

MULTIWALL CARBON NANOTUBES UNDER HIGH HYDROGEN PRESSURE

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Introduction

The storage of hydrogen has been intensively studied for many years and recent demand for efficient fuel cells for automotive applications has intensified the research in this field. Because of safety reasons, energy efficiency and relatively low weight density the well known storage technologies do not meet the desired requirements. Hydrogen storage in carbon materials may lead to the solution of above stated problems. Recently Rodriguez group reported remarkably high values of hydrogen adsorption (up to 67 weight %) on graphite nanofibers [1]. Temperature-programmed desorption measurements by Dillon et al. [2] performed on a single-wall nanotube containing sample gave reversible hydrogen capacities up to 5-10 wt % assuming solely nanotubes to contribute to the hydrogen storage. Electrochemical storage of hydrogen (110 mAh/g - 0.39 wt %) in the nanotube-containing material was reported by Nuetzenadel et al. [3]. Here we report room temperature hydrogen absorption by multiwall carbon nanotubes (MWNT) at hydrogen pressures up to 2000 atm.

Experimental

Synthesis: Synthesis: Catalytic multiwall carbon nanotubes were synthesized by decomposition of acetylene over a silica supported cobalt catalyst and then silica and cobalt were eliminated by hydrofluoric (73%) and nitric (3M) acids treatments [4].

Hydrogen absorption: 119 mg MWNT sample was loaded into stainless steel hydrogen pressure cell and evacuated to 10^{-2} Torr while heating to 500 K. After the sample was allowed to cool down, hydrogen was introduced into the sample chamber at pressures 100, 300, 1000 and 2000 atm. and the drop in pressure of the system was measured at regular intervals. The equilibrium was considered to be reached at pressure drop saturation. The equilibrium was reached in 0.5-3 hours depending on pressure value and the prolongation of sample exposure to the hydrogen pressure (up to 24 hours) did not yield any additional sorption. Due to the limited sample weight the accuracy of determination of MWNT sorption capacity

directly from the system pressure drop appeared to be insufficient for the pressures above 100 atm., so for higher pressure ranges the following procedure was applied: after the saturation was reached the sample was cooled down to liquid nitrogen temperature, hydrogen pressure was released and then the sample chamber was evacuated. The amount of hydrogen stored in the sample was measured via hydrogen desorption into vacuum (via absolute pressure increment) while heating the sample chamber to room temperature.

Results and discussion

The amount of hydrogen desorbed into vacuum while heating (from 77K to room temperature) of MWNT samples saturated with hydrogen at different pressures is presented in the table:

Pressure, atm.	Amount of hydrogen desorbed, wt%		
	1 st stage	2 nd stage	Total
100	0.2	0.3	0.5
300	0.3	0.3	0.6
1000	0.5	0.3	0.8
2000	1.0	0.4	1.4

Two stages in the desorption process could be clearly distinguished. The first, more rapid one, corresponded to the sample heating from 77K to room temperature (or to 500K). The amount of hydrogen desorbed during the first stage was the same when heating to room or 500K temperature, did not depend on the heating rate, but was significantly affected by the pressure of hydrogen treatment. The second stage, more slow one was over in 24 hours, did not depend on the conditions of the first stage heating and the value of hydrogen treatment pressure.

It should be noted that there was a significant hydrogen desorption observed during the pressure release and evacuation of frozen hydrogen treated MWNT samples which we were unable to measure quantitatively due to technique limitations. This observation was proved by direct measurements of MWNT sorption capacity from the system pressure drop after 24 hours of sample

exposure to 100 atm. hydrogen pressure at room temperature. The calculations showed that the amount of hydrogen sorbed at 100 atm. was about 1 wt % - the value two times higher than that obtained via desorption into vacuum procedure. Thus we could propose two forms of sorbed hydrogen different in the character of binding with carbon matrix. The first one, representing the major amount of hydrogen sorbed, has low binding energy and readily desorbs even at low temperature. The second one, having higher binding energy is trapped in MWNT sample at 77 K and is responsible for slow desorption process at room temperature.

There was another observation worth to be mentioned. Sorption-desorption cycling seems to increase rather significantly the amount of the first form of sorbed hydrogen (with low carbon matrix-hydrogen binding energy). This form of hydrogen is not trapped in the sample at 77 K and therefore, unfortunately, we were unable to measure it quantitatively in the current set of experiments.

Conclusions

At 100 atm. hydrogen pressure and room temperature catalytic carbon nanotubes sorb up to 1 wt% of hydrogen. We propose two forms of hydrogen dissolved in MWNT differing in binding energy with carbon matrix. The amount of hydrogen sorbed increases with pressure, but for higher hydrogen pressures (300, 1000, 2000 atm.) we were able to measure only the second form of sorbed hydrogen, trapped in the sample at 77K temperature and representing the minor fraction of hydrogen sorbed.

More experiments are needed to measure the total quantity of hydrogen sorbed in MWNT at high pressures and to clear out the nature of proposed forms of hydrogen sorbed.

References

1. Chambers A, Park C, Baker RTK, Rodriguez NM. Hydrogen storage in graphite nanofibers. *J. Phys. Chem.* 1998; B 102: 4253-4256.
2. Dillon AC, Jones KM, Bekkedahl TA, Kiang CH, Bethune DS, Heben MJ. Storage of hydrogen in single-walled carbon nanotubes. *Nature* 1997; 386: 377-379.
3. Nuetzenadel Ch, Zuetzel A, Chartouni D, Schlapbach Louis. Electrochemical storage of hydrogen in nanotube materials; *Electrochem. and Solid State Lett.* 1998; 2 (1): 30-32.
4. Gaucher H, Pellenq R, Bonnamy S, Béguin F, Nalimova V, Grillet Y. Characteristics of catalytic carbon nanotubes: their evolution after thermal and chemical modifications. In: Kuzmany H, Fink J, Mehring M, Roth S, editors. *Electronic properties of novel materials - Progress in molecular nanostructures*, New York: Woodbury, 1998: 395-398.

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