HYDROGEN STORAGE IN GRAPHITE NANOFIBERS

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Abstract

Graphite nanofibers (GNF) are a type of material that is produced by the decomposition of carbon containing gases over metal catalyst particles at temperatures around 600°C. These molecularly engineered structures consist of graphene sheets perfectly arranged in a parallel, perpendicular or at angle orientation with respect to the fiber axis. The most important feature of the material is that only edges are exposed. Such an arrangement imparts the material with unique properties for gas adsorption because the evenly separated layers constitute the most ordered set of nanopores that can accommodate an adsorbate in the most efficient manner. In addition, the non-rigid pore walls can also expand so as to accommodate hydrogen in a multilayer conformation. Of the many varieties of structures that can be produced we have discovered that when gram quantities of a selected number of GNF are exposed to hydrogen at pressures of ~2,000 psi, they are capable of adsorbing and storing up to 40 wt % of hydrogen. It is believed that a strong interaction is established between hydrogen and the delocalized p-electrons present in the graphite layers and therefore a new type of chemistry is occurring within these confined structures.

Introduction

The ever growing demand for energy, as well as the increase in environmental concerns, are exerting pressure for the development of cleaner fuels and more efficient engines. The conventional internal combustion engine currently used in most automobiles produces an array of

pollutants including, particulate materials, nitrogen oxides, sulfur oxides, hydrocarbons and carbon monoxide as well as large amounts of carbon dioxide. Although reduction of toxic emissions has been achieved to some degree by the use of the catalytic converter unit, this approach puts great demands on supported noble metal systems, which are required to operate with maximum efficiency over extreme temperature ranges (Taylor 1984).

It has been predicted that oil reserves will peak in about 15 years and therefore, in order to sustain the energy demand it is necessary to find new fuels and more efficient processes. A new technology that is becoming the subject of increasing research effort, is that of fuel cells. In this method, direct conversion from chemical into electrical energy is realized, and consequently, the efficiency of the process is enhanced by almost a factor of three over that of the conventional internal combustion engine, where most of the energy is wasted as heat. Hydrogen and oxygen are the essential reactants for the PEM fuel cells that are being developed for electric vehicles (Appleby 1989, Kordesch 1995). A number of factors contribute to the choice of hydrogen as a fuel, not least being the fact that it is one of the most abundant elements found in nature and during its reaction with oxygen the only product is water. Unfortunately, due to the lack of a suitable storage system and a combination of both volume and weight limitations, the driving range of electric vehicles is restricted to about 100 miles. This is one of the shortcomings that has prevented this very promising technology from reaching the commercial arena.

Currently, four methods are being considered for hydrogen storage in commercial applications; pressurized gas storage, liquefied hydrogen, selected metal hydrides and refrigerated super-activated carbon. Pressurized gas offers the advantage of being simple, however, in mobile applications the large volume coupled with the small capacity (8.7 wt. % at 5,000 psi and 7.6 wt. % at 10,000 psi) will limit its practicality. Liquefied hydrogen is expensive since it requires constant refrigeration and loss of the gas by evaporation is inevitable. While the latter two approaches may offer benefits over the other technologies with regard to safety aspects, they do however, have their own set of associated drawbacks. Metal hydrides are heavy, expensive, release heat during the hydrogen absorption process (Lynch 1991) and require the use of about one third of the stored energy during the release of the hydrogen fuel.

Because of their extremely high surface area, active carbons constitute without any doubt the preferred adsorbent in many processes (Noh 1987, Mattson 1971, Puri, 1970, Wigmans 1986). Carbon molecular sieves have been known for several decades (Walker 1966, Koresh 1980, Koresh 1981, Kappor,1989, Walker 1990, Cabrera 1993, Hynek 1997) and present an alternative choice for many commercial gas separation processes. These structures are produced from a variety of carbonaceous solids of different origins, including active carbons, cokes, and chars. Activated carbons possess a wide pore size distribution, where the fraction of micro- and nanopores is rather small. While these materials are very effective for the adsorption of a variety of molecules, one has to consider that the interaction between the adsorbent and the adsorbate is only of a physical nature, and as a consequence, the retention of gases is only achieved at extremely low temperatures. The use of activated carbons for gas storage at high temperatures has been found to be ineffective since the solid takes up storage volume without appearing to add any substantial benefits to the overall capacity.

In more recent years there has been a growing interest in the effects of confinement and the influence of the walls of the solid on the gas adsorption process. Indeed, theoretical studies carried out by Gubbins (Cracknell 1995, Rhykerd 1975, Balbuena 1993) using modern statistical mechanic fluids theory indicate that when fluids are restricted within narrow pores, their behavior does not conform to that predicted by classical thermodynamic methods. Non local density functional theory method calculations and molecular simulations have been employed to determine the optimum pore size of carbons for gas adsorption and it was concluded that the ideal system consisted of slit pores bounded by parallel single layers of graphite (Cracknell 1995). One of the reasons for this requirement is that in such a configuration, the solid will exhibit the highest ratio of nanopore volume to total volume and as a consequence void space will be eliminated.

In addition, since adsorption of gas molecules on the wall of the pore can cause profound perturbations in the system it is perhaps this aspect that might allow retention of the adsorbate at higher temperatures and at low pressures. It is well known that certain solids, particularly metals, chemisorb gases at room temperature and indeed, this property is routinely used to determine the metal surface area in supported catalyst systems (Anderson 1975). In contrast to physical adsorption, chemisorption requires energy in order to release the adsorbed molecules.

Graphite, is a layered solid in which the various planes are bonded by van der Waals forces where the minimum distance possible between the carbon layers for single crystal graphite is 0.335 nm. In this crystalline structure delocalized π-electrons form a cloud above and below the basal plane and it is this arrangement that imparts a certain degree of metallic character to the solid that results in a relatively high electrical conductivity across each carbon layer. The interlayer spacing in graphitic materials is a property dependent on a number of parameters including, the nature and the thermal history of the precursor, and can vary between 0.335 and 0.342 nm, which by appropriate intercalation procedures can be expanded up to values of 0.9 nm (Dresselhaus 1993, Dresselhaus 1981). Unfortunately, in its conventional form of flat sheets, graphite has an extremely low surface area (~ 0.5 m^2/g) resulting from the very small number of edges that are exposed and this aspect has tended to limit its usefulness as a practical selective adsorption agent for small diameter molecules due to diffusion restrictions.

Graphite nanofibers, GNF, are a novel material that has been developed in our laboratory from the metal catalyzed decomposition of certain hydrocarbons (Baker 1987, Kim 1991). These structures possess a cross-sectional area that varies between 5 to 100 nm and have lengths ranging from 5 to 100 mm (Rodriguez 1993). High-resolution transmission electron microscopy studies have revealed that the nanofibers consist of extremely well-ordered graphite platelets (Rodriguez 1995), which are oriented in various directions with respect to the fiber axis. The arrangement of the graphene layers can be tailored to a desired geometry by choice of the correct catalyst system and reaction conditions, and it is therefore possible to generate structures where the layers are stacked in a "ribbon", "herring-bone", or "perpendicular" orientation with respect to the direction of the fiber axis.

Experimental

Synthesis and Characterization of Graphite Nanofibers

GNF were prepared from the decomposition of ethylene, carbon monoxide and hydrogen mixtures over selected metal powders at temperatures between 500 and 700°C as described in previous publications (Baker 1987, Kim 1991). The solids were demineralized by immersing them in a mineral acid solution for a period of a week, washed and dried before testing. GNF were examined by high resolution transmission electron microscopy, temperature programmed oxidation, X-ray diffraction and nitrogen adsorption techniques.

Hydrogen Adsorption/Desorption

Hydrogen adsorption experiments were performed in a custom built unit that consists of two stainless steel vessels. The sample vessel, which is 100 cm^3 in volume is connected to the hydrogen reservoir vessel via a high pressure bellows valve. GNF are loaded in the sample container and the entire system evacuated in an oil free environment for about 5 hours at 150°C. The connecting valve is then closed and the sample cooled to room temperature for several hours. Hydrogen is permitted to enter the reservoir vessel and the pressure allowed to reach thermal equilibrium over a two hour period. The connecting valve is then opened and hydrogen immediately gains access to the sample and undergoes adsorption at room temperature. Blank experiments to determine the various parameters involved during gas expansion were conducted in the absence of GNF and also in the presence of other solids. Approximately 1 gram of GNF was placed in the adsorption unit and allowed to react with hydrogen at 1800 psi at room temperature for a several hours. Changes in pressure were carefully monitored as a function of time. Following adsorption hydrogen was allowed to exit the system and the volume carefully measured by displacement of water. Throughout these processes the adsorption unit was continuously monitored with a high sensitivity H$_2$ detector to ensure a complete absence of leaks in the system.

Results and Discussion

TEM examinations of the carbon deposited during the catalytic formation of GNF indicated that under the conditions described above, nanofibers were the only product of the reaction, with no other forms of carbon being present. A high resolution transmission micrograph of the typical appearance of the nanofibers is presented in Figure 1, where the graphene layers that are separated at a distance of ~ 0.34 nm can be observed. A schematic rendition illustrating the arrangement of graphite platelets within the structure is shown in Figure 2a.

When samples of catalytically grown GNF were placed in the adsorption unit, hydrogen uptake to unprecedented levels was obtained. Certain types of graphite nanofibers were found to be capable of adsorbing and storing extremely high quantities of hydrogen at room temperatures in amounts that were over an order of magnitude higher than those found with conventional materials such as metal hydrides (Chambers 1998). Figure 3 shows two typical isotherms for the adsorption of the hydrogen over a sample of GNF. Following the first adsorption, hydrogen was

released from the specimen and a second adsorption was carried out. Based on the pressure drop of the second uptake it is estimated that this sample of GNF adsorbs over 40 wt % of hydrogen.

The extraordinary hydrogen adsorption behavior exhibited by GNF is believed to be due to the unique structure of this molecularly designed solid. The material consists of graphite platelets possessing a small cross-sectional area, which is estimated to be on average 20 nm, combined with an abundance of exposed edges. In addition, since hydrogen possesses a kinetic diameter of 0.289 nm, a value slightly smaller than that of the interlayer spacing in graphite nanofibers, 0.342 nm as measured by X-ray diffraction, adsorption occurs due to the gas being able to readily gain access to the inner regions of the solid (Figure 2b). Another aspect of significance in this regard is that the solid consists entirely of non-rigid wall nanopores that extend across the nanofiber.

Following adsorption we found that a significant amount of hydrogen was still retained within the structure and the presence of this stored gas caused the lattice to expand as determined by X-ray diffraction. The interaction of hydrogen with graphite surfaces has been investigated using various techniques including neutron scattering (Nielsen 1980). It has been concluded that a commensurate $\sqrt{3} \times \sqrt{3}$ structure is achieved at low coverage and an incommensurate layer is observed at monolayer coverage. Following the formation of a second monolayer, a lattice parameter of 0.35 nm is observed. This value is smaller than the measured bulk hexagonal closed packed of 0.376 nm, which suggests that the presence of graphite causes hydrogen to adopt an unusually highly packed structure, thus accounting for the high storage levels measured in the current experiments.

Changes in the Structure of GNF Following Hydrogen Desorption

Pore size distribution and X-ray diffraction studies have indicated that following hydrogen adsorption experiments, the solid undergoes tangible structural perturbations. Figures 4a - 4c illustrate the changes in the pore size distribution of a GNF sample prior to exposure to a high pressure of hydrogen (4a), immediately following adsorption/desorption experiments (4b) and after 8 days (4c). X-ray diffraction experiments were conducted on a sample preceding the hydrogen treatment and ensuing desorption (Figures 5). It can be observed that hydrogen induces an expansion of the lattice from 3.40Å (prior to adsorption) to 3.47 following a decrease in the pressure. The structure seems to revert to the original value after a few hours.

We interpret these changes according to the notion that as hydrogen enters the graphene layers, a concomitant expansion of the lattice takes place to accommodate the gas molecules. Furthermore, we believe that following desorption, sufficient hydrogen still remains within the structure so as to generate a structure where the layers are separated to a greater extent than encountered in the initial state, (prior to hydrogen adsorption experiments) and that the residual amount is bound in a relatively strong form within the nanofiber structure being slowly released over a period of time. This process is consistent with the finding that both the pore size distribution and X-ray diffraction patterns gradually relax back to their initial state. Clearly, if the desire is to release all the hydrogen in a single burst then we must explore the potential of utilizing additional procedures to enhance this step. While raising the temperature is one option, other more sophisticated methods that can be operated at room temperature will be explored.

Future Studies

Given the extraordinary performance of GNF towards hydrogen storage, coupled with the extreme sensitivity of the material to the presence of impurities, we intend to continue our research in order to optimize the parameters associated with both adsorption and desorption phenomena. The objectives for the second part of the project are as follows:

- To scale up the production (100 grams) quantities of GNF that possesses the optimum hydrogen adsorption properties

- To examine the impact of controlled gasification treatments (activation) of GNF on the hydrogen storage capacity

- To investigate the effect of interlayer expansion of GNF via selected intercalation methods on the hydrogen adsorption/desorption characteristics

- Independent testing has been conducted by scientists in our laboratory and we plan to invite other organizations to conduct testing in our facilities following our protocol.

Acknowledgments

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Figure Captions

Figure 1. High resolution electron micrograph of a graphite nanofiber, showing the graphite platelets in a parallel arrangement.

Figure 2. (a) Schematic representation of the structure of graphite nanofiber; (b) enlarged section showing details of the hydrogen adsorption process.

Figure 3. Change in hydrogen pressure as a function of time in the presence of 1.1285 g of GNF H-200 at room temperature.

Figure 4. Pores size distribution of an H-500 GNF: (a) before hydrogen adsorption; (b) immediately following adsorption/desorption; and (c) 8 days after hydrogen treatment.

Figure 5. X-ray diffraction patterns of a GNF H-200 sample (a) prior to hydrogen adsorption; (b) immediately following adsorption/desorption; (c) 24 hours after hydrogen treatment, and (d) 48 hours following hydrogen treatment.
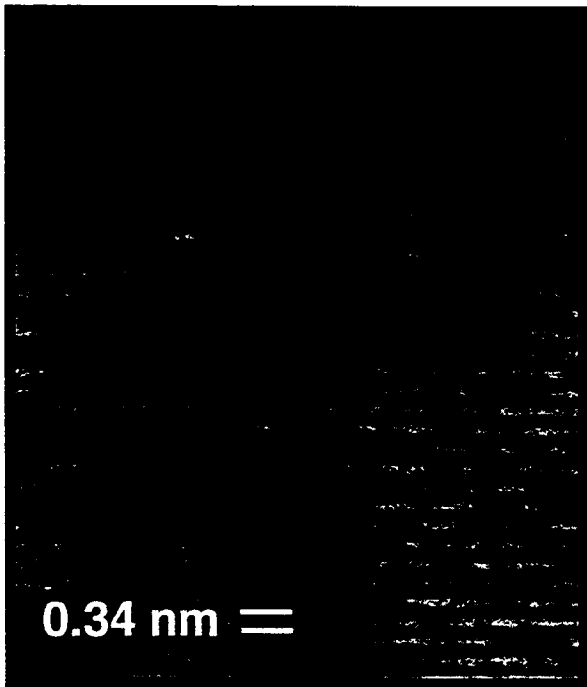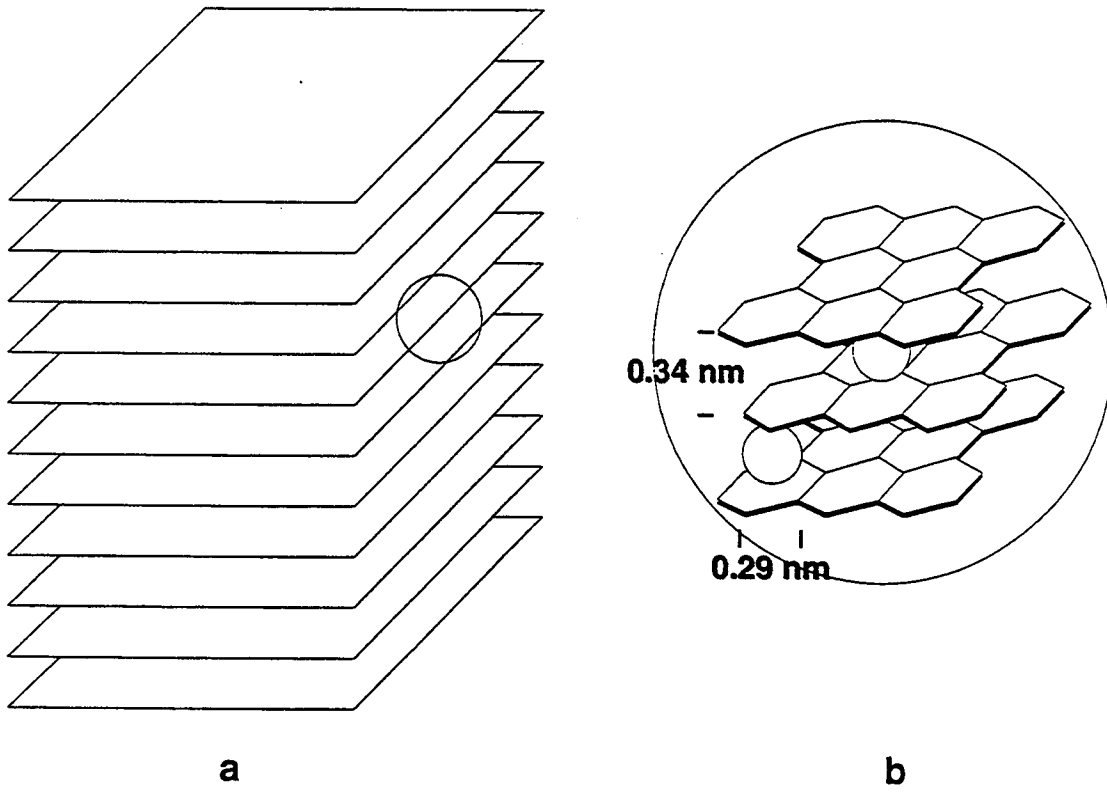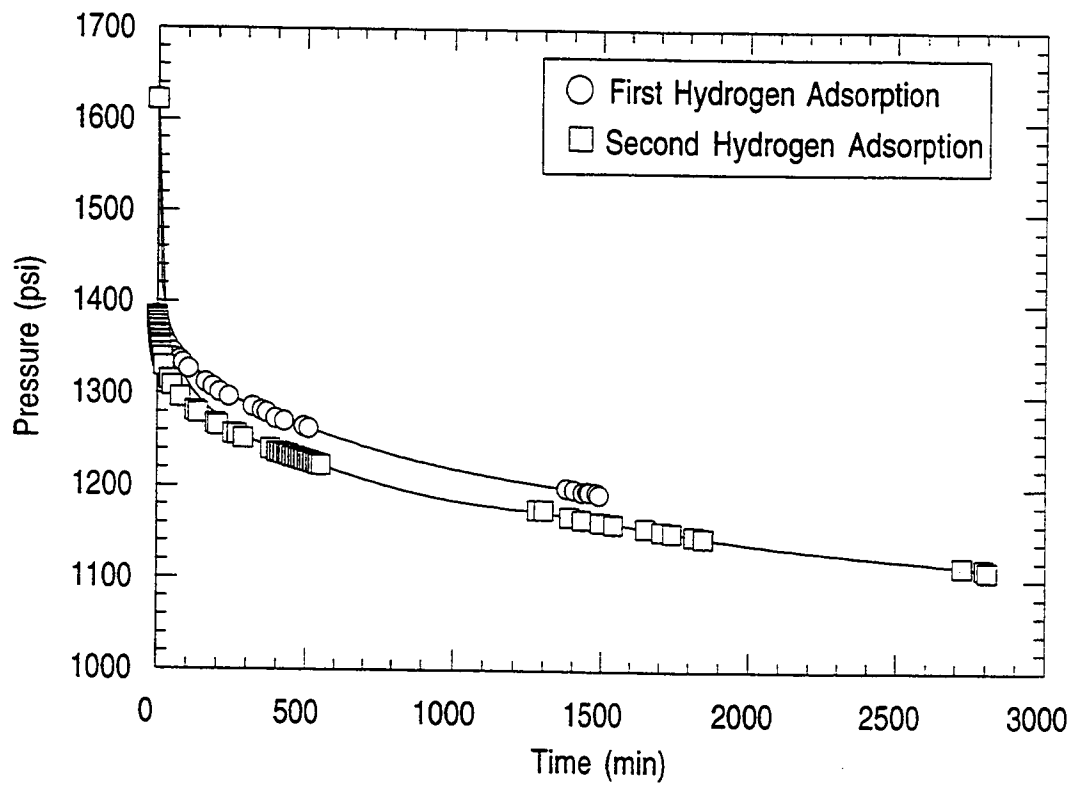
0.34 nm ⚌

Figure 1

a

b

0.34 nm

0.29 nm

Figure 2

Figure 3

Figure 4

Figure 5