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Hydrogen storage in carbon nanostructures

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Abstract

The paper gives a critical review of the literature on hydrogen storage in carbon nanostructures. Furthermore, the hydrogen storage of graphite, graphite nanofibers (GNFs), and single-walled carbon nanotubes (SWNTs) was measured by thermal desorption spectroscopy (TDS). The samples were ball milled under Ar or D_2 atmosphere in order to modify the microstructure which was characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. These investigations show a reversible hydrogen storage only for SWNTs and in addition indicate that an opening of the SWNTs is essential to reach high storage capacities.

Keywords: Hydrogen storage; Graphite nanofibers; Carbon nanotubes

1. Introduction

The time span for commercializing fuel cell vehicles may be drastically shortened if an adequate hydrogen storage device will be found in the near future. The first report [1] on hydrogen storage in single-walled carbon nanotubes (SWNTs) estimated a high possible storage capacity for purified material and initiated a tremendous research activity on SWNTs as well as graphite nanofibers (GNFs) concerning their hydrogen uptake. In the present paper we will give a critical review of the literature. Furthermore, own measurements of the hydrogen storage on SWNTs and GNFs will be shown.

2. Carbon nanostructures

The three well-known forms of carbon are diamond, graphite and fullerenes. In diamond each carbon has four bonds to its neighbors and forms a three-dimensional lattice. Graphite is built up of two-dimensional hexagonal sheets of carbon atoms where the carbon carbon distance in plain is 1.42 Å and the distance between the sheets is 3.35 Å.

In the 70s graphite nanofibers (GNFs) were discovered which consist of graphite platelets stacked together in various orientations to the fiber axis with an interlayer spacing similar to bulk graphite. The length of these GNFs can vary between 5 and 100 μm and their diameter between 5 and 200 nm. For details on the structure see Refs. [2,3]. In the present paper we only mention one configuration of GNFs the so-called herringbone type where graphite sheets are stacked with a certain angle to the fiber axis or conically shaped graphite sheets are stacked. In transmission electron microscopy investigations both structures yield in projection a fish-bone like image. Concerning a possible hydrogen uptake, geometrically, this structure possesses advantages due to the accessibility of all sheets from the outside and short diffusion paths into the nanostructure.

The discovery of the fullerenes opened the door to a new class of carbon materials. Carbon nanotubes were first observed in 1991 by Iijima [4]. Simply speaking these nanotubes are built of a finite graphite sheet which is rolled to a tube. A variety of types exists which is either made of one layer and therefore called single-walled nanotube (SWNT) or more than one layer called multi-walled nanotube (MWNT) (for details see Ref. [5]). Here we focus on SWNTs which can be prepared with diameters between 1 and 2 nm. Typically, these SWNTs have caps at the end which have structures related to the fullerenes.

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Furthermore, SWNTs form bundles owing to the Van der Waals forces between the tubes. These arrays of SWNTs form a regular triangular array with a distance of about 1.7 nm and are called nanoropes. These nanoropes typically grow in lengths of several μm. Concerning the hydrogen storage the structure has two possible sites: (i) inside the tubes and (ii) in the interstitial sites between the tube array. In the case of a long SWNT closed with fullerene-like caps at the end, the hydrogen can only get access to the tube interior via the six ring of the graphite-like tube wall. An opened tube with removed caps may give an easier access for the hydrogen molecule into the tube. Typically, the tubes are very long and therefore a good diffusivity of the hydrogen inside the tube will be required in order to fill the whole tube volume. Furthermore, one can imagine that a structural defect in the tube or a sharp bend of the tube may block the hydrogen diffusion. Therefore, cutting the tubes in shorter pieces may help to overcome this problem. Concerning the interstitial sites of the rope array similar arguments hold. The access from the side requires diffusion between the closest tube–tube distance whereas the interstitial sites are directly accessible from the rope ends. To fill the whole volume of these interstitial sites or better cylinders, owing to its extension in one dimension along the whole rope, will require a good hydrogen diffusivity inside these cylinders. Again cutting the rope in short pieces may help to improve hydrogen storage and its kinetics.

3. Measurement of hydrogen storage

Mainly, three different techniques are applied to study the hydrogen storage in solids. The volumetric method measures the pressure drop owing to hydrogen absorption after applying a hydrogen pressure to the specimen contained in a constant volume, e.g. Refs. [6,7]. Similarly the pressure increase due to desorption can be measured. For good accuracy and reliable results, this method requires typically specimen masses of 500 mg or higher. Furthermore, any leakage or temperature instability of the apparatus may give rise to large experimental errors. The advantage of this technique is that both absorption and desorption can be measured and that the conditions are similar to usage in a storage tank.

The gravimetric method measures the weight changes of the specimen due to absorption or desorption of hydrogen. In specially designed devices a high accuracy can be achieved even at sample masses of 10 mg, e.g. Refs. [8,9]. However, this technique is sensitive to all gasses absorbed or desorbed since it is only based on weighing.

Thermal desorption spectroscopy (TDS) measures only the hydrogen desorption in high vacuum utilizing mass spectrometry. Moreover, the method is selective and highly sensitive allowing to study samples with masses even below 1 mg, e.g. Refs. [1,10]. The sensitivity and selectivity can be even improved by using deuterium loaded specimens [10]. In this case no disturbing background from water or other hydrogen containing adsorbents occurs.

4. Experiments in literature

4.1. Graphite nanofibers

In 1998 Baker et al. [11] reported extremely high hydrogen uptake in GNFs. They applied a pressure of 12 MPa at 300 K and monitored the pressure drop utilizing the volumetric method. Several groups and companies succeeded in fabricating GNFs. However, they could not confirm the high hydrogen storage capacity; e.g. Ahn et al. [12] found in GNFs applying the volumetric method with a pressure of 8 MPa at 77 K and 18 MPa at 300 K less than 0.01 wt.% hydrogen storage. Ströbel et al. [8] measured the hydrogen adsorption on different carbon materials using a microbalance at 12.5 MPa and 296 K and observed a maximum weight increase corresponding to a hydrogen uptake of 1.6 wt.%. A group from the Chinese Academy of Science [6] reported a hydrogen uptake of 10–13 wt.% at 11 MPa and room temperature after boiling the GNFs in HCl. In a further publication [13] the same group reduces the values for the hydrogen storage capacity of GNFs by a factor of two. Up to now none of these experiments could be repeated or confirmed by other groups. We performed volumetric experiments at 14 MPa using GNFs prepared by catalytic chemical vapour deposition (CVD) at the IFW in Dresden, Germany and observed a hydrogen uptake lower than 0.05 wt.%. Loading GNFs at ambient pressure with deuterium and measuring the desorption utilizing TDS showed values of the hydrogen storage below 0.02 wt.%.

In 1999 Chen et al. [14] reported a large hydrogen uptake in GNFs and even graphite doped by the alkali metals. They measured with a thermo-gravimetric method the weight changes of the carbon samples heated up in a continuous hydrogen flow. However, their results have been taken into doubt by Yang [15]. Yang attributed most of the weight uptake to moisture by repeating the experiment under wet and dry hydrogen flow. Chen et al. [14] performed the alkali metal doping by – as they call it – a solid state reaction using nitrate and carbonate salts of the alkali metals. It is known that heating the mixture of carbon or GNFs with $LiNO_3$, and Li_2CO_3 under hydrogen flow results in the formation of LiO_2 [16,17]. By reproducing the experiments of Chen et al. we could confirm the following chemical reactions

$$2\,LiNO_3 + C + H_2 \rightarrow Li_2CO_3 + H_2O + 2\,NO \qquad (1)$$

and then

$$Li_2CO_3 + H_2 \rightarrow Li_2O + H_2O + CO, \qquad (2)$$

by X-ray diffraction and gas analysis. As LiO_2 is highly hygroscopic the mixture used by Chen et al. may indeed be very sensitive to moisture in the thermo-gravimetric experiment. This interpretation is supported by the fact that we did not find any hydrogen desorption in graphite doped with Li or K.

4.2. Single-walled nanotubes

Dillon et al. [1] investigated by thermal desorption spectroscopy the hydrogen storage capacity of non-purified bundles of SWNTs. The amount of hydrogen desorbed from the total sample was 0.01 wt.% and they estimated for pure SWNTs a hydrogen storage capacity of 5–10 wt.% at pressures less than 0.1 MPa near room temperature by assuming that this hydrogen content is due to the small fraction of SWNTs present in the sample. Recent results yielded about 7 wt.% for purified SWNTs treated by a special opening method [18]. Ye et al. [19] reported a storage capacity of 8 wt.% for purified single-walled carbon nanotubes. This high value was obtained at 80 K and for a hydrogen pressure of 12 MPa. Prior to the measurement, some of the material was sonicated for 10 h in dimethyl formide then vacuum degassed for 10 h at about 500 K. Liu et al. [20] showed by volumetric measurements on SWNTs with large mean diameters of 1.85 nm a reproducible storage capacity of 4.2 wt.% at room temperature and 10 MPa H_2 pressure. The SWNTs were soaked in hydrocloric acid and then heat-treated in vacuum. Furthermore, they reported that most of the stored hydrogen can be released under ambient pressure at room temperature. Again it should be noted, that none of these experiments could be repeated or confirmed independently in other laboratories up to now.

5. Own experiments

5.1. Experimental

Three different forms of carbon were used as starting material, graphite powder with an average particle size of 50 μm purchased from Merck, GNFs prepared by catalytic chemical vapour deposition (CVD) with ferrocene as catalyst at the IFW Dresden, Germany, and SWNTs produced by arc discharge with Ni and Y catalysts at the University of Montpellier II, France. The material containing SWNTs was taken from the so-called collerette region in the reaction chamber and contains in this unpurified state less than 50% of SWNTs plus amorphous carbon and metallic catalyst particles.

The microstructure of all starting materials was modified by ball milling with a stainless steel bowl and balls utilizing a plenatary ball mill (Fritsch). After filling, the bowl was evacuated and then pressurized by Ar (0.9 MPa) to avoid adsorption of reactive gases or water during the milling process. For reactive ball milling the bowl was pressurized with deuterium (0.9 MPa, purity 99.7%). Typically the milling time was 24 h and the rotation speed of the bowl 440 rpm. After milling the samples were shortly exposed to air in order to weigh and transfer to the TDS equipment. In the TDS apparatus the samples can be heated by a radiation furnace up to 1000 K in high vacuum (10^{-4} Pa). Without air contact the samples can be exposed to D_2 atmosphere (0.08 MPa, purity 99.7 %) for deuterium uptake. The typical loading time is 15 min. The desorption and loading procedure can be repeated several times to test reversibility. Using deuterium the TDS apparatus has an extremely high sensitivity and more or less no disturbing background is observed (for details see Ref. [10]). It should be noted, that although deuterium was used in our experiments the values of the storage capacity are given in weight percent of hydrogen (wt.%) in order to compare the hydrogen storage capacity with other publications.

5.2. Results and discussion

5.2.1. Ball milling under Ar

During the ball milling process the carbon materials get mechanically damaged when hit between balls or ball and bowl wall. The acceleration of the balls may reach up to 16 times the earth acceleration. In the transmission electron microscope (TEM) damages in the bundle structure and strongly bent or broken ropes can be observed. SWNTs were ball milled under Ar, shortly exposed to air to transfer into the TDS apparatus and after evacuating exposed 15 min to 0.08 MPa D_2 atmosphere. The following TDS measurement up to 1000 K shows no deuterium desorption within the experimental error limits. However, after heating in high vacuum (10^{-4} Pa) and exposure to D_2 atmosphere of 0.08 MPa at room temperature, the subsequent TDS run shows a desorption maximum at 558 K (Fig. 1). The amount of deuterium desorbed corresponds to a gravimetric storage capacity for hydrogen of lower than 0.1 wt.%. The desorption maximum is reversible, i.e. after heating and exposure to D_2 atmosphere at room temperature it occurs again. For the first few cycles the maximum temperature shifts to lower temperatures and after more than five cycles is almost stable. Exposing the deuterium loaded sample to air results in a desorption maximum at higher temperatures (Fig. 1), however, the deuterium content remains about the same. This stability under air at room temperature was tested for 48 and 1000 h without showing any significant change of the maximum and deuterium content. The reversibility of adsorption and desorption cycles allows to study the kinetics of the desorption maximum by applying different heating rates from 0.8 to 19.6 K min^{-1}. The position of the desorption peaks shifts to higher temperature with increasing heating rate (Fig. 2). This shift of the maximum temperature can be analysed by assuming a first order desorption reaction. This reaction is described by $\ln(T_m^2/\beta) = E_D/RT_m$, where

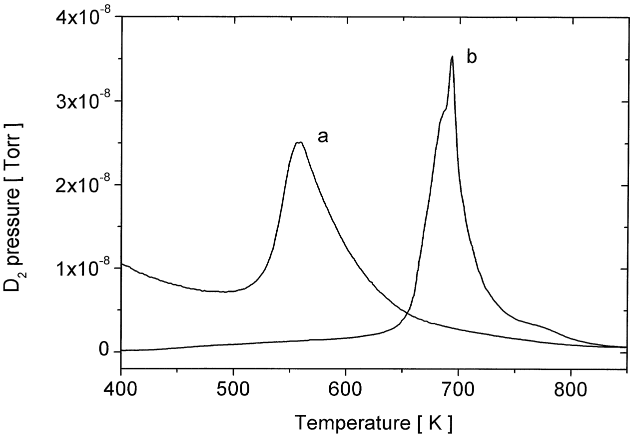

Fig. 1. Thermal desorption rate of deuterium in high vacuum plotted against temperature for SWNTs ball milled under Ar atmosphere for 24 h and exposed to D_2 atmosphere (0.08 MPa at RT for 15 min). Curve **a** represents the measurement without exposing the sample to air after deuterium loading and curve **b** after exposing the sample for 1000 h to air (heating rate 4.9 K min^{-1}).

T_m denotes the maximum temperature, E_D the activation enthalpy of desorption, β the heating rate and R the universal gas constant [21]. The Arrhenius representation yields an activation enthalpy of $E_D = (145 \pm 20)$ kJ mol^{-1} (see inset Fig. 2).

For comparison we applied the same loading procedures (1. D_2 0.08 MPa, RT and 2. heating to 1000 K in high vacuum with successive D_2 exposure) to SWNTs prior to ball milling and GNFs prior as well as after ball milling. However, within the experimental error no desorption maximum was observed and the total deuterium release was at least 20 times lower if not negligible.

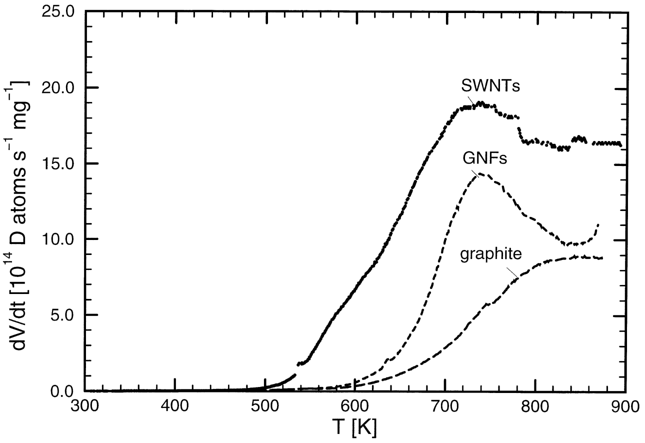

Fig. 3. Thermal desorption rate of deuterium in high vacuum plotted against temperature for SWNTs, GNFs and graphite ball milled under D_2 atmosphere of 0.9 MPa for 24 h (heating rate 4.9 K min^{-1}).

5.2.2. Reactive ball milling under D_2

By ball milling the carbon materials under D_2 atmosphere, in addition to the mechanical damage, a reaction between the carbon and deuterium may take place, e.g. formation of covalent bonds. Fig. 3 shows the deuterium desorption rates into high vacuum of the three carbon materials after ball milling under 0.9 MPa D_2 atmosphere (heating rate 4.9 K min^{-1}). For GNFs and SWNTs in the desorption spectrum a maximum is observed at 720 K, whereas graphite reaches its maximum desorption rate at 900 K. It should be noted, that all samples show a fairly high desorption rate up to 900 K, which is the highest temperature of heating. Therefore, the determined hydrogen storage capacities correspond to the amount of

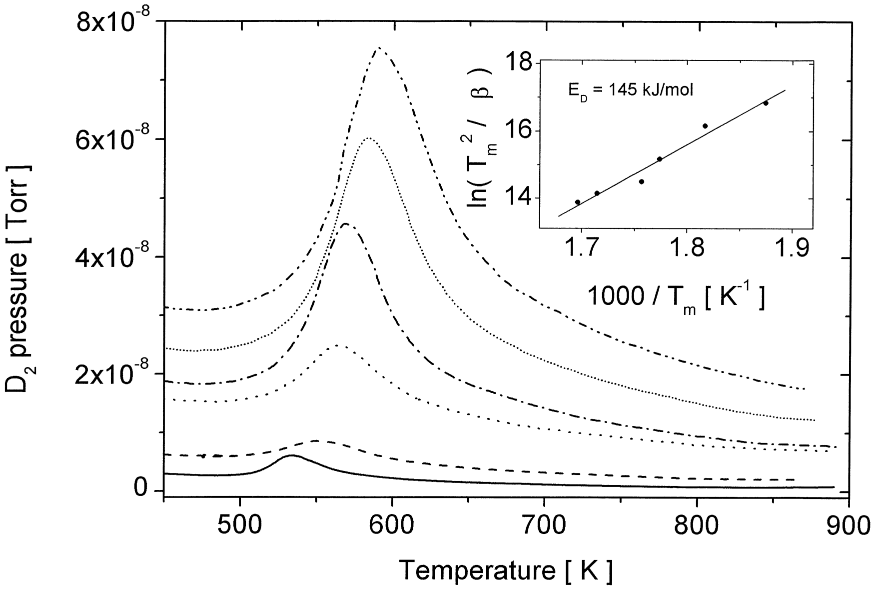

Fig. 2. Thermal desorption rate of deuterium in high vacuum plotted against temperature for SWNTs ball milled under Ar atmosphere for 24 h and exposed to D_2 atmosphere (0.08 MPa at RT for 15 min). The different curves represent different heating rates, 0.8 K min^{-1} (lowest curve), 1.7, 4.9, 9.8, 14.7 and 19.6 K min^{-1} (highest curve). The inset shows an analysis of the activation enthalpy according to Ref. [21] (see text).

deuterium released up to 900 K. Accordingly, we found for SWNTs 1.0 wt.%, for GNFs 0.5 wt.% and for graphite 0.3 wt.% hydrogen storage capacity. The actual deuterium content of the materials is higher since there is still desorption at 900 K. Orimo et al. [22] reported a storage capacity of 5 wt.% for graphite ball milled 24 h under 1 MPa H_2 atmosphere. This content was determined by oxygen-combustion hydrogen analysis, which measures the total amount of hydrogen by burning the sample.

After the first TDS measurements, i.e. heating in high vacuum up to 900 K, the samples are exposed to D_2 atmosphere (0.08 MPa for 15 min at RT) without air contact. However, for all three carbon structures the following TDS measurements do not show any deuterium release up to about 850 K. Reaching 900 K an increasing deuterium desorption rate is observed, which may be due to deuterium still present from the ball-milling process under 0.9 MPa D_2. This remaining deuterium may block sites for reloading in the carbon structure.

6. Conclusions

Hydrogen storage in carbon nanostructures is a very attractive topic since owing to the small mass of carbon and its newly found nanostructures high potential storage capacities are expected. Nevertheless, up to the present day none of the promising experiments on hydrogen storage in GNFs as well as SWNTs could be repeated by an independent group in another laboratory. For GNFs most of the experiments showing large storage capacity have been taken into doubt and therefore only little hope is left.

SWNTs are more difficult to prepare in large quantities and high purity. The experiments of Ye et al. [19] and Dillon et al. [1] are not yet independently confirmed. Our experiments on ball milled graphite GNFs and SWNTs show a small reversible hydrogen uptake only for SWNTs. This suggests that SWNTs can store hydrogen and an opening or cutting of the tubes and ropes is essential. Owing to the unpurified materials used the observed total storage capacities are relatively low up to now. Preliminary experiments on purified SWNTs cut by ultra sonication yielded higher storage capacities.

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References

[1] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.

[2] M.S. Dresselhaus, G. Dresselhaus, K. Sugihara, I.L. Spain, H.A. Goldberg, in: U. Gonser, A. Mooradian, K.A. Müller (Eds.), Graphite Fibers and Filaments, Springer, Berlin, 1988.

[3] N.M. Rodriguez, J. Mater. Res. 8 (1993) 3233.

[4] S. Iijima, Nature 354 (1991) 56.

[5] P.M. Ajayan, T.W. Ebbesen, Rep. Prog. Phys. 60 (1997) 1025.

[6] Y.-Y. Fan, B. Liao, Y.-L. Wei, M.-Q. Lu, H.M. Cheng, Carbon 37 (1999) 1649.

[7] G. Friedlmeier, M. Schaaf, M. Groll, Z. Phys. Chem. NF 183 (1994) 185.

[8] R. Ströbel, L. Jörissen, T. Schliermann, V. Trapp, W. Schütz, K. Bohmhammel, G. Wolf, J. Garche, J. Power Sources 84 (1999) 221.

[9] M.J. Benham, D.K. Ross, Z. Phys. Chem. NF 163 (1989) 25.

[10] N. Mommer, M. Hirscher, F. Cuevas, H. Kronmüller, J. Alloys Comp. 266 (1998) 255.

[11] A. Chambers, C. Parks, R.T.K. Baker, N.M. Rodriguez, Phys. Chem. B 102 (1998) 4253.

[12] C.C. Ahn, Y. Ye, B.V. Ratnakumar, C. Witham, R.C. Bowman Jr., B. Fultz, Appl. Phys. Lett. 73 (1998) 3378.

[13] H.M. Cheng, C. Liu, Y.Y. Fan, F. Li, G. Su, L.L. He, M. Liu, Z. Metallkd. 91 (2000) 306.

[14] P. Chen, X. Wu, J. Lin, K.L. Tan, Science 285 (1999) 91.

[15] R.T. Yang, Carbon 38 (2000) 623.

[16] M. de Forcrand, Ann. Chim. Phys. 15 (1908) 433.

[17] Gmelin Handbuch der anorganischen Chemie, Verlag Chemie, Berlin, 1927, p. 71.

[18] M.J. Heben, at the International Winterschool on Electronic Properties of Novel Materials in Kirchberg, Austria, 2000.

[19] 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 (1999) 2307.

[20] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, Science 286 (1999) 1127.

[21] R.J. Madix, in: R. Vanselov (Ed.), Chemistry and Physics of Solid Surfaces, CRC, Boca Raton, 1979, p. 63.

[22] S. Orimo, G. Majer, T. Fukunaga, A. Züttel, L. Schlapbach, H. Fujii, Appl. Phys. Lett. 75 (1999) 3093.