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Hydrogen-Carbon Studies

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Work on Hydrogen Storage Alloys

Our work on hydrogen storage alloys is published in several papers [1,3,6] and is not repeated in this report. We focus in this report on the work on carbon nanostructure materials with a short review of the literature and a summary of our recent results.

State of the Art of Hydrogen in Carbon

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 to 100 µm. The CNT's 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 much higher values were also found due to a change from nested to rolled type of the nanotubes [2]. The diameter of SWNT's varies from 1 to 3 nm, whereas MWNTs show typical diameters of 30 to 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 minutes 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 temperature (298 K). The hydrogen storage capacity was found to be 11.26 mass% for tubular CNT's, 67.55 mass% for herringbone CNT's, 53.68 mass% for platelet CNT's, and 4.52 mass% for graphite. These extraordinary high values, which are roughly one order of magnitude higher than anything known to date caused an avalanche of research on hydrogen storage in carbon nanotubes. So far, 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. Later,

Nutzenadel et al. [7, 8] measured by low current electrochemical discharge up to 2 mass% on purified SWNT samples.

Hydrogen gas adsorption on purified SWNT samples was performed by Ye et al. [9]. The BET surface area of the SWNT sample was found to be 285 m^2g^{-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^2g^{-1}). At high hydrogen pressures (7 MPa) and a temperature of 80 K, the hydrogen to carbon ratio reached H/C = 1 (8.25 mass%) in the initial absorption. In the following absorption cycles the absorption isotherm was shifted to considerably higher pressure and a hydrogen-to-carbon ratio of H/C = 0.8 was reached at 12 MPa. Liu et al. [10] 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 minutes 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. [11] investigated the hydrogen absorption of vapor-grown carbon nanofibers with a diameter of 5 nm to 300 nm. The fibers absorbed hydrogen up to 12.38 mass% when a hydrogen pressure of 12 MPa was applied. The absorption equilibrated within 200 - 300 minutes.

Chen et al. [12] reported that a high hydrogen uptake of 14 to 20 mass% can be achieved for K- and Li-doped MWNT, respectively, 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. [13] for hydrogen absorption and desorption. Graphite was ballmilled for a maximum of 80 hours 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.

A large variety of carbon samples was investigated by Ströbel et al using a high-pressure microbalance. [14]. The BET (N_2) surface area of the samples ranged from 100 m^2g^{-1} up to 3300 m^2g^{-1}. The absorbed amount of hydrogen (p = 12.5 MPa, T = 296 K) correlates with the surface area according to the equation x [mass%] = $0.0005 \cdot S[m^2g^{-1}]$ (taken from their figure) except for the nanofiber samples. The latter exhibit a rather low surface area of approximately 100 m^2g^{-1}; however, the increase in mass upon hydrogen absorption corresponds to about 1.2 mass%. The adsorption isotherms measured follow approximately the Langmuir adsorption model. Some isotherms intercept the mass-axis (p = 0) at x = 0, other intercept at a finite mass between 0.2 and 0.4 mass%.

Rzepka et al. [15] 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 at 300 K.

Stan and Cole [16] 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.

Williams and Eklund [17] performed Monte Carlo simulation of H_2 physisorption in finite-diameter carbon SWNT ropes and found an increasing amount of adsorbed hydrogen with decreasing temperature from 1.4 mass% (p = 10 MPa, T = 300 K) to 9.6 mass% (p = 10 MPa, T = 77 K). For lower hydrogen pressure, this range is shifted to considerably lower amounts of adsorbed hydrogen, i.e. 0.2 mass% (p = 1 MPa, T = 300 K) to 5.9 mass% (p = 10 MPa, T = 77 K).

Experiments

Synthesis of Nanotubes

The nanotube (NT) samples were synthesized in a vacuum furnace at 920 K by pyrolysis of acetylene (12 vol% acetylene in nitrogen, p = 50 kPa). The base pressure of the furnace was 1 Pa. Therefore, the oxygen concentration in the furnace during the synthesis was less than 5 ppm. Nanotubes were grown on Al and Si substrates pretreated with a solution of $Fe(NO_3)_3$ in ethanol. Large quantities of nanotubes (1 g per day) were synthesized on stainless steel (INOX) substrate without any pretreatment. 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.

Gas Phase Hydrogen Absorption

Gas phase absorption and desorption was performed in a system equipped with a mass flow controller (max. flow = 5 sccm H_2 per minute) and pressure gauges ranging from 25 Pa to 10 MPa. The volume of the system is 30 cm^3. Therefore, the detection limit of the system is $3 \cdot 10^{-7}$ mol H_2. The system works in a temperature range starting from 78 K up to 800 K.

Temperature Programmed Desorption Spectroscopy

The system is equipped with a liquid nitrogen cooled furnace, turbomolecular pump and a mass spectrometer (QMG 64 from Balzers). The furnace operates over a temperature range from 78 K to 900 K. The heating rate ranges from 1 $K \cdot min^{-1}$ to 30 $K \cdot min^{-1}$. The samples are first degassed in ultra high vacuum (base pressure $1 \cdot 10^{-6}$ Pa) at 773 K for several hours. Subsequently, the samples are loaded with hydrogen gas (<10 MPa). Then the samples are cooled with liquid nitrogen (77.4 K). The sample reactor is then connected to the UHV system and the remaining hydrogen is removed until the base pressure of the system is below $1 \cdot 10^{-5}$ Pa. The temperature is then increased at a constant rate and the desorbed gases are analyzed in the mass spectrometer. Partial pressure measurements for hydrogen are recorded every second, full mass spectra every minute.

BET Surface Area Measurements

The surface areas of the CNT samples are measured by means of the B.E.T.-method (Brunauer-Emmett-Teller) [18]. Prior to the 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 recorded. The surface area is calculated using the conversion factor of 102 $m^2 \cdot mol^{-1}$ N_2 [14].

Nanotube Samples Investigated

The following nanotube samples were investigated for hydrogen absorption:

1. MER Corporation – as-produced soot containing a few % of SWNT. The residuals are traces of C_{60}, C_{70} and amorphous carbon. The catalyst used was 25% Ni and Fe. Nanotubes were synthesized in an arc furnace.
2. Carbolex – selected grade containing 85% of SWNT. The remainder is amorphous carbon. The catalyst used was Ni. Nanotubes were synthesized in an arc furnace.

3. Dynamic Enterprises Ltd. (DEL) – purified soot containing 50% SWNT. The residuals are traces of C_{60}, C_{70} and amorphous carbon. The catalyst used is 25% Ni and Fe. Nanotubes were synthesized in an arc furnace.
4. Ching-Hwa Kiang, UCLA – Nanotubes were synthesized in an arc furnace.
5. Patrick Bernier, University Montpelier – purified (Colorette 218) containing 70% SWNT. The reminder is amorphous carbon. The catalyst used was Ni and Y. Nanotubes were synthesized in an arc furnace.
6. Rice University, (Tubes@Rice) – purified containing 95% SWNT (bundles). The reminder is amorphous carbon. The catalyst used was Ni and Co. Nanotubes were synthesized by means of laser vaporization.
7. Hoechst – C_{60}, C_{60} lab grade.
8. Timcal AG – HSAG 100, high purity graphite (<0.22% ash) with a specific surface area of 100 $m^2 g^{-1}$.
9. Timcal AG – HSAG 300, high purity graphite (<0.22% ash) with a specific surface area of 300 $m^2 g^{-1}$.
10. FK, University of Fribourg – MWNT, as produced. The catalyst used was Fe. Nanotubes were synthesized by pyrolysis of hydrocarbons in a furnace.

Table 1: List of nanotube and carbon samples that were investigated in an electrochemical system. The data measured on very small samples (few mg) are printed in *italic*.

Producer	SWNT	Catalyst	H [mass%]	C [mAh/g]
MER Corporation	a few %	"25% Ni, Fe"	0.37	98
Carbolex	0.85	Ni	0.65	175
Carbolex	0.5..0.7	Ni	0.71	191
Ching-Hwa Kiang, UCLA	0.5	"25% Ni, Fe"	2	552
Dynamic Enterprises Ltd. (DEL)	0.5	"25% Ni, Fe"	0.9	245
Dynamic Enterprises Ltd. (DEL)	?	?	0.23	62
Patrick Bernier, Univ. Montpelier	0.7	"Ni, Y"	2	550
Patrick Bernier, Univ. Montpelier	0.7	"Ni, Y"	0.1	26
Rice University (Tubes@Rice)	0.95	"Ni, Co < 1%"	0.31	84
Hoechst	0	?	0.04	12
Timcal AG	graphite	-	0.13	36
Timcal AG	graphite	-	0.25	66
FK, Univ. of Fribourg	MWNT	Fe	0.13	34

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 mass% up to 2.0 mass%. For the electrochemical measurements a constant current was applied and the time, on the order of minutes to hours, measured. The results are reproducible with less than 1% error. However, the measured capacity is a sum of the capacities from all of 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 of 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 that have been 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 gram, and the inhomogenity of the samples. Electron microscope images (e.g. SEM, TEM) allow us to investigate only a few nanotubes that are not necessarily representative. Global analysis methods, (e.g., surface area

measurements [BET]) and diffraction methods (e.g., X-ray, neutron) result in averaged values of the physical parameters and do not necessarily exhibit 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^2g^{-1} for all samples. The maximum possible specific surface area of graphite is 2600 m^2g^{-1}, with the 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, or in case the inner surface of the tube is also accessible for the gas (nitrogen) the maximum specific surface area is 5200 m^2g^{-1}. The much smaller surface areas measured can be explained by the formation of bundles of SWNT or the samples 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.

Table 2: Surface area determined by the BET method, 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]	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

The hydrogen absorption properties of the samples in the gas phase were investigated by means of a high-pressure (2 MPa) absorption and a subsequent temperature programmed desorption spectroscopy (TDS). The samples 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 decreasing, showing 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 compared to the pressure of the graphite sample. Around 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. Around 100 K the total pressure was mostly molecular hydrogen and hydrogen still contributed significantly to the total pressure up to 200 K. At higher temperatures the hydrogen partial pressure becomes 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 to 18 u, 28 u and 42 to 44 u. The reason for the occurrence of the large masses is hydrocarbons (e.g. CH_4, C_2H_4, C_3H_8), which are preferably formed at higher temperatures and desorb or decompose in the range of 300 K to 800 K. Therefore much of the absorbed hydrogen binds covalently to the carbon sample. Orimo [13] came to the same conclusion for graphite samples that 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 and 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.

Conclusions

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 USD per kilogram [19]. Orimo [13] has shown that nanocrystalline graphite is able to store a large quantity of hydrogen (7.4 mass%); however, that 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, as these results are inconsistent and not reproducible.

Acknowledgment

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