali metals, even theoretical simulations predict that the experimental intercalation would not be effective. Therefore, the idea was to combine alkali metal and hydrogen intercalation. The alkali intercalation causes the graphitic layers to be widened and may facilitate the hydrogen diffusion into the carbonic material.

In 1999 Chen et al. [35] tried to intercalate different carbonic materials by mixing them with alkali salts and performing a so-called solid state reaction. The mixture was heat treated under hydrogen flow. The following gravimetric measurements performed under hydrogen flow yield dramatic and reversible weight changes of the alkali treated carbon samples which have been attributed to hydrogen adsorption and release. The related storage capacities reached up to 20 wt% for Li treated multi-walled carbon nanotubes and even up to 14 wt% for Li treated graphite. However, these measurements were subsequently put into doubt by Yang and Pinkerton et al. [36,37]. They found that the majority of the weight changes are due to adsorption and release of water.

If the gravimetric experiment on lithium treated graphite is reproduced under hydrogen flow the results shown in Fig. 3 are obtained. The heating rate was 5 K/min and the measured weight changes are very similar to those obtained by Chen et al. The characterisation of the intercalation product by X-ray diffraction, however, did not show any evidence of intercalated graphite. The so-called solid state reaction yields a mixture of graphite, lithium oxide, and lithium hydroxide (see Fig. 4). A complicated chemistry is occurring during the heat treatment under hydrogen flow. The Lithium oxide is highly hygroscopic and the release and re-absorption of crystal water can be observed [38–40]. Furthermore, Lithium oxide can adsorb carbon dioxide so that a possible hydrogen uptake cannot be inferred from the observed weight changes.
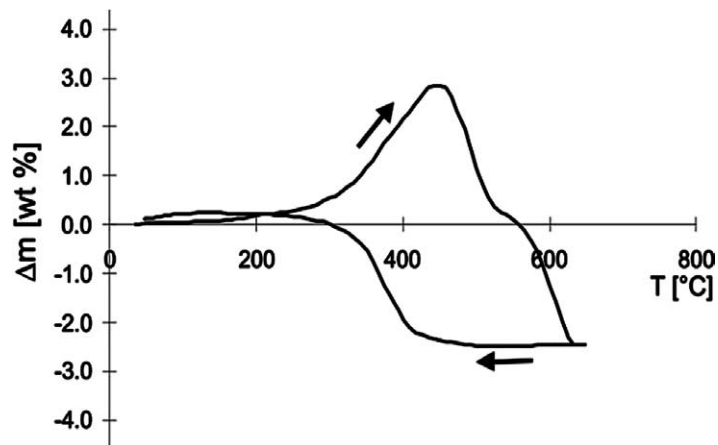
Fig. 3. Weight changes versus temperature obtained by a gravimetric measurement under flowing hydrogen performed on a mixture of graphite and lithium salts heat treated under hydrogen flow.
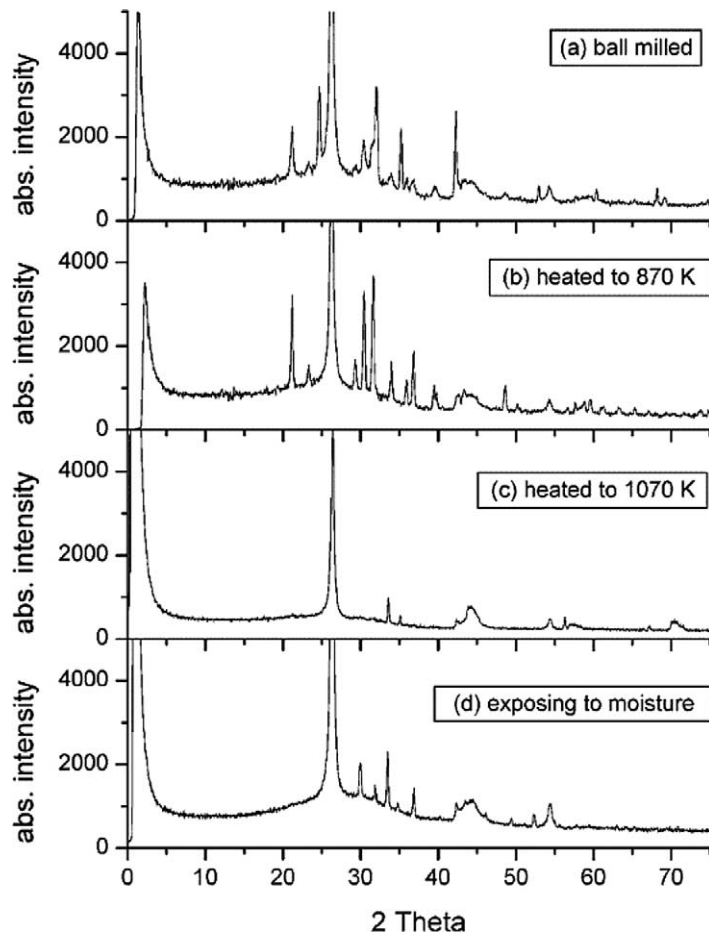

Fig. 4. X-ray diffraction spectra (Cu Kα radiation) of graphite mixed with LiNO$_3$ and Li$_2$CO$_3$ and heat treated under hydrogen flow. (a) After ball milling under air for 5 h showing a superposition of the diffraction peaks of the different components; (b) after heating to 900 K under hydrogen flow the diffraction peaks of Li$_2$CO$_3$ increase at the cost of those of LiNO$_3$ according to C + 2LiNO$_3$ + H$_2$ $\rightarrow$ Li$_2$CO$_3$ + H$_2$O + 2NO; (c) after further heat treating under hydrogen flow up to 1070 K the diffraction peaks of Li$_2$CO$_3$ vanish and those of Li$_2$O appear according to Li$_2$CO$_3$ + H$_2$ $\rightarrow$ Li$_2$O + H$_2$O + CO; (d) after exposure to wet hydrogen, i.e., moisture LiOH is formed from Li$_2$O.

5. Low pressure hydrogen storage in carbon nanotubes

The first publication concerning the hydrogen storage capacity of carbon nanotubes by the group of M. Heben [41] caused enormous interest. The authors claimed that hydrogen can condense to high density inside narrow single-walled carbon nanotubes. They estimated a storage capacity of 5–10 wt% which is highly interesting for automotive applications. However, the total amount of hydrogen desorbed from a sample with only a small concentration of nanotubes and determined with thermal desorption spectroscopy (TDS) was about 0.01 wt%. The large storage values were obtained after 'normalizing' to 100% nanotube concentration. Three years later the same group affirmed that they have directly measured a hydrogen storage capacity of about 7 wt% after purifying the samples and opening the SWNTs [42]. However, the temperature at which the hydrogen releases now was significantly higher than that observed in the first measurements. Heben's group reported that after heating in high vacuum the opened SWNTs could adsorb this high amount of hydrogen within a few minutes at ambient pressure and room temperature. The hydrogen could be released at moderate temperatures. The procedure for opening the carbon nanotubes was high power ultra-sonication in acid. A few milligrams of the SWNTs were dispersed in HNO_3 and sonicated with an ultrasonic horn active in the liquid. Typically an ultrasonic horn made of Ti-6Al-4V is used because of its chemical resistance.

Within the joint BMBF project we carefully tried to reproduce the results of the group of M. Heben [42]. Various carbonic materials treated by ultra sonication have been systematically investigated [43]. We could more or less reproduce the data of Heben's group; however, the storage capacity of the sonicated SWNTs was reduced by a factor of three. However, further investigations have shown that hydrogen was not stored in the carbonic material. Owing to cavitation, the high-power ultra-sonication for opening the nanotubes incorporated metal particles of the horn into the samples. Applying the Ti-alloy horn to the samples hydrogen desorption could be observed in all investigated carbonic materials, e.g., purified SWNTs, graphite and diamond powder. The maximum storage capacity observed with TDS was 1.5 wt% measured in purified SWNTs sonicated 24 h with the Ti-alloy horn. In contrast, no hydrogen storage has been found (below 0.005 wt%) if the SWNTs had been sonicated with a stainless steel horn.

The desorption spectra of purified SWNTs sonicated for different times using the Ti-alloy horn are shown in Fig. 5. With increasing sonication time the hydrogen storage capacity increases as well as the titanium content in the carbon samples. The loading and activating conditions were nearly the same as used by Heben's group [42], exposing the samples to deuterium atmosphere (0.8 atm) at room temperature for 15 min directly after heating the sample in high vacuum. But all hydrogen storage of the examined sonicated samples can be attributed to hydrogen storage in the Ti-alloy particles. The heat treatment under high vacuum before hydrogen loading the samples is a well known activation procedure of titanium removing the natural oxide layer [44]. Furthermore, the TDS spectra of all different carbon samples sonicated with the Ti alloy horn are very similar indicating a fingerprint of the Ti-alloy hydride. X-ray analysis yields clear evidence of the formation of titanium hydride (see Fig. 6). The obvious way to resolve the apparent contradiction between these results and that of the group of M. Heben would
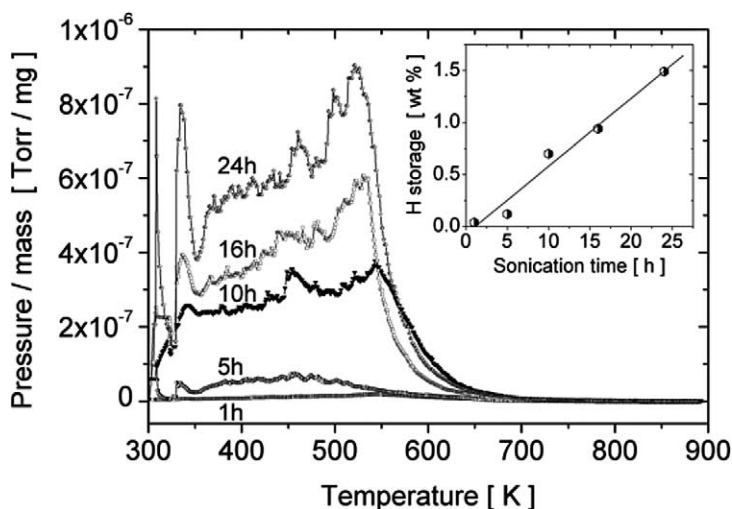

Fig. 5. Thermal desorption of deuterium into high vacuum versus temperature (heating rate 5 K/min) for purified SWNTs from Tubes@Rice sonicated in 5 M HNO_3 for different times using a Ti-alloy horn, heated to 900 K under high vacuum and then deuterium loaded at room temperature and 0.8 atm for 15 min. The inset shows the total storage capacity converted to wt% of hydrogen versus the sonication time [43] (originally Fig. 1, published with permission from Springer).
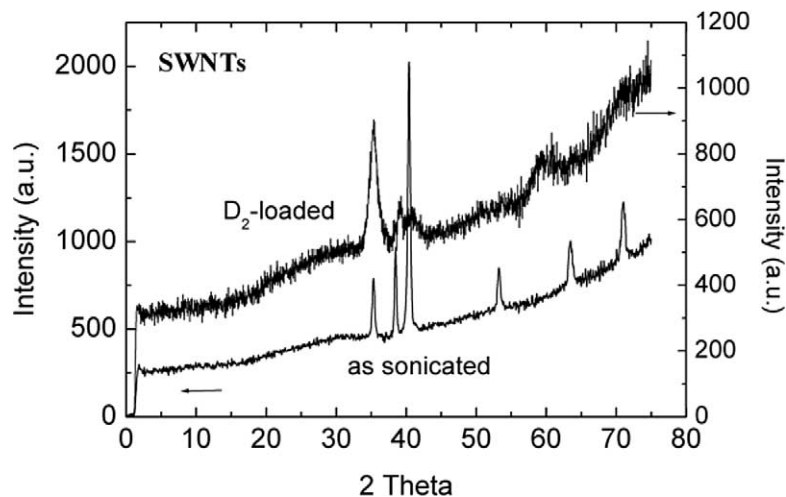
Fig. 6. X-ray diffraction spectra (Cu Kα radiation) of the SWNTs sonicated 16 h in 5 M HNO₃ using a Ti-alloy horn. The as-sonicated sample shows the diffraction peaks of titanium, after loading with deuterium the diffraction peaks of titanium deuteride appear [43] (originally Fig. 3, published with permission from Springer).

be to reproduce the experiments with the same single-walled carbon nanotubes in an independent laboratory. However, the exchange of samples was said to be prohibited by industrial contracts. Furthermore, new investigations of the group of M. Heben on newly produced SWNTs showed significantly lower hydrogen storage capacities of 2–3 wt% [45,46].

6. Summary and outlook

From today's viewpoint low pressure hydrogen storage in carbon nanostructures is not very promising. None of the theoretical calculations shows a high hydrogen storage capacity at ambient temperature and, aside from the the results of Cheng et al. [18], none yields any evidence for an intermediate adsorption state between physisorption and chemisorption. The exciting experimental data published by several groups could be primarily reproduced, but they have to be interpreted in a different way. Hydrogen was either stored in contaminations or, instead of hydrogen, water or other environmental gases have been adsorbed. High pressure hydrogen storage is confirmed in carbon nanotubes, but the very high values could not be reproduced. The volumetric measurements allow the rough estimate that at room temperature a hydrogen uptake of about 1 wt% per 100 atm can be obtained if the surface area of the nano-structured carbon is some 500 m² per gram. The storage capacity can probably be increased by applying higher hydrogen pressures or by lowering the temperature. Furthermore, a higher storage capacity can be obtained in carbon materials with a larger specific surface area. In future studies, an emphasis should be given to develop reliable purification and characterization methods for carbon nanotubes.

For high pressure storage one has to discuss whether the presence of the carbon materials in a hydrogen pressure tank is really advantageous. Hydrogen adsorption by the carbonic material in the pressure tank may help to reduce the pressure necessary for an adequate storage capacity but the presence of this material reduces the volume available for hydrogen. Supposing a hydrogen storage capacity of the available carbonic material at ambient temperature of about 1 wt% each 100 atm, an optimistic linear extrapolation yields at about 700 atm the DOE target of 6.5 wt% or 62 kg·H₂·m⁻³ for the storage medium. However, at ambient temperatures, this hydrogen density can be obtained just by pressurizing in this high pressure range. The density of liquid hydrogen of 71 kg·m⁻³ is setting the upper limit for compressed hydrogen below 900 atm at ambient temperature. Today pressure tanks up to 350 atm and associated components are state of the art. The corresponding storage capacity of the total system is about 3.5 wt%. Up to now it is not clear whether at this pressure the available carbonic material is helpful. Another question is whether it is more effective to look for new carbonic materials with higher specific surface areas or rather to develop better designed pressure tanks and related components?

The above considerations are relevant for automotive applications requiring the DOE benchmark for the hydrogen storage capacity. Another (but smaller) market is the use of the carbonic material in fuel cells for portable electronics, e.g., laptops or cellular phones. In this case other considerations have to be taken into account. Besides the prize the consumer's comfort is decisive. The low weight of fuel cells with carbonic hydrogen storage media as well as an easy and quick loading procedure favours the substituting of conventional rechargeable batteries.

Acknowledgements

References

[1] V. Meregalli, M. Parrinello, Appl. Phys. A 72 (2001) 143.
[2] Q. Wang, J.K. Johnson, J. Chem. Phys. 110 (1) (1998) 577.
[3] Q. Wang, J.K. Johnson, J. Phys. Chem. B 103 (2) (1999) 277.
[4] Q. Wang, J.K. Johnson, J. Phys. Chem. B 103 (23) (1999) 4809.
[5] M. Rzepka, P. Lamp, M.A. de la Casa, J. Phys. Chem. B 102 (1998) 10894.
[6] F. Darkrim, J. Vermesse, P. Malbrunot, D. Levesque, J. Chem. Phys. 110 (8) (1999) 4020.
[7] F. Darkrim, D. Levesque, J. Phys. Chem. B 104 (29) (1999) 6773.
[8] Y.F. Yin, T. Mays, B. McEnaney, Langmuir 16 (2000) 10521.
[9] K.A. Williams, P.C. Eklund, Chem. Phys. Lett. 320 (2000) 352.
[10] S.M. Lee, Y.H. Lee, Appl. Phys. Lett. 76 (20) (2000) 2877.
[11] S.M. Lee, K.S. Park, Y.C. Choi, Y.S. Park, J.M. Bok, D.J. Bae, K.S. Nahm, Y.G. Choi, S.C. Yu, N. Kim, T. Frauenheim, Y.H. Lee, Synthetic Metals 113 (2000) 209.
[12] S.M. Lee, L.H. An, W.S. Kim, Y.H. Lee, Y.S. Park, G. Seifert, T. Frauenheim, Synthetic Metals 121 (2001) 1189.
[13] S.M. Lee, K.H. An, Y.H. Lee, G. Seifert, T. Frauenheim, J. Am. Chem. Soc. 123 (21) (2001) 5059.
[14] Y. Ma, Y. Xia, M. Zhao, R. Wang, L. Mei, Phys. Rev. B 63 (2001) 115422.
[15] K. Tada, S. Furuya, K. Watanabe, Phys. Rev. B 63 (2001) 155405.
[16] C.W. Baulischer, Chem. Phys. Lett. 322 (2000) 237.
[17] C.W. Baulischer, Nano Lett. 1 (5) (2001) 223.
[18] H. Cheng, G. Pez, A.C. Cooper, J. Am. Chem. Soc. 123 (2001) 5845.
[19] A. Chambers, C. Park, R. Baker, N.M. Rodriguez, J. Phys. Chem. B 102 (1998) 4253.
[20] C. Park, P.E. Anderson, A. Chambers, C.D. Tan, R. Hidalgo, N.M. Rodriguez, J. Phys. Chem. 103 (1999) 10572.
[21] C.C. Ahn, Y. Ye, B.V. Ratnakumar, C. Witham, R.C. Bowman, B. Fultz, Appl. Phys. Lett. 73 (23) (1998) 3378.
[22] Y.Y. Fan, B. Liao, M. Liu, Y.L. Wie, M.Q. Lu, H.M. Cheng, Carbon 37 (1999) 1649.
[23] H.M. Cheng, C. Liu, Y.Y. Fan, F. Li, G. Su, L.L. He, M. Liu, Z. Metallkunde 91 (2000) 306.
[24] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, Science 286 (1999) 1127.
[25] B.K. Gupta, O.N. Srivastava, Int. J. Hydrogen Energy 26 (2001) 857.
[26] G.G. Tibbetts, G.P. Meisner, C.H. Olk, Carbon 39 (2001) 2291.
[27] Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Smith, R.E. Smalley, Appl. Phys. Lett. 74 (16) (1999) 2307.
[28] X. Chen, M. Haluska, U. Dettlaff-Wegliskowska, M. Hirscher, M. Becher, S. Roth, Mat. Res. Soc. Symp. Proc. 706 (2002) Z9.11.1.
[29] M. Ritschel, M. Uhlemann, O. Gutfleisch, A. Leonhardt, A. Graff, C. Täschner, J. Fink, Appl. Phys. Lett. 80 (16) (2002) 2985.
[30] M.G. Nijkamp, J. Raaymakers, A.J. van Dillen, K.P. de Jong, Appl. Phys. A 72 (2001) 619.
[31] A. Züttel, C. Nützenadel, P. Sudan, P. Mauron, C. Emmenegger, S. Rentsch, L. Schlapbach, A. Weidenkaff, T. Kiyobayaschi, J. Alloys Comp. 676 (2002) 320.
[32] A. Züttel, P. Sudan, P. Mauron, T. Kiyobayaschi, C. Emmenegger, L. Schlapbach, Int. J. Hydrogen Energy 27 (2002) 203.
[33] L. Schlapbach, A. Züttel, Nature 414 (2001) 353.
[34] M.S. Dresselhaus, G. Dresselhaus, Adv. Phys. 30 (1981) 139.
[35] P. Chen, X. Wu, J. Lin, K.L. Tan, Science 285 (1999) 91.
[36] R.T. Yang, Carbon 38 (2000) 623.
[37] F.E. Pinkerton, B.G. Wicke, C.H. Olk, G.G. Tibbetts, G.P. Meisner, M.S. Meyer, J.F. Herbst, J. Phys. Chem. 104 (2000) 9460.
[38] M. de Forcrand, Ann. Chim. Phys. 15 (1908) 433.
[39] Handbuch der anorganischen Chemie, Verlag Chemie, Berlin, 1927, p. 71.
[40] V. Skakalova, A. Quintel, Y.M. Choi, S. Roth, M. Becher, M. Hirscher, Chem. Phys. Lett. 365 (2002) 333.
[41] A.C. Dillon, K.M. Jones, A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.
[42] A.C. Dillon, T. Gennett, K.M. Jones, J.L. Alleman, P.A. Parilla, M.J. Heben, Proceedings of the 2000 Hydrogen Program Review NREL/CP-507-28890, 2000.
[43] M. Hirscher, M. Becher, M. Haluska, U. Dettlaff-Weglikowska, A. Quintel, G.S. Duesberg, Y.M. Choi, P. Downes, M. Hulman, S. Roth, I. Stepanek, P. Bernier, Hydrogen storage in sonicated carbon materials, Appl. Phys. A 72 (2) (2001) 129.
[44] IEA/DOE/SNL On-line database, http://hydpark.ca.sandia.gov.
[45] A.C. Dillon, K.E.H. Gilbert, J.L. Alleman, T. Gennett, K.M. Jones, P.A. Parilla, M.J. Heben, Proceedings of the 2001 U.S. DOE Hydrogen Program Review NREL/CP-570-30535, 2001.
[46] A.C. Dillon, K.E.H. Gilbert, P.A. Parilla, J.L. Alleman, G.L. Hornyak, K.M. Jones, M.J. Heben, Proceedings of the 2002 U.S. DOE Hydrogen Program Review NREL/CP-610-32405.