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Hydrogen sorption by carbon nanotubes and other carbon nanostructures

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Abstract

We have analyzed the hydrogen storage capability of a set of carbon samples including a variety of carbon nanotubes, in the gas phase and in the electrolyte as well. The nanotube samples synthesized in our laboratory by pyrolysis of acetylene are of the multi-wall type. The hydrogen sorption properties of our synthesized nanotubes were compared with the properties of commercially available nanotubes and high surface area graphite as well. The nanotube samples and the high surface area graphite as well absorb hydrogen up to 5.5 mass% at cryogenic temperatures (77 K). However, at room temperatures this value drops to ≈0.6 mass%. The electrochemical experiments on the carbon samples showed a maximum discharge capacity of 2.0 mass% at room temperature (298 K). The hydrogen tends to covalently bind to carbon when the absorption takes place at elevated temperatures (>573 K). Therefore, hydrocarbons desorbed from the sample were analyzed by means of temperature programmed desorption measurements. We conclude that the adsorption of hydrogen on nanotubes is a surface phenomenon and is similar to the adsorption of hydrogen on high surface area graphite. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen sorption; Carbon nanotubes; Graphite

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1. Introduction

The discovery of carbon nanotubes (CNT) in 1991 by Iijima [1] has stimulated research on a large variety of physical properties of the nanotubes. Carbon nanotubes are formed by rolled graphite sheets, with an inner diameter starting from 1 nm up to several nm and a length of 10–100 μm. The CNTs are described as usually closed on both sides by a hemisphere, i.e. half of a fullerene. Tubes formed by only one graphite layer are called single wall nanotubes (SWNT). Tubes consisting of multiple concentric graphite layers are called multi-wall nanotubes (MWNT). The interlayer distance in MWNTs is close to the interlayer distance in graphite ($0.5 \cdot c = 0.3355$ nm). But also much higher values were found due to a change from nested to rolled type of the nanotubes [2]. The diameter of SWNTs varies from 1 to 3 nm, whereas MWNTs show typical diameters of 30–50 nm.

In 1997, Dillon et al. [3] reported for the first time excellent hydrogen storage properties of SWNT. The SWNT samples were exposed to hydrogen gas ($P = 40$ kPa) at 273 K for 10 min and subsequently cooled to 133 K. The temperature programmed desorption spectroscopy of the SWNT sample shows two hydrogen peaks, the major peak at 150 K and a second peak at 300 K. Activated carbon and non activated SWNT exhibit only the low temperature peak. The hydrogen storage capacity was estimated to range between 5 and 10 mass%. However, measured hydrogen desorption was only 0.01 mass% of the sample and the content of SWNT in the sample was estimated to be 0.2 mass%. Furthermore, it was assumed that only the SWNT in the sample contribute to the hydrogen adsorption. This measurement was made on a very dilute SWNT sample, so the analysis required a large correction for 99.8 mass% of material that was assumed inert. However, the hydrogen adsorption in high porosity carbon (AX-21 carbon) is as high as 5.3 mass%, or 0.64 H/C, at a temperature of 77 K and a hydrogen pressure of 1 MPa [4]. Therefore, not only SWNT adsorb reasonable amounts of hydrogen at low temperatures but also other forms of carbon.

In spring 1998, Chambers et al. [5] described their findings on various carbon nanostructures. Hydrogen gas applied at $P = 11.35$ MPa was absorbed at room tempera-

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ture (298 K). The hydrogen storage capacity was found to be for tubular CNTs 11.26 mass%, for herringbone carbon nanofibres 67.55 mass%, for platelet carbon nanofibres 53.68 mass%, and finally for graphite 4.52 mass%. These extraordinary high values, which are roughly one-order of magnitude higher than everything known up to date caused an avalanche of research on hydrogen storage in carbon nanotubes. Until today nobody has been able to reproduce these results.

Nützenadel et al. [6] investigated the hydrogen sorption properties of nanotubes at room temperature (298 K) in an electrochemical system and found a maximum desorption (electrochemical discharge) capacity of 0.41 mass% with a SWNT sample from MER Corporation, Tucson, AZ, USA.

Hydrogen gas adsorption on purified SWNT samples was performed by Ye et al. [7]. The BET surface area of the SWNT sample was found to be 285 $m^2 g^{-1}$ and remained unchanged upon the hydrogen absorption and desorption process. The hydrogen adsorption obtained at a temperature of 80 K and a pressure of 0.32 MPa was $H/C=0.04$ for the SWNT sample and $H/C=0.28$ for the high surface area saran-carbon (1600 $m^2 g^{-1}$). At high hydrogen pressures (7 MPa) at a temperature of 80 K the hydrogen to carbon ratio reached $H/C=1$ (7.7 mass%) in the initial absorption. In the following absorption cycles the absorption isotherm was considerably shifted to higher pressure and a hydrogen to carbon ratio of $H/C=0.8$ was reached at 12 MPa. Liu et al. [8] applied high pressure (12 MPa) hydrogen gas at room temperature (298 K) to SWNT and followed the pressure change in time. The samples equilibrated after approximately 300 min and reached a maximum absorption of 4.2 mass% ($H/C=0.5$). About 20% of the absorbed hydrogen remained in the sample after desorption at room temperature. Fan et al. [9] investigated the hydrogen absorption of vapor-grown carbon nanofibers with a diameter of 5–300 nm. The fibers absorbed hydrogen up to 12.38 mass% when a hydrogen pressure of 12 MPa was applied. The absorption equilibrated upon 200–300 min.

Chen et al. [10] reported that a high hydrogen uptake of 14–20 mass% can be achieved for K- and Li-doped MWNT at a pressure of 0.1 MPa. The K-doped MWNT absorb hydrogen at room temperature, but they are chemically unstable, whereas the Li-doped MWNT are chemically stable, but require elevated temperatures (473–673 K) for maximum absorption and desorption of hydrogen.

Nanostructured graphite was investigated by Orimo et al. [11] for hydrogen absorption and desorption. Graphite was ballmilled for a maximum of 80 h in a 1-MPa hydrogen atmosphere. The hydrogen absorbed in the sample was determined by means of oxygen-combustion hydrogen analysis and turned out to be as high as 7.4 mass% ($C/H=0.95$). This result shows that high hydrogen absorption can also be realized without the hollow structure of nanotubes.

Rzepka et al. [12] calculated the amount of absorbed hydrogen for a slit pore and a tubular geometry. The amount of absorbed hydrogen depends on the surface area of the sample and the maximum is at 0.6 mass% ($T=300$ K, $P=6$ MPa). The calculation was verified experimentally with an excellent agreement. At a temperature of 77 K the amount of absorbed hydrogen is about one-order of magnitude higher than 300 K.

Stan and Cole [13] used the Feynman (semiclassical) effective potential approximation to calculate the adsorption potential and the amount of hydrogen adsorbed on a zigzag nanotube (13.0). The adsorption potential was found to be 9 $kJ\,mol^{-1}$ for hydrogen molecules inside the nanotubes at 50 K, the potential is about 25% higher as compared to the flat surface of graphite due to the curvature of the surface and therefore the increased number of carbon atoms interacting with the hydrogen molecule. The ratio of hydrogen adsorbed in the tube to that on a flat surface decreases strongly with increasing temperature and is 55 at 50 K and 11 at 77 K.

We have analyzed the hydrogen absorption and desorption of several nanotube and graphite samples in the gas phase and in the electrolyte as well. The results are compared with the well known properties of high surface area carbon materials.

2. Experimental

The carbon nanotube (CNT) samples were synthesized in a vacuum furnace at 920 K by pyrolysis of acetylene (12 vol% acetylene in nitrogen). Several other samples were purchased from the companies indicated. Most of the nanotube samples were investigated in their as produced state. A few samples were treated with diluted nitric acid (35%) in order to open the caps on the end of the nanotubes and therefore to make the void of the tube accessible for the hydrogen gas.

The hydrogen absorption and desorption properties of the nanotube samples were investigated by means of pressure–concentration isotherms ($P–C–T$), temperature programmed desorption spectroscopy (TDS), surface area measurement (BET) and electrochemical charge/discharge measurements.

Gas phase absorption and desorption were performed in a system equipped with a mass flow controller and pressure gauges ranging from 0.25 mbar to 100 bar. The volume of the system was 30 cm^3.

Temperature programmed desorption spectroscopy was performed with a liquid nitrogen cooled furnace at a heating rate of 4 $K\,min^{-1}$. The samples were first degassed in ultra high vacuum (base pressure 1×10^{-8} mbar) at 773 K for several hours. Subsequently the sample was loaded with hydrogen gas (12 bar) for 1–180 min at temperatures between 300 and 773 K. Then the samples were cooled with liquid nitrogen (77.4 K). The sample reactor was then connected to the UHV system and the remaining hydrogen was removed until the base pressure of the system was below 1×10^{-7} mbar. Subsequently the temperature was increased starting at 90 up to 800 K with a constant rate of 4 K min^{-1} and the desorbed gases were analyzed in a mass spectrometer (QMG 64 from Balzers).

The surface area of the CNT samples was measured by means of the BET method (Brunauer–Emmett–Teller) [14]. Before absorption, the samples were degassed at 773 K for at least half an hour at 10^{-2} mbar. A constant flow (0.5 standard cm^3 N_2 min^{-1}) of nitrogen gas was adsorbed at 77.4 K and the pressure was recorded. The surface area was calculated using the conversion factor of 102 $\text{m}^2\ \text{mol}^{-1}\ N_2$.

Electrodes of the nanotube material for the electrochemical investigation were manufactured by mixing 10 mg of the nanotubes with 90 mg of gold powder (Goodfellow, <53 μm) an cold pressed (500 MPa) in air to a pellet (7 mm in diameter). The nanotube suspension purchased from Tubes@Rice [15] was filtered and washed with distilled water and ethanol and dried in air. The resulting buckypaper was 250 μm thick. Discs of 7 mm in diameter were cut out and used as electrodes. The negative electrodes were tested in a half cell with a nickel plate as counter electrode, Hg/HgO reference electrode and 6 mol l^{-1} KOH as electrolyte. The charge/discharge experiments were conducted at constant current (20 mA g^{-1}), a capacity of 1000 mAh g^{-1} was charged and after a pause of 180 s the electrodes were discharged until the cut-off potential of 0.0 V versus the Hg/HgO electrode was reached.

3. Results and discussion

The common three units used to describe the hydrogen contents of a storage material are: [H/C] the ratio of hydrogen atoms per atom of storage material (carbon), [mass%] (old: [wt%]) the ratio of the mass of hydrogen to the mass of storage material also called the gravimetric density and [$\text{kg H}_2\ \text{m}^{-3}$] the volumetric density. The conversion between the units for carbon is as following:

$$x[\text{H/C}] = x/(x + M_\text{C}) \cdot 100\%\ [\text{mass\%}]$$
$$= x/(x + M_\text{C}) \cdot d[\text{kg m}^{-3}][\text{kg H}_2\ \text{m}^{-3}]$$

where M_C stands for the molecular mass of carbon ($M_\text{C} = 12$ g mol^{-1}) and d for the density of the host material at the hydrogen concentration x.

Fig. 1 shows the volumetric and the gravimetric hydrogen density of several low and high temperature hydrides, including predicted values for SWNT taken from Dillon et al. [3]. Hydrocarbons, i.e. octane and methane, are also shown because hydrocarbons represent the major fuel for mobile applications today. However, hydrocarbons are not reversible hydrogen storage materials because of the covalent bonds between carbon and hydrogen with a binding energy of 300–400 kJ mol^{-1}. For metal hydrides the binding energy is 30–80 kJ mol^{-1}. An improvement of hydrogen storage devices demands materials which store at least 8 mass% of hydrogen and have a density of approximately 2000 kg m^{-3}. The absorption should occur at a pressure below 5 bar and a temperature below 620 K. In order to prevent major energy loss the thermodynamic

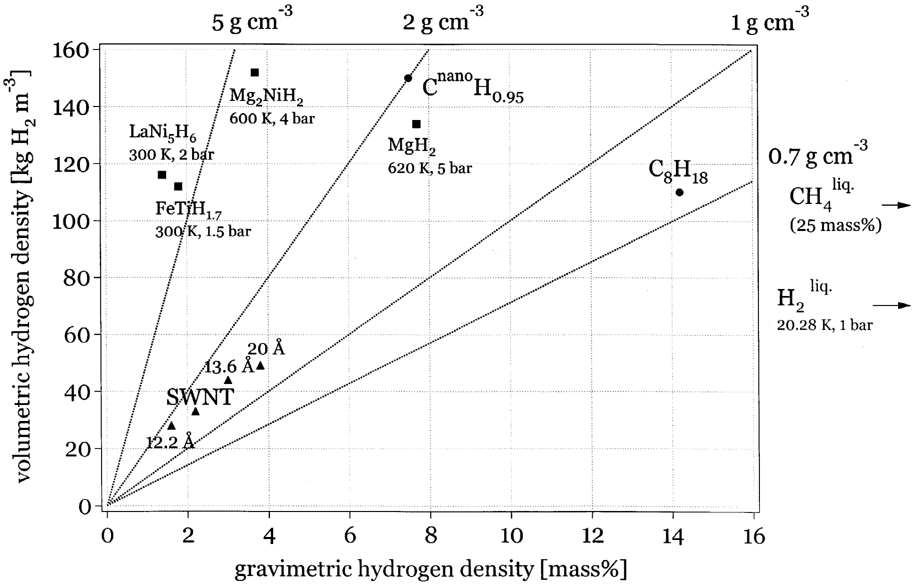

Fig. 1. Volumetric hydrogen density [$\text{kg H}_2\ \text{m}^{-3}$] versus gravimetric hydrogen density [mass%] for several hydrogen storage metals [16]. Dotted lines stand for the density of the host material. SWNT data taken from the Fig. 2 in Ref. [2]. Data for nanocrystalline graphite from Ref. [10].

parameters for the desorption should be roughly the same as for adsorption (reversibility of the system). The nanostructured graphite [10] almost fulfills the above mentioned storage density requirements. All other carbon materials described in the introduction with a storage density greater than 8 mass% are either very poorly defined and therefore the amount of hydrogen absorbed is only guessed or the results were not reproducible by any other group.

Table 1 shows a summary of the set of samples we analyzed in an electrochemical half cell at room temperature (298 K). The gravimetric hydrogen density was calculated from the measured discharge capacity using the real mass of the sample, i.e. no correction for the purity of the sample was applied. The storage densities found range from 0.04 up to 2.0 mass%. For the electrochemical measurements, a constant current was applied and the time in the order of minutes to hours is measured. The results are reproducible with less than 1% error. However, the measured capacity is a sum of the capacities from all the reducible species in the electrode during the discharge. As a rough estimation 1 mg of a metal, e.g. Ni, Co, leads to a discharge capacity of 0.5 mAh. In other words, metallic impurities could increase the measured capacity. Therefore, the electrochemical discharge capacity is a measure for the upper limit of the amount of desorbed hydrogen at room temperature. Several batches from the same producer show significant differences in their desorbed capacities. This problem could not be investigated further because of the very small amounts of samples which were available in the past.

The characterization of the nanotube samples is rather difficult, because of the large amount of nanotubes in a sample, approximately 10^{16} nanotubes per g, and the inhomogeneity of the tubes itself. Electron microscope images (e.g. SEM, TEM) allow to investigate only a few nanotubes which are not necessarily representative. Global analyzing methods, e.g. surface area measurements (BET), diffraction methods (e.g. X-ray, neutron) result in averaged values of the physical parameters and do not exhibit necessarily the intrinsic properties of nanotubes. Therefore, the characterization of the carbon samples investigated in this work is based on the unverified information from the producers (Table 1) and on surface area measurements shown in Table 2. The surface areas measured are less than 400 $m^2\ g^{-1}$ for all samples. The maximum possible specific surface area of graphite is 1315 $m^2\ g^{-1}$, with the

Table 1
List of nanotube and carbon samples which were investigated in an electrochemical system (producer data in italics were measured on very small samples (few mg))

Producer	Sample	SWNT	Remainder	Catalyst	Process	H [mass%]	C [mAh g^{-1}]
MER Corporation	SWNT soot, as produced	A few %	Traces of C60, C70, amorphous carbon	25% Ni, Fe	Arc	0.37	98
Carbolex	Carbolex	85%	Amorphous carbon	Ni	Arc, selected grade	0.65	175
Carbolex	Carbolex, AP-Grade-1	50–70%	Amorphous carbon	Proprietary Basically Ni	Modified arc	0.71	191
Dynamic Enterprises Ltd. (DEL)	SWNT purified	50%	Traces of C60, C70, amorphous carbon	25% Ni, Fe	Arc, purified	2.0	552
Dynamic Enterprises Ltd. (DEL)	SWNT purified	50%	Traces of C60, C70, amorphous carbon	25% Ni, Fe	Arc	0.9	245
Ching-Hwa Kiang, UCLA	?	?	?	?	Arc	0.23	62
Patrick Bernier University Montpelier	–	70%	Amorphous carbon	Ni, Y	Arc, as produced	2.0	550
Patrick Bernier, University Montpelier	Colerette 218	70%	Amorphous carbon	Ni, Y	Arc	0.1	26
Rice University, (Tubes@Rice)	SWNT	95%	Amorphous carbon	Ni, Co$<$1%	Laser vaporisation	0.31	84
Hoechst	C60 lab grade	0	?	?	?	0.04	12
Timcal AG	HSAG 100	Graphite	$<$0.22% ash	–	Calcination	0.13	36
Timcal AG	HSAG 300	Graphite	$<$0.22% ash	–	Calcination	0.25	66
FK, University of Fribourg	MWNT	?	?	Fe	Pyrolysis	0.13	34

Table 2
Surface area determined by the BET method including the mass of material used for the measurement and the amount of desorbed hydrogen (electrochemically) for several graphite and nanotube samples

Sample	Sample mass m [mg]	Surface area S [$m^2 g^{-1}$]	Desorbed hydrogen H_2 [mass%]
HSAG 100 (graphite)	1000.8	104	0.13
HSAG 300 (graphite)	957.1	297	0.25
MER	298.4	237	0.36
MER (acid treatment)	535.5	377	0.58
Rice	53.3	197	0.31
Rice (acid treatment)	–	–	0.24
FK, University of Fribourg	489.6	73	0.13

assumption, that every C-atom is at the surface of bulk graphite. Therefore, isolated single wall nanotubes should theoretically exhibit the same large surface area and in case the inner surface of the tube is also accessible for the gas (nitrogen) the maximum specific surface area is 2630 $m^2 g^{-1}$. The considerably smaller surface area measured can be explained by the formation of bundles of SWNT or the sample contain a major amount of MWNT with at least 12 shells and other graphitic and amorphous carbon structures as impurities. The measured desorption capacities correlates with the surface area of the samples.

The hydrogen absorption properties of the samples in the gas phase were investigated by means of a high pressure (2 MPa) absorption and subsequent temperature programmed desorption spectroscopy (TDS). Fig. 2 shows the hydrogen partial pressure as a function of temperature of a high surface area graphite (HSAG) sample and a SWNT sample from MER. Both sample exhibit the low temperature peak at 105 K of the physisorbed hydrogen followed by a much smaller peak at 136 K. Above this temperature the hydrogen pressure was continuously decreased showing only a small shoulder at 300 K. The spectra of the SWNT and the graphite are similar, however the hydrogen partial pressure for the SWNT sample was always higher as compared to the pressure of the graphite sample. Upon 500 K, the spectra show an increase in hydrogen pressure. We observed, that the increase of the hydrogen pressure in the desorption spectrum becomes more pronounced if the absorption of hydrogen is performed at elevated temperatures ($T > 500$ K). Therefore, the HSAG sample (high surface area graphite from Timcal) was heated to 600 K for the hydrogen absorption. The total pressure and the hydrogen partial pressure of the HSAG sample are shown in Fig. 3 together with the mass spectra for five temperatures. Around 100 K the total pressure is given by the molecular hydrogen partial pressure and hydrogen still contributes significantly to the total pressure up to 200 K. At higher temperatures the hydrogen partial pressure is insignificant. The main contribution at temperatures greater than 300 K to the total pressure are molecules or fragments of molecules with an atomic mass of 12–18, 28 and 42–44 u. The reason for the

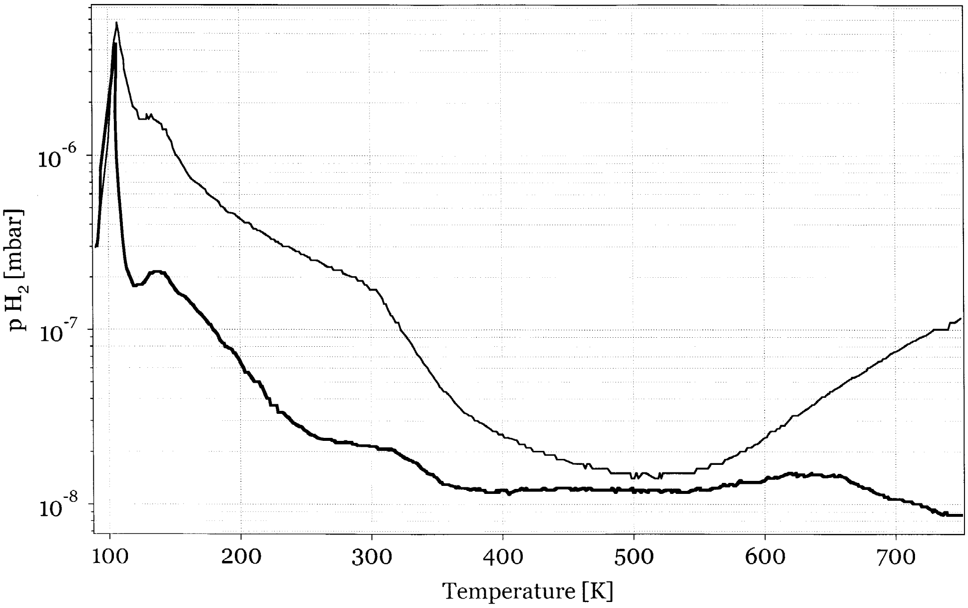

Fig. 2. Temperature programmed desorption spectra for a nanotube sample from MER and a high surface area graphite (HSAG 300) sample from Timcal (bold line). Sample was evacuated at 88 K before the experiment started with a heating rate of 4 K min^{-1}.

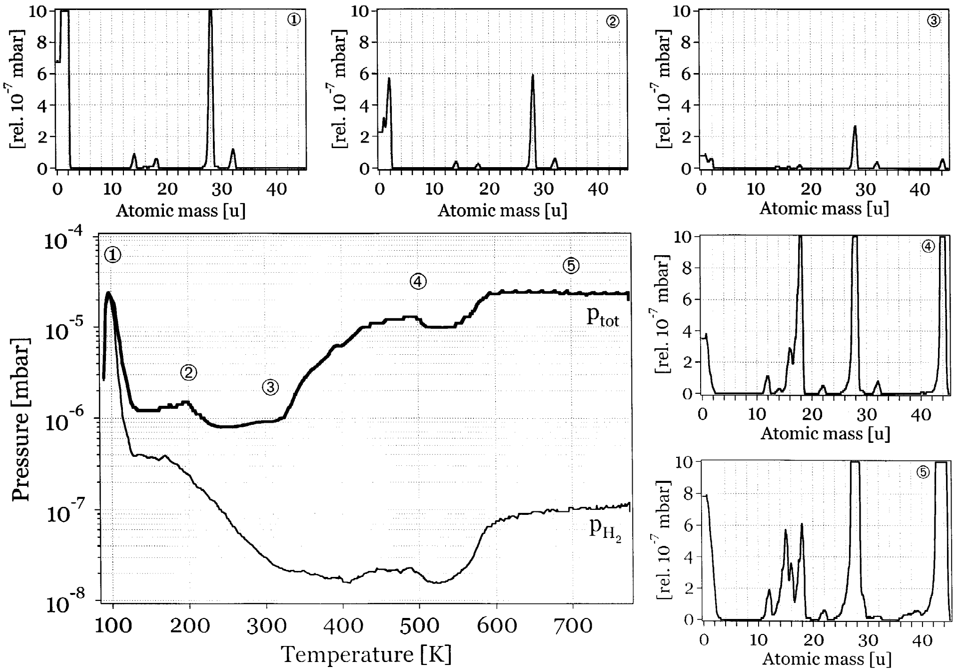

Fig. 3. Temperature programmed desorption spectra for a high surface area graphite (HSAG 300) sample from Timcal. Total pressure (bold line) and partial pressure of hydrogen. The mass spectra for the temperatures 100, 200, 300, 500, and 700 K are also shown. Sample was evacuated at 88 K before the experiment started with a heating rate of 4 K min^{-1}.

occurrence of the large masses are hydrocarbons e.g. CH_4, C_2H_4, C_3H_8, which are preferentially formed at higher temperatures and desorb or decompose in the range of 300–800 K. The hydrocarbons are only observed if the absoption of hydrogen is performed at elevated temperatures and not in case of hydrogen absorption at room temperature. Therefore, a considerable high amount of the absorbed hydrogen binds covalently to the carbon sample. Orimo et al. [11] came to the same conclusion for graphite samples which were heavily ball milled in a hydrogen atmosphere.

A very simple test for a hydrogen storage material is to apply a hydrogen pressure to the sample, then cool it to liquid nitrogen temperature and pump the residual hydrogen off. The hydrogen absorbed in the sample is then determined by the pressure increase upon heating of the sample. The largest amount of hydrogen desorped was 12 sccm g^{-1} which corresponds to 0.1 mass% for the SWNT from MER.

4. Conclusion

Carbon materials, e.g. high surface area graphite, single- and multi-wall nanotubes, physisorb hydrogen gas up to 5.5 mass% at low temperatures ($T=77$ K). The amount of adsorbed hydrogen is mainly a function of the surface area and the temperature. At room temperature the gravimetric storage density drops to 0.6 mass% ($T=300$ K, $P=6$ MPa) [12]. Larger storage densities at room temperature are possible, however the hydrogen then binds covalently to the carbon and can only be desorbed at elevated temperatures ($T>350$ K). Nanotubes do not behave significantly different from high surface area graphite powder in view of their hydrogen storage capability. The synthesis of nanotubes is a rather difficult and an expensive procedure. Today, purified SWNT are sold for 1 million US$ per kg [15]. Orimo et al. [11] has shown, that nanocrystalline graphite is able to store a large quantity of hydrogen (7.4 mass%), however the hydrogen is at least partially covalently bond to the graphite. The extraordinary large hydrogen storage densities of nanotube materials published in the last few years have to be viewed with skepticism because the overall results are inconsistent and not reproducible.

Acknowledgements

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