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Assessment of Hydrogen Storage on Different Carbons

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Abstract

We have measured the hydrogen uptake of several samples of carbon nanofibers, inserted and exfoliated compounds, as well as of one sample of unopened SWNTs. Using three different systems, the experiments were carried out in both the low-pressure limit and the higher-pressure range (3 MPa –10 MPa) at temperatures ranging from 70 K to room temperature. At one atmosphere and 273 K, our best results show physisorbed densities of about 0.03 wt%. At 35 atmospheres and room temperature this amount increased to about 0.1 wt%; whereas AX-21 activated carbon gave 0.3 wt%. A further increase of pressure up 100 atmospheres along with a dramatic increase of exposure time up to 24 hours led to sorption densities of 0.7 wt% for GNF and to about 1.4 wt% for exfoliated carbon.

Introduction

Due to its low density, one of the main obstacles to the widespread use of hydrogen in the energy sector is an efficient storage technology. A promising avenue in this field is adsorption storage, which could allow the storage of a high density of hydrogen at much lower pressures than compression and higher temperatures than liquefaction. Several carbon structures have been proposed as adsorbents for hydrogen. Some of these are ordered, such as the fullerene family (includes bucky balls, single- and multi-wall nanotubes, as well as nanohorns) and the recently proposed nanofibers. Activated carbons, on the other hand, are sets of graphite planes of various sizes, forming a disordered, highly-porous three-dimensional structure characterized by a pore distribution. In general, the search for better adsorbents involves looking for a high specific surface per unit of mass and a large energy of adsorption. While H_2 adsorption data on activated carbon are fairly well accepted and understood, those on structured carbons vary quite widely. Sometimes they are contradictory and, in some cases, they have yet to be determined.

The main objective of this work was to carry out a comparative study of hydrogen adsorption properties on different carbon nanostructures under the same experimental conditions of pressure and temperatures and using the same experimental systems.

Materials

More than two-dozen samples were characterized; they may be classified in the following five different categories: *a)* carbon nanofibers; *b)* intercalated compounds; *c)* exfoliated compounds; *d)* super activated carbon; and *e)* single wall nanotubes.

The nanofibers were synthesized by INRS-E&M via the decomposition of a hydrocarbon gas over a catalyst (Ni, Cu) maintained at an appropriate temperature. A nanostructural carbon deposit is obtained, having the structure of nanofibers. The catalyst is prepared from the precipitation of the metal nitrate with sodium carbonate. After washing the precipitate, it is calcined at 500°C for 4 hours under oxygen and reduced for 20 hours in hydrogen at the same temperature. Then, in order to obtain nanofibers, the catalyst is used with acetylene at 500°C or ethylene at 600°C. Both gases have also been used in mixtures with hydrogen and/or argon because hydrogen seems to affect the orientation of the graphene planes that in turn influences the specific area of the nanofibers. Both gases were used, as were several proportions of Ni and Cu.

Some of the nanofibers produced above were inserted with $MnCl_2$, H_2SO_4, or Br. The insertion of such an agent into a graphitized carbon increases the distance between its graphene planes. It should, therefore, facilitate the introduction of hydrogen and its adsorption on the material. If there is an obstacle to the accumulation of hydrogen into the intercalated graphite, it is possible to exfoliate it, which is equivalent to producing a de-insertion reaction. This reaction is performed by heating the intercalated compound at temperatures varying from 600 to 1500°C and gradually reducing the temperature of the material to room temperature. Doing so, de-insertion occurs but the graphene planes have a tendency to maintain the spacing they have in the intercalated compound. Lowering the temperature too quickly results in smaller distances between the graphene planes.

The SWNT sample originated from the group of Professor Bernier at the Université de Montpellier. The 122 mg sample had an estimated purity of about 30% and was characterized without further treatment and with the ends still closed by the fullerene caps. Therefore, the interior of the tubes, where most of the adsorption occurs, was not readily accessible to H_2.

The super activated carbon used in the experiment is the well-known AX-21 that has a surface area of about 2800 m^2g^{-1}. The purity of all of the gases used in the experiments was 99.999%.

Results

Surface area: The BET surface area of the samples was measured, with an estimated accuracy of ±10%, at liquid nitrogen temperature (77 K) using an Autosorb Automated Gas Sorption System model, Autosorb-1 from Quantachrome. The surface area varied from 40-300 m^2g^{-1} for nanofibers, and from 20-155 m^2g^{-1} for the inserted and exfoliated compounds. The surface area of the SWNT was 266 m^2g^{-1}. This value is about an order of magnitude lower than for the super activated carbon AX-21.

Hydrogen adsorption in the range 0 - 1 atmosphere: The same autosorb apparatus was used for measuring hydrogen adsorption at low pressure and three discrete temperatures: 77 K, 195 K, and 273 K. Prior to measurements, the samples were degassed *in-situ* under vacuum at 200°C for several hours. Most, if not all, of the results obtained at 273 K and near atmospheric pressure fall below 0.01 wt%, many were even below the detection limits of the apparatus. Only the SWNT sample (pure) and one nanofiber sample showed an adsorption density of about 0.03 wt%, which is slightly higher than that of AX-21 (see Table 1). This particular nanofiber sample was grown at 500°C by passing acetylene over a Ni_{70}-Cu_{30} catalyst. Table 1 also shows that AX-21 adsorbs 3.4wt% of H_2 at 77 K and 1 atmosphere.

Table 1
Measured physical and H_2 adsorption properties of the selected carbons

Adsorbent	BET Surface (m^2/g)	Micropore Volume (cc/g)	Adsorption (H_2) Wt%@750 torr		
			77 K	195 K	273 K
Activated carbon AX-21	2800	1.1	3.4	0.63	0.02
Activated carbon CNS 201	1100	0.4	1.9	0.27	0.01
SWNT, 30% pure, unopened	266	0.1	0.6	0.02	0.01
Nanofiber Ni_{70}-Cu_{30}	143				0.02

Hydrogen adsorption in the range 0-35 atmospheres: The measurements were carried out in an experimental system based on the traditional volumetric expansion method. The system, which is fully automated, covers the range of temperatures, 77-300 K, and pressures up to 7MPa. Although initially conceived for large samples, the system was extensively modified to measure the adsorption of much smaller samples (around 100 mg). Mainly the dead volume was drastically reduced; the volume of the sample holder was reduced from 150 ml to 5 ml and that of

the reference cell was reduced in the same proportions. Depending on the size of the available samples, the estimated accuracy of the measurements varied between 10% and 20%. The isothermal measurements were carried out at 77 K and 273 K. Again, like the previous results at low pressure, many of the adsorbed densities at 35 atmospheres were below the reliability limits of the measuring system, only a few were around 0.1 wt% (see table 2), and the remaining were much lower. Table 2 also shows that activated carbon was much superior to nanofibers.

Table 2
H_2 adsorption on AX-21 and nanofibers

Adsorbent	Adsorption (H_2) Wt%@3 MPa	
	77 K	273 K
Activated carbon AX-21	4.7	0.37
Nanofiber **Ni_{70}-Cu_{30}, acetelyne, 500°C**	0.46	0.14
Nanofiber **Ni_{70}-Cu_{30}, ethelyne, 500°C**	0.17	0.08
Nanofiber **Ni_{80}-Cu_{20}, ethelyne, 450°C**		0.10
Inserted Nanofiber		0.08

Hydrogen adsorption at high pressure and long exposure time: The experimental system used for this type of measurement is also based on the volumetric approach, but it was specially designed to minimize hydrogen leaks over a prolonged period of time; i.e. days instead of hours. The maximum measured leak rate of the system was 0.028% per day at a H_2 pressure of 12 MPa; this is less than the 0.05% rated full-scale accuracy of the 13.8 MPa transducer. This kind of leak proofing is needed to reliably measure the extremely slow H_2 adsorption processes that were reported for some graphite nanofibers. From all the samples characterized above, we chose three to undergo the high-pressure long-time exposure measurement. As shown in Table 3 two of the samples are nanofibers with different surface areas and the third one is an inserted nanofiber. Prior to adsorption measurements, the samples were heat treated in a quartz tube oven at 1250 K under a flow of He gas and then transferred to the adsorption cell in an He glove box. The adsorption results for an H_2 exposure of 20 hours are shown in the last two columns for two different pressures. Results are accurate to ± 10%.

From Table 3, we can see some increase in the adsorption values that is probably due to slow diffusion of the H_2 between the graphene layers. However, the results of the last sample were not reproducible, neither when the same sample underwent another heat treatment at 1250 K, nor when a fresh sample was used.

Table 3
Adsorption after long time exposure

Sample	Surface area (m^2/g)	Wt% Ads. @ 3 MPa	Ratio Ads (3MPa)/ Surface Area	Wt% Ads. @7.5 MPa	Wt% Ads. @10.5 MPa
Nanofiber Ni_{80}-Cu_{20}, ethelyne, 450 C	70	0.10	0.01	0.3	0.5
NF73 Eth+H_2(10)	289	0.024	8.3×10^{-4}	0.4	0.8
Inserted nanofiber	32	0.08	0.03	0.6	1.4

Conclusions

Our study shows that the capped SWNTs, nanofibers and inserted carbon compounds that we measured may hold more H_2 per unit surface area, but activated carbons are better storage material given their much higher surface area.