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Are carbon nanostructures an efficient hydrogen storage medium?

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Abstract

Literature data on the storage capacities of hydrogen in carbon nanostructures show a scatter over several orders of magnitude which cannot be solely explained by the limited quantity or purity of these novel nanoscale materials. With this in mind, this article revisits important experiments. Thermal desorption spectroscopy as a quantitative tool to measure the hydrogen storage capacity needs an appropriate calibration using a suitable hydride. Single-walled carbon nanotubes that have been treated by ultra-sonication show hydrogen uptake at room temperature. However, this storage can be assigned to metal particles incorporated during the sonication treatment. Reactive high-energy ball milling of graphite leads to a high hydrogen loading, however the temperatures for hydrogen release are far too high for application. In view of today's knowledge, which is mainly based on experiments with small quantities and poorly characterised samples, carbon nanostructures at around room temperature cannot store the amount of hydrogen required for automotive applications.

Keywords: Hydrogen storage; Carbon nanotubes; Nanostructured graphite

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1. Introduction

Hydrogen storage in carbon materials is a very attractive topic since high gravimetric storage capacities may be possible owing to the low specific weight of carbon. For automotive applications, a hydrogen storage capacity of greater than 6.5 wt% is required as set by the US Department of Energy [1]. Besides the capacity, industrial applications require ambient temperatures for hydrogen release and moderate pressures for storage.

Today, different nanostructured carbon materials are available, e.g. carbon nanofibers, carbon nanohorns, multi-walled carbon nanotubes, and single-walled carbon nanotubes. All these new carbon structures exhibit a nanoscale extension in two dimensions. These new geometries, which have been discussed in several reviews [2], may give rise to new interactions of carbon with hydrogen.

Very promising publications reporting high hydrogen storage capacities in carbon nanotubes resulted in enormous research activity, yielding much experimental data. These data, however, exhibit a large scatter, as exemplified for single-walled carbon nanotubes (SWNTs) in Fig. 1. For graphitic nanofibers the results are even more scattered and storage capacities from 67 down to 0.1 wt% have been reported. However, the extremely high storage capacities have never been independently reproduced in another

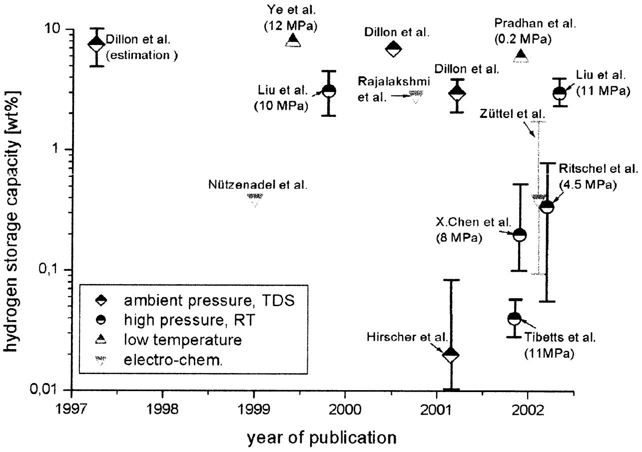

Fig. 1. Experimental data for hydrogen storage capacities (logarithmic scale) in SWNTs versus publication year for different methods, pressures and temperature regimes.

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laboratory. Considering the experimental results for metal hydrides, the storage capacities of which have been reported to vary only within a few percent since their discovery many years ago, why it is so difficult to determine the hydrogen storage capacity of carbon nanostructures? One reason may be the limited quantity and purity of carbon nanotubes. Furthermore, a reliable characterisation of carbon nanostructures and the determination of their purity is extremely difficult. But can these difficulties really explain the extreme discrepancies between different research groups?

In view of the above, this article assesses the following: (i) the quantitative analysis of the storage capacity by thermal desorption spectroscopy; (ii) hydrogen storage in SWNTs at ambient pressure and temperature; (iii) the dependence of the storage capacity on the specific surface area; and (iv) hydrogen loading of nanostructered carbon by reactive ball milling. Finally, we conclude by giving a summary and outlook with respect to technical applications.

2. Quantitative thermal desorption spectroscopy

In thermal desorption spectroscopy (TDS), hydrogen desorption is determined while heating the sample in high vacuum. The desorbed gases are selectively analysed utilising a quadrupolar mass spectrometer. This highly sensitive method allows the study of small samples of less than 1 mg. The sensitivity can be improved by using deuterium-loaded samples and thereby avoiding any background disturbance from water or other hydrogen-containing adsorbents [3].

For quantitative analysis the TDS apparatus can be calibrated by introducing a known amount of hydrogen molecules into the high vacuum system. This amount of hydrogen must give rise to a pressure increase which is within the range of operation of the mass spectrometer. Ideal materials are metal hydrides containing weighable amounts of hydrogen which release it under heating. For easy handling the hydride should be stable at room temperature and non-reactive under atmospheric conditions. Ti hydride, for example, is stable for years under laboratory conditions owing to the high desorption temperature. Using commercially available TiH_2, the TDS apparatus can be consistently calibrated for quantitative analysis with an error of less than ±5% [4].

A critical factor is the use of hydrides which react with moisture, e.g. CaH_2. Fig. 2 shows the desorption spectrum of CaH_2 briefly exposed to air during weighing. Compared with TiH_2 the spectrum consists of two maxima and, during the first desorption maximum, water is detected in addition to hydrogen [4]. On exposure to air, CaH_2 absorbs moisture [5]:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

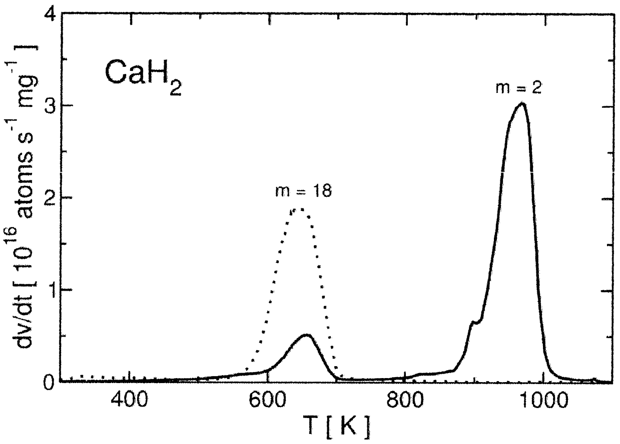

Fig. 2. Thermal desorption spectrum of hydrogen ($m = 2$) and water ($m = 18$) in high vacuum versus temperature (heating rate 5.0 K/min) for CaH_2 briefly exposed to air.

During the TDS heating run, $Ca(OH)_2$ decomposes above 520 K:

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

One part of the water evaporates and the other reacts with CaH_2, leading to the evolution of hydrogen:

$$H_2O + CaH_2 \rightarrow CaO + 2H_2$$

Decomposition of the remaining CaH_2 into Ca and H results in the hydrogen desorption peak at 970 K. Owing to this hygroscopic behaviour of CaH_2, exposure to air changes the composition depending on the humidity and time. Therefore, using this kind of hydride for calibration is erroneous and may cause an error exceeding a factor of 2 [4].

3. Hydrogen storage in SWNTs at ambient pressure

In 1997, Dillon et al. [6] first published investigations on the hydrogen storage capacity of single-walled carbon nanotubes. Non-purified samples containing only a trace of SWNTs were exposed to hydrogen at ambient pressure and room temperature. The amount of hydrogen in the overall sample was measured at 0.01 wt% by thermal desorption spectroscopy. Based on this measurement the authors estimated a hydrogen storage capacity of 5–10 wt% for pure SWNTs, assuming that the small hydrogen content was due to the small fraction of SWNTs present in the sample. In further work, Dillon et al. [7] developed a special opening and cutting procedure and measured a storage capacity of about 7 wt% for purified SWNTs after loading at 0.07 MPa and at room temperature by prior heating to 900 K in high vacuum. However, the temperature of hydrogen release was now significantly higher (double maximum at 450 and 600 K) compared to their former investigations (single maximum at 300 K). The opening and cutting method was high-power ultra-sonication in HNO_3, which results in contamination of the sample with metal particles due to cavitation of the sonicator horn [8]. The material of this horn has the composition 90 wt% Ti, 6 wt% Al, and 4 wt% V, which is commonly used because of its chemical resistance. The authors proposed that the introduced Ti alloy particles 'somehow' stimulates hydrogen adsorption of the SWNTs [9–11].

In a joint project of the German Ministry of Education and Research (BMBF) we carefully tried to reproduce the experiments of Dillon et al., but obtained contrary results [12]. Various carbonic materials, e.g. SWNTs purified by various methods, graphite, and diamond powder, were suspended in 5 M HNO_3 and treated by high-power sonication (50 W/cm^2) for different times. An ultra-sonic horn made of Ti alloy as well as of stainless steel was used for the opening and cutting procedure. Prior to hydrogen storage the samples were heated in high vacuum (10^{-5} Pa) up to 900 K and then, without air contact, exposed to a deuterium atmosphere of 0.08 MPa for 15 min. The hydrogen storage capacity was analysed by TDS. All carbon materials treated by the Ti alloy sonicator horn showed hydrogen desorption, i.e. hydrogen storage. In contrast, no hydrogen desorption (below 0.005 wt%) was observed if the SWNTs were sonicated with a stainless steel horn.

The desorption spectra for purified SWNTs (from Tubes@Rice, produced by laser ablation) sonicated for different times using the Ti alloy horn are shown in Fig. 3. The inset shows the total deuterium content desorbed (given in units of wt% hydrogen), which increases linearly with sonication time. The maximum storage capacity was 1.5 wt% in purified SWNTs sonicated with a Ti alloy horn for 24 h.

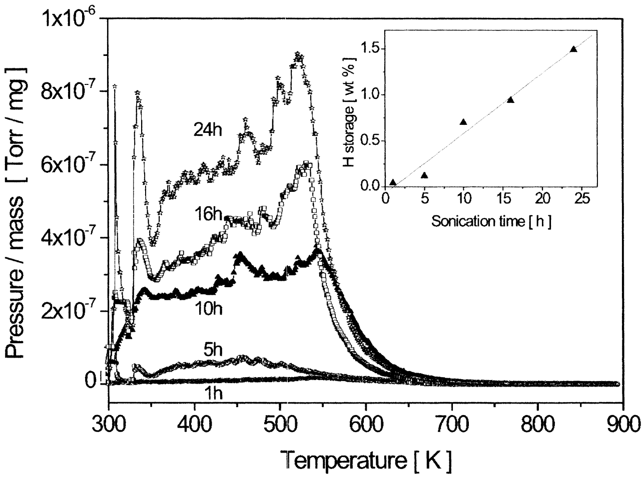

Fig. 3. Thermal desorption rate of deuterium in high vacuum plotted against temperature (heating rate 4.8 K/min) for SWNTs sonicated in 5 M HNO_3 for different times using a Ti alloy probe, heated to 900 K in high vacuum and then deuterium loaded (0.08 MPa D_2 at room temperature for 15 min). The inset shows the total hydrogen content (note that storage capacity is given in wt% of hydrogen) plotted versus the sonication time [12].

Transmission electron microscopy (TEM) investigations and X-ray diffraction (XRD) measurements show metal particles of the ultra-sonic tip material incorporated in the SWNTs. After loading with deuterium, the XRD spectrum shows characteristic diffraction peaks for Ti deuteride [12]. Furthermore, chemical analysis of the samples yields a linear increase of the Ti content with sonication time. After 24 h sonication the sample contained about 60 wt% Ti, as determined by inductively coupled plasma (ICP) using optical emission spectroscopy (OES). By applying indirect methods such as thermo-gravimetric analysis (TGA) the titanium content may be underestimated, since TiC may be formed during heating of the mixture of carbon nanostructures with Ti alloy particles (e.g. see Ref. [13]). TiC is very stable and is not oxidised in air. In TGA, this may cause a deviation of the Ti content of up to 30% from the real Ti concentration.

Assuming that all hydrogen is stored in the Ti alloy particles, the hypothetical hydrogen content of the metal particles lies in the range 0.4–3.3 wt%, which may be compared to the storage capacity of the Ti alloy of 3.4 wt%. Heat treatment under high vacuum prior to hydrogen loading is a well-known activation procedure for Ti, by removing the natural oxide layer [14]. Ti then readily takes up hydrogen at ambient pressure and room temperature. Furthermore, the TDS spectra of all different carbon samples, e.g. graphite and even diamond powder with Ti alloy particles introduced during sonication, are very similar, indicating the fingerprint of Ti alloy hydride powder with a particle size between several nanometers and 1 μm.

The apparent contradiction between our results and those of Heben's group led to a controversy [15,16], which could easily be resolved by reproducing the results on the same single-walled carbon nanotubes in an independent laboratory. However, the exchange of samples is prohibited by industrial contracts. The latest reports from Dillon et al. show lower hydrogen contents if measured by a volumetric method [9] or if using new SWNT material prepared utilizing a different laser [10], which typically yield 2.3 wt% absorption or 2–4 wt% desorption, respectively. Furthermore, by applying an unknown cutting method, which avoids contamination by metal particles, they recently reported a hydrogen content below 1 wt% [11].

4. Specific surface area and hydrogen storage capacity

At high pressure and ambient temperature, none of the results claiming high hydrogen storage could be independently reproduced, and recent carefully performed experiments reported values below 1 wt% [17,18]. Ströbel et al.

measured a maximum storage capacity of 1.3 wt% for graphitic nanofibers using the gravimetric method at hydrogen pressures up to 12.5 MPa. Furthermore, they proposed a correlation between specific surface area and storage capacity [25]. At low temperature, all experiments typically show an increased hydrogen storage capacity [19–22]. The correlation between the specific surface of carbonic materials and hydrogen adsorption was examined by Nijkamp et al. [21]. They investigated different adsorbents for hydrogen at 77 K and atmospheric pressure using the volumetric method. For carbonic materials they found an approximately linear correlation between the specific surface area determined by BET measurements and the hydrogen adsorption. The highest storage capacity, about 2 wt%, was obtained for activated carbon with about 2000 m^2/g specific surface area, whereas GNFs, possessing lower surface areas, showed less than 1 wt%. Schlapbach and Züttel [24] included their values of the hydrogen storage capacities, obtained for different carbon nanostructures by the electrochemical method at room temperature [23], in one plot together with the low-temperature adsorption data measured by Nijkamp et al. [21]. All experimental data could be described by a storage capacity of 1.5 wt% per 1000 m^2/g specific surface area [24]. Chen et al. [22] examined the hydrogen storage capacity of different nanostructured carbonic materials at 77 K and a higher pressure of 5 MPa and therefore determined slightly higher values.

5. Hydrogen loading by reactive ball milling

One effective method for preparing defective structures in carbonic materials, which may act as trapping centers for hydrogen, is mechanical ball milling. Orimo et al. [26] investigated the hydrogen storage capacity of nanostructured graphite which had been high-power ball milled under hydrogen pressure. This reactive ball milling leads to a high hydrogen concentration of up to 7.4 wt% after milling for 80 h, as determined by oxygen combustion [26]. For technological applications the dehydriding temperature and kinetics of this nanostructured carbon material are important and may be examined by TDS.

Orimo et al. [26] prepared a sample by the ball milling of high-purity graphite powder with an initial particle size of 200 μm in a small steel vial (30 cm^3) with 20 steel balls of 7 mm diameter. After evacuation of the vial using a turbomolecular pump, an initial deuterium or hydrogen pressure of 1.0 MPa was introduced. The sample was milled using a planetary ball mill apparatus at 400 rpm for periods of 1 to 80 h and handled under argon atmosphere prior and after milling. TDS measurements showed two hydrogen or deuterium desorption peaks starting at about 650 and 950 K, respectively [27]. The low-temperature hydrogen peak was accompanied by the desorption of hydrocarbons such as CH_4 and C_2H_6.

Hirscher et al. [28] and Haluska et al. [29] investigated, by TDS, the hydrogen storage capacities of different carbon nanostructures ball milled under deuterium, hydrogen and argon pressure. Using Raman spectroscopy and transmission electron microscopy they observed that the structure of SWNTs is destroyed within a few minutes of ball milling [29]. These results indicate that, for long-time high-energy ball milling, a highly defective carbon nanostructure is obtained independently of the initial structural form of the carbon material.

Former investigations yielded a storage capacity of 0.3 wt% for graphite ball milled for 24 h using a planetary mill with a larger stainless steel bowl (85 cm^3) and 12 balls [28]. However, using 30 stainless steel balls the hydrogen uptake was strongly increased after long-time high-energy ball milling. Fig. 4 shows the thermal desorption spectrum of hydrogen ($m = 2$) and CH_4 ($m = 16$) for graphite ball milled under 0.8 MPa hydrogen atmosphere for 48 h. Hydrogen evolution starts at around 600 K and exhibits its first maximum at 863 K, which is accompanied by the desorption of CH_4 at a slightly higher temperature with a maximum at 850 K. At 1066 K, a second sharp hydrogen desorption maximum is observed. Using thermal desorption, a storage capacity of 1.53 wt% is measured for the total sample. Chemical analysis yielded a hydrogen concentration of 2.4 wt%, a carbon content of 44 wt% and Fe and Ni metallic impurities at 40.6 and 3.6 wt%, respectively. These high levels of metallic contamination are caused by abrasive wear of the milling tools. Taking the fraction of metal into account the hydrogen content of the carbon material is greater than 5 wt%, which is consistent with the observation of Orimo et al. [26,27]. Reloading by exposing the samples to a hydrogen atmosphere was not possible after the initial desorption. Owing to the high local energy transfer during the milling process, C–H bonds are formed, which can only be broken by high temperature. For

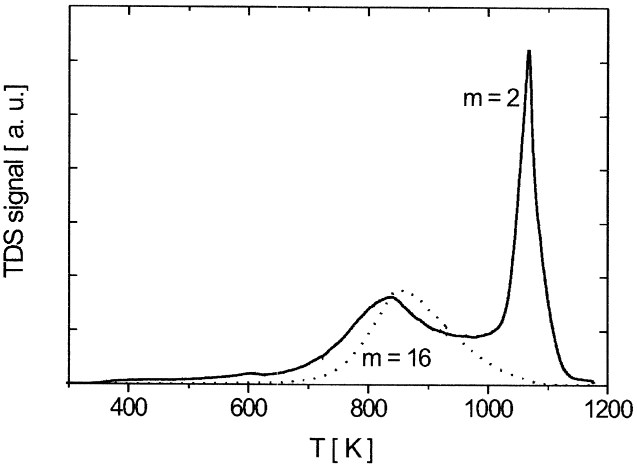

Fig. 4. Thermal desorption rate of hydrogen ($m = 2$) and CH_4 ($m = 16$) in high vacuum as a function of temperature (heating rate 4.8 K/min) for graphite ball milled under hydrogen atmosphere (0.8 MPa) for 48 h.

technological applications, therefore, hydrogen release is at too high temperatures and the loading process is irreversible.

6. Conclusions

The large scatter in the experimental data for hydrogen storage capacities in nanostructured carbon cannot by explained by the limited quantity or quality of the samples and, therefore, we revisited some key experiments.

1. For a quantitative measurement of the hydrogen storage capacity by TDS, calibration by an appropriate hydride is essential. Using stable hydrides, e.g. TiH_2, a reliable calibration is possible. However, hygroscopic hydrides, e.g. CaH_2, are not reliable.
2. High-power ultra-sonication incorporates metal particles into the sample. SWNTs sonicated using a Ti alloy horn show hydrogen uptake at ambient pressure and room temperature. However, the hydrogen storage can be assigned to the Ti alloy particles incorporated during processing.
3. At low temperature the hydrogen storage capacity increases and is proportional to the specific surface area of the nanostructured carbon material, indicating physisorption.
4. Using high-energy reactive ball milling under a hydrogen atmosphere graphite can be loaded with large amounts of hydrogen (above 5 wt%). However, the desorption temperature is high (above 700 K) and re-loading in a hydrogen atmosphere is impossible.

Summarizing, at the present stage of development, no carbon nanostructure fulfills the requirements for storage capacity or release temperature for technical applications.

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