

# Carbon nanostructures

Carbon nanostructures, seen as promising materials for many applications, could become one of the more innovative paths for hydrogen storage.

Two categories of carbonaceous nanomaterials stand out as regards hydrogen storage: nanotubes, (1) which are the target of much research work, and activated carbons, (2) which, paradoxically, have attracted little investigation, compared to the former, for this application.

## Nanotubes: properties awaiting confirmation

Since A. C. Dillon reported, (3) in 1997, the ability to store hydrogen in nanotubes, a large number of investigations have been devoted to this topic. Some twenty papers, over the past few years, have noted significant values (> 3 % by weight), some of which, announced quite recently, have come from laboratories of renown (6 wt% at 2 MPa and 77 K, as claimed by Honda and Lawrence Livermore National Laboratory; 3 wt% at 10 MPa [100 bars] and ambient temperature by Osaka Gas). In a majority of cases, however, it unfortunately proved impossible to obtain samples to verify the properties announced. Tests carried out on available materials, from outside laboratories or synthesized at CEA, in the Saclay and Le Ripault centers, have not found any significant adsorption (see Table), whether these materials had been subjected to opening, purification or doping treatments, or not. (4) This, however, does not warrant drawing any conclusion, since nanotubes can exhibit highly diverse characteristics, which may lead to varying behavior. The results from modeling do not allow the issue to be decided either, since many authors, depending on the models adopted and the data used, find values that may be very low (< 1 wt%), or very high (~10 wt%). Research workers at CEA are actively following developments, and are looking to obtain materials of interest, for test purposes.

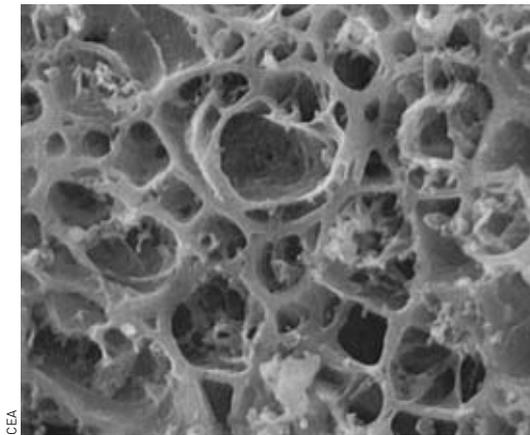
(1) Nanotubes: crystalline carbon structures, comprising one or more rolled-up graphite sheets, of nanometric diameter but having a length that may attain several micrometers, or even hundreds of micrometers. They may be either metallic or semiconductors, exhibiting conductivity which is not dependent on length, and, among other properties, mechanical strength six times higher than that of steel wire.

(2) Activated carbons: materials exhibiting high adsorption capacity, obtained by pyrolysis (activation) from high-carbon-content materials (coal, hydrocarbons, wood...): the more volatile constituents are removed, leaving a microporous carbonaceous structure having a specific surface area in the range 300-1,500 m<sup>2</sup>/g. Main applications: water or air treatment, the agricultural and food industry, the pharmaceutical industry.

(3) A. Dillon et al., Nature 386 (1977), p. 377.

(4) T. Piquero, Y. Pierre, P. David (CEA /Le Ripault); S. Begin-Colin, K. Lebbou, P. Perriat, O. Tillement (Claude-Bernard University), "Ouvrir les nanotubes de carbone augmente-t-il leur capacité de stockage d'hydrogène?", Proceedings of the Convention "Matériaux 2002, de la conception à la mise en œuvre", Tours (France), 21-25 October 2002.

(5) N. Texier-Mandoki, T. Piquero, J. Dentzer, P. David, C. Vix-Guterl, "Hydrogen storage in activated carbon materials: role of the porous structure", Carbon, in press.



Structure of activated carbon, observed under scanning electron microscopy.

material	adsorption conditions	storage (wt%)
nanotubes (single wall)	77 K ; 1 MPa	~ 0.7
	300 K ; 10 MPa	< 0.2
activated carbon	77 K, 1 MPa	6
	300 K, 1 MPa	< 0.5
tank with no adsorbent	77K, 1 MPa	~ 0.7

Table. Hydrogen adsorption capacity of various carbon materials.

## Activated carbons: the CASH Program

Activated carbon materials are known for their adsorption properties. Notable values found for semi-industrial products (see Table) warrant their being considered for cryogenic tank applications (see Figure 1). The CEA team at Le Ripault recently set up the CASH Program (Charbons actifs pour le stockage de l'hydrogène: Activated Carbons for Hydrogen Storage), as a partnership with société Pica (activated carbon manufacturers, a subsidiary of Veolia Water) and the Nantes mine engineering school. This program, endorsed by the PACo Network and supported by the French Ministry for research, aims at securing improved understanding in this area, and enhanced performance for such materials. The CEA team was able to establish very good correlation between the hydrogen-adsorption capacity of materials, and their microporous volume (corresponding to pores with a diameter of under 0.8 nm) (5) (see Figure 2). The team was also able to

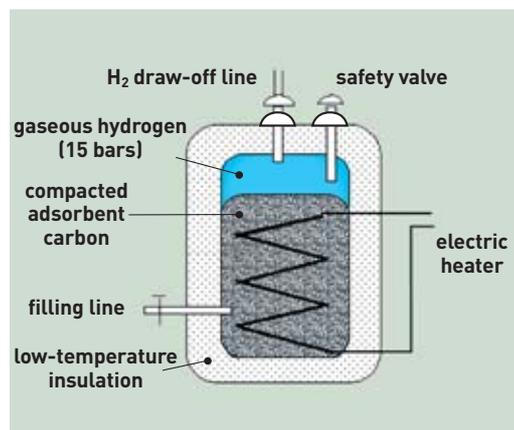
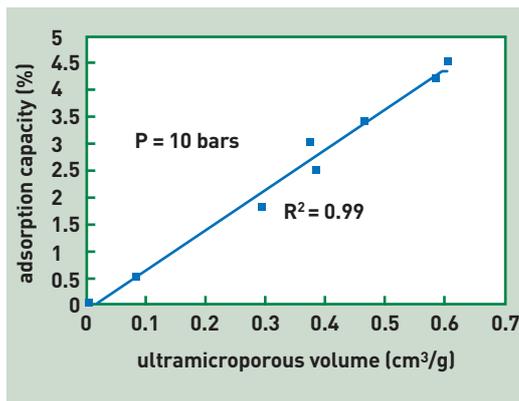


Figure 1. Theoretical schematic of a cryogenic pressure tank for hydrogen storage. The tank is filled using liquid or cooled hydrogen, the gas being recovered by reducing pressure and, in some cases, by heating.



Figure 2. Correlation between adsorption capacity and ultramicroporous volume (pore diameter < 10 nm). Adsorption capacity does not include compressed H<sub>2</sub> in the intergrain porosity.



synthesize activated carbons exhibiting storage capacities that rank among the highest, of all the materials tested (5.5 wt% at 1 MPa [10 bars] and 77 K) (see Figure 3). These materials exhibit an exceptional proportion of effective pores (90% microporosity), which should make them the most advantageous in terms of compactness; 30 kg hydrogen per cubic meter of material should be achieved.

(6) General Motors have recently announced they were investigating the selfsame solution (cryogenic tank containing activated carbons, Inside Fuels and Vehicles, 18 December 2003). One major Japanese manufacturer considered compressed or liquid hydrogen was not a satisfactory solution, banking rather on hydrides and carbon materials (Inside Fuels and Vehicles, 12 February 2004).

(7) Aerogel: a solid, porous (90-99% empty space), ultralight material (exhibiting a density of the order of tens of milligrams per cubic centimeter), formed when the liquid is removed from a gel, leaving as residue a lattice of nanoparticles. Aerogel exhibits outstanding thermal and sonic insulation properties. Silica aerogels, the most widely-used form, consist in microspheres of porous, amorphous silicon dioxide-based glass. Carbon aerogels may be used as host material for hydrogen storage, but equally as electrode material (fuel cells, supercapacitors).

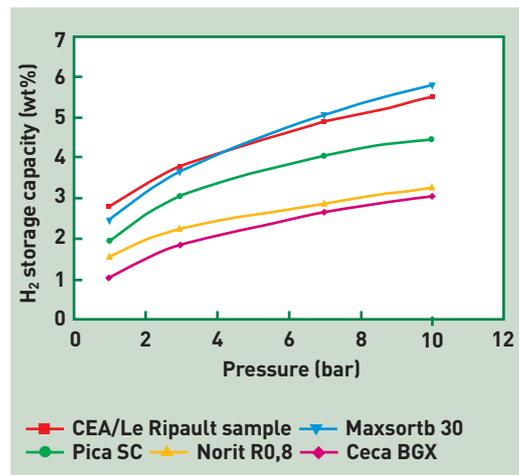


Figure 3. Influence, at 77 K, of pressure on the H<sub>2</sub> storage capacity of industrial (Pica, Norit, Ceca) or prototype (Maxsortb 3, CEA test sample) activated carbons.

This solution, while it does not as yet allow DOE targets for automotive applications to be achieved, is beginning to gain recognition as being competitive, as witness recent pronouncements by automotive manufacturers. (6) The next stage will involve development, with a manufacturer, of a prototype cryogenic tank containing activated carbons.

Other programs have also been initiated with academic laboratories and the French CNRS: participation in excellence networks, "Nano Hydro" concerted incentivizing initiative (action concertée incitative) for energy, funded by Ademe, and collaboration on electrochemical hydrogen storage in carbon aerogels. (7)

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## Liquid hydrogen storage in personal vehicles

Liquid hydrogen storage is one of the solutions available to automobile manufacturers, whether to feed a fuel cell, or directly to supply fuel to an internal combustion engine, as German manufacturer BMW is doing.



Robot-operated liquid-hydrogen filling station at Munich Airport.

In the context of an intensive research effort, spanning over twenty years, BMW AG have brought forward solutions for the major aspects of hydrogen technology. All hydrogen-burning BMWs are powered by internal combustion engines, fed from liquid hydrogen storage units. One recent instance being the 750hL, shown at Expo 2000, and further operated during the CleanEnergy World Tour, in 2001 and 2002. The auxiliary power required for the electrical system was generated by a PEMFC fuel cell. A fleet of vehicles of this type covered an overall distance of about 200,000 km in hydrogen mode, with no notable problem arising.

Currently, onboard hydrogen storage in automobiles is carried out in the liquid or pressurized gaseous form. Liquid hydrogen exhibits the higher energy

density. Hydrogen compressed at over 1,200 bars (120 MPa), for instance, would exhibit an energy density comparable to that of liquid hydrogen (LH<sub>2</sub>) stored at 5 bars (0.5 MPa). Owing to low-pressure operation, liquid-hydrogen tanks offer a major weight reduction potential, and allow new concepts to be put forward, yielding shape geometries (free-form tanks) that are better suited to a variety of vehicle designs. Maximum working pressure in LH<sub>2</sub> storage systems is 5 bars. Tank insulation must meet severe constraints, since liquid hydrogen temperature is around -250 °C. The LH<sub>2</sub> tank is located behind the vehicle's rear bench seat. With a capacity of 120 liters, it holds about 8 kg LH<sub>2</sub>, equivalent to 32 L gasoline.

The tank structure comprises an inner and an outer shell, each fabricated from 2-mm, low-temperature-resistant special-steel plate (see Figure). To achieve a high level of insulation, a 30-mm wide super-insulation space - equivalent to some 3.5 m polystyrene - acts as separation between the two shells. This space holds a vacuum (at 10<sup>-6</sup> mbar, once cold conditions pertain), and 70 layers of aluminum foil, alternating with glass-fiber fleece. The outer shell mounts an encapsulated auxiliary system, monitored by the "gas" warning system, comprising the valves, hydrogen heater and sensors (pressure, temperature, and tank level). At engine start up, gas is drawn from the tank. As soon as tank pressure drops beneath a given threshold, the pressure-restoration system is activated. An electric element, positioned inside the inner tank, heats the liquid hydrogen, which, by evaporation, builds up the pressure to ensure engine fuel supply. Hydrogen, drawn off at very low temperature, is heated to ambient temperature in a heat exchanger, fed by the engine coolant. The engine is fed via a pressure regulator. A capacity sensor determines the LH<sub>2</sub> level inside the tank, this value then being displayed on the dashboard.

The tank features two redundant safety systems, to prevent overpressure. If, for instance, tank insulation is damaged following a serious accident, the resulting rising heat transfer leads to intense evaporation, which ultimately triggers the pressure-limiting safety valve. The hydrogen is then bled off through pipes venting it directly outside the vehicle. In the event of a malfunction of this pressure-relief system, the inner tank's rupture disc breaks before pressure can overstress the tank. In this case also, pressure is lowered in a pre-defined manner.

In order to limit and evaluate the effects of potential damage, worst-case scenarios were examined and tested. It was shown the LH<sub>2</sub> tanks exhibit, even in extreme conditions, noncritical behavior.

### Filling up in three minutes

Refueling with LH<sub>2</sub> may be carried out either manually or in fully automated fashion in robot-operated service stations. While the two-piped coaxial coupling docks with the vehicle, the space between filler couplings, on the supply side and vehicle side, is flushed out with helium to preclude any air being included. Once docking is completed, the ball valves in both couplings are opened. Overpressure in the service-station tank causes LH<sub>2</sub> to flow into the vehicle tank. Transfer is effected through a vacuum-insulated, coaxial hose.

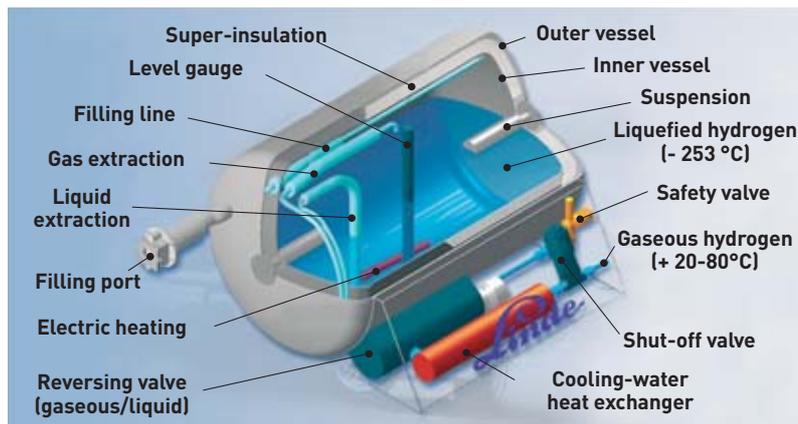
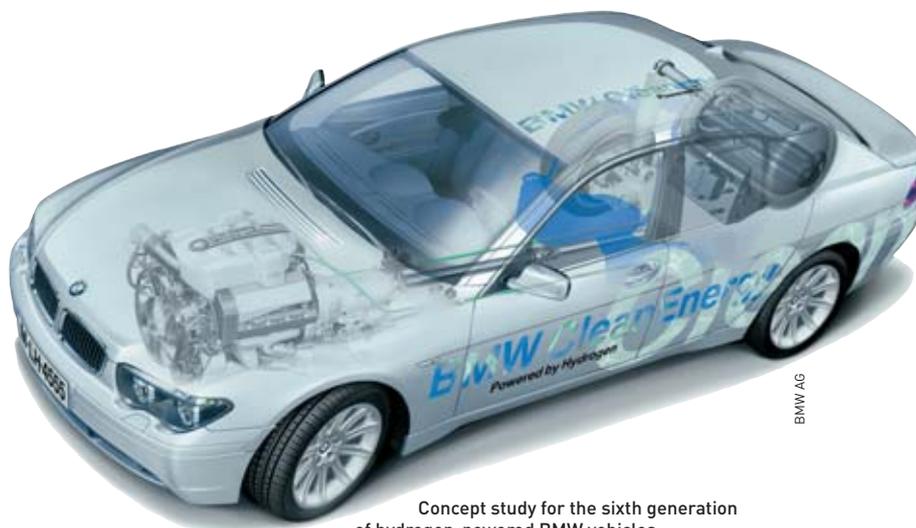


Figure: Schematic of the structure of a liquid-hydrogen tank.

During the refueling procedure, any gas generated is routed back to the supply tank. On completion of the procedure, the ball valves are closed, and the filler couplings disconnected.

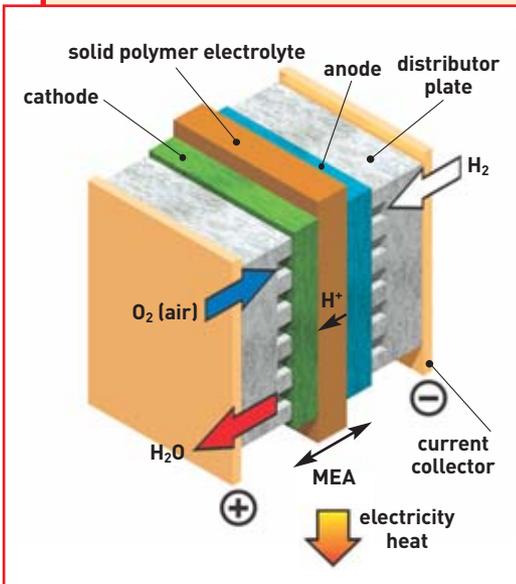
The potential of hydrogen as an energy source for vehicle engines, with respect to driving performance, energy efficiency, emission rate, safety, comfort and economy, can be further developed. There will be a requirement, however, when future generations of vehicles are defined, to take on board the characteristics of hydrogen from the initial layout stage of a vehicle and drivetrain design. A further step in that direction will be taken with the development of the sixth generation of hydrogen BMWs. This model, due to be offered to customers, initially, in the guise of the current 7 Series, is to be fitted with a hydrogen-burning internal combustion engine and liquid-hydrogen storage system.

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Concept study for the sixth generation of hydrogen-powered BMW vehicles.

## C How does a fuel cell work?



Operating principle of the fuel cell: the example of the proton-exchange membrane fuel cell. MEA stands for membrane-electrode assembly.

The fuel cell is based on a principle discovered quite some time ago, since it was in 1839 that Sir William Grove constructed the first electrochemical cell working with **hydrogen** as its **fuel**, thus demonstrating the ability to generate electric current through direct conversion of the fuel's chemical energy. Since the fuel cell has the special characteristic of using two gases - hydrogen  $H_2$  and oxygen  $O_2$  - as its electrochemical couple, the **oxidation-reduction** reactions occurring inside the fuel cell are particularly simple. The reaction takes place inside a structure (the **basic electrochemical cell**), consisting essentially in two **electrodes** (the **anode** and **cathode**), separated by an **electrolyte**, i.e. a material that lets **ions** through. The electrodes employ **catalysts**, to activate, on the one side, the hydrogen **oxidation** reaction, and, on the other, the oxygen **reduction** reaction.

In the case of an acid-electrolyte cell (or **proton** exchange membrane fuel cell), the hydrogen at the anode is dissociated into protons (or hydrogen ions  $H^+$ ) and **electrons**, in accordance with the oxidation reaction:  $H_2 \rightarrow 2 H^+ + 2 e^-$ . At the cathode, the oxygen, the electrons and the protons recombine to yield water:  $2 H^+ + 1/2 O_2 + 2 e^- \rightarrow H_2O$ . The principle of the fuel cell is thus the converse of that of water **electrolysis**. The thermodynamic potential for such an electrochemical cell, consequently, stands at around 1.23 volt (V). However, in practice, the cell exhibits a voltage of about 0.6 V for **current densities** of 0.6-0.8 A/cm<sup>2</sup>. The efficiency of such a fuel cell is thus equal to about 50%, the energy dissipated naturally being so dissipated in the form of heat.