HYDROGEN STORAGE BY ADSORPTION ONTO DIFFERENT ACTIVATED CARBONS

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Abstract

The objective of this work was to evaluate the hydrogen storage capacities of various activated carbon materials in form of granules, powders, fibers and clothes under cryogenic and ambient temperature conditions (77K - 293K), at pressures up to 30Bar. The experimental data were analyzed for carbon samples covering a wide range of BET surfaces and microporous volumes. At 293K, the storage capacities of all the materials tested were found to be very low, and to result mainly from compression of the gas within the external voidage of the bulk solid sample and the internal porous volume of the material. Under these conditions, the storage capacity varies linearly with the pressure increase. At 77K, the contribution of physisorption becomes significant and was shown to represent nearly 60% of the maximum storage capacity measured à 20Bar. The experimental set of data enabled to propose a model to predict the weight of hydrogen stored in the carbonaceous sample. This model assumes the superposition of the two phenomena : physisorption within the material's micropores and gas compression in the external and internal voidage of the sample The model was deduced from the Langmuir equation and a non ideal gas law. According to this model, the maximum weight percentage of hydrogen that could be stored in a tank filled with a material having a BET surface equals to $2600m^2/g$ and a bulk density of 200 kg.m^{-3} would be as high as 9% in weight at 20Bar.

Introduction

Hydrogen is a renewable and environmentally friendly energy source. It has been considered as an ideal energy medium for replacing fossil fuels such as oil and coal. For instance, an electrical vehicle powered by a hydrogen fuel cell will requires 3.1 kg of hydrogen to achieve a range of 500 km. However, hydrogen storage is the bottleneck for the breakthrough of hydrogen as the energy carrier in automotive applications. In the last years, different storage technologies were investigated in order to develop a secure and cheap way to save hydrogen. Storage by gas compression, hydrogen liquefaction, or in the form of metallic hydrides and complex hydrides, possess several disadvantages (Zhou, 2005). These drawbacks have induced the study of storage concepts as physical adsorption on carbon materials. Although physisorption of hydrogen on carbon nanotubes and carbon nanofibers seems now hopeless, the microporous activated carbons possessing abundant slit-like micropores (<2 nm) appear as very good candidates for the development of packed bed hydrogen storage tanks. (Zhou et al., 2004). According to Zhou (2005), the cryoadsorption of hydrogen on activated carbons allows to reach a storage capacity of more than 10 wt% , which agrees with the 2015 target of the Department Of Energy (DOE) applied to automobile transport (Table 1), and enables to obtain a reasonable volumetric density of 41 kg/m^3 at a relatively low cost.

Table 1. DOE targets for automobile applications (from Bouza et al., 2004).

Storage parameter	2005	2010	2015
Gravimetric capacity (wt%)	4.5	6	9
Volumetric capacity (kgH_2/m^3)	36	45	81

In this paper, we present a survey of the storage capacity of hydrogen in various microporous carbon materials, having different forms (granules, powders, fibers and clothes) and representative of a wide range of specific surface areas and microporous volumes.

Experimental

Carbon materials

A large number of activated carbons (Table 2) were selected to represent a wide range of surface areas and micropore volumes. The porosity properties of the activated carbon samples were characterized using N_2 physisorption at 77K under atmospheric pressure. From the N_2 physisorption data, obtained with a Micromeritics ASAP 2010 apparatus, the BET surface area, and the micropore volume (MV), defined for pore widths less than 2nm were derived. The BET surface area (S_{BET}; m^2/g) is the surface area of the sorbent according to the model formulated by Brunauer et al. (1938) for planar surfaces. The bulk density of the carbon materials (ρ_{bulk}) was determined from the mass of the activated carbon (m_{carbon}) introduced into the storage tank having a volume equals to 254 mL. This data was also confirmed by the determination of the total pore volume deduced from Mercury intrusion porosimetry (Micromeritics AutoPore IV 9500) and N_2 adsorption measurements.

Table 2. Physical characteristics of the carbon materials investigated for hydrogen storage.

Activated carbons		S_{BET} (m^2/g)	MV (cm^3/g)	ρ_{bulk} (kg/m^3)
Material	shape			
PICA 70	granule	1207	0.517	463
PICA BC120	granule	1812	0.772	241
PICA SC	granule	2075	0.877	223
PICA SC	powder	2162	0.915	189
NORIT row 0,8 supra 3708-1	granule	900	0.409	381
ACTITEX SC-1501	fiber	1397	0.597	330
KYNOL	fiber	1299	0.555	144
ACTITEX WWP3	clothe	455	0.195	255

Hydrogen storage measurement

The hydrogen storage capacity of the carbon materials was measured by a gravimetric method. The experimental setup presented in Figure 1 was composed by a loading circuit with a $8.8m^3$ hydrogen bottle *(1)* at 200Bar (purity 99.99%), linked through a pipe to the storage tank *(8)*. The circuit was equipped with a pressure monitoring system *(6)* and a mass flowmeter *(5)* Brooks 5850S which allowed to regulate the hydrogen flow at the desired value (200 NmL/min). The storage tank was a cylindrical stainless steel reactor equipped with an internal thermocouple which allowed to know the temperature within the bed of the activated

carbon. The data were acquired by means of the Test Point software and the acquisition frequency for temperature (T), pressure (P) and hydrogen mass flow was 1Hz. The apparatus was previously tested for leak absence and for accuracy through calibration with the empty tank.
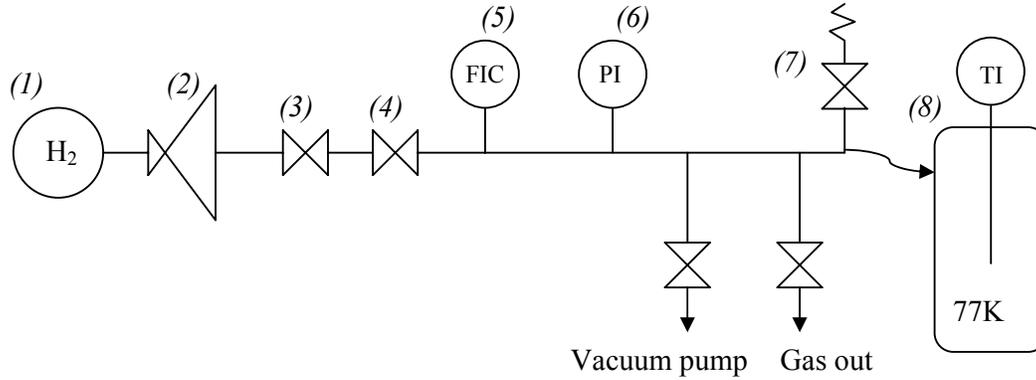

Figure 1. Experimental setup for hydrogen storage. *(1)* hydrogen bottle, *(2)* regulator, *(3)* stop valve, *(4)* gate valve, *(5)* mass flowmeter, *(6)* pressure indicator, *(7)* security valve, *(8)* storage tank.

Experiments were carried out at 77 and 293 K and the pressure was increased step by step up to 30Bar. Before each experiment, the gas inside the circuit was extracted using a vacuum pump to reach a pressure around few mbar. The loading process was started by opening valve *(3)* and the gas flowing was regulated by the mass flowmeter. During the loading process, the tank was cooled either in liquid nitrogen (77K) or in water regulated at a constant temperature (293K). The gas flow rate and the time required to reach the equilibrium conditions at constant pressure and temperature were continuously recorded. The integration of the data flow rates with the time gave the mass of hydrogen filling the tank and the *dead volume* (V_{dead}) which was the part of the circuit downstream the flowmeter, equivalent to 38 mL.

At equilibrated pressure and temperature, the mass of hydrogen stored in the tank completely filled with the carbon sample, was deduced by difference between the total mass of gas measured and the mass of gas filling the dead volume (eq.1). This last quantity was computed from the ideal gas law corrected with the compressibility factor Z, from Zhou and Zhou (2001).

$$\left(M_{H_2}^{PT} \right)_{stored} = \left(M_{H_2}^{PT} \right)_{measured} - \left(M_{H_2}^{PT} \right)_{V_{dead}} \tag{1}$$

The hydrogen storage capacity in the tank filled with carbon materials results from the adsorption within the micropores on the solid surface and the compression in the void spaces in the tank. In order to assess the gain obtained from the part of the gas physically adsorbed onto the material, the mass of the gas filling the tank by compression in the space non occupied by the carbon skeleton was evaluated and deduced from the mass stored in the tank (eq 2). In this equation the "skeleton" carbon density (ρ_{carbon}) was 2267 kg/m^3.

$$\left(M_{H_2}^{PT}\right)_{adsorbed} = \left(M_{H_2}^{PT}\right)_{stored} - \frac{M_{H_2}^{molar}P}{ZRT}\left(V_{tank} - \frac{m_{carbon}}{\rho_{carbon}}\right) \qquad (2)$$

From eqs (1) and (2), the storage gravimetric capacities as well as the adsorption capacities of the materials were derived (eq. 3 and 4). It is important to note that the gravimetric capacities given by eqs (3) and (4) do not take into account the mass of the tank.

$$wt\%_{stored} = 100 * \frac{\left(M_{H_2}^{PT}\right)_{stored}}{m_{carbon}} \qquad (3)$$

$$wt\%_{adsorbed} = 100 * \frac{\left(M_{H_2}^{PT}\right)_{adsorbed}}{m_{carbon}} \qquad (4)$$

The volumetric capacity (VC) of the tank corresponding to the mass of hydrogen stored in a 1m^3 reservoir was given by eq (5) :

$$VC = \frac{wt\%_{stored}}{100}\cdot\rho_{bulk} \qquad (5)$$

Results and analyses

Figure 2 shows typical results of the changes in the mass of hydrogen stored in the tank as a function of the pressure measured at 77 and 293K. The results are showed for a granular material (PICACTIF SC) having a BET surface in the upper range (2075 m^2.g^{-1}) among the selected materials. At 293K, due to low hydrogen adsorption capacities of the tested material, the storage capacity was found to be a linear function of the pressure. Thus, at ambient temperature, the storage is mainly due to the compression of hydrogen in the external voidage and internal pore volume of the material. In such conditions, there's no advantage to use an activated carbon adsorbent for hydrogen storage, as shown in the Figure. At 77K, the the physisorption process is predominant at pressures below 5Bar, and increases significantly the storage capacity of the tank compared to pure compression under identical temperature and pressure conditions. Beyond 5Bar, the contribution of the gas compression in the sample void spaces becomes larger and larger, and represents 50% of the mass of hydrogen stored in the tank at the highest pressure 30Bar. Similar observations were made for the other tested materials.

From the previous experimental data, the adsorbed and storage gravimetric capacities were deduced and modelled using a Langmuir model to account for the part of hydrogen adsorbed onto the carbon surface and a linear regression function of the pressure to represent the quantity of gas compressed, according to the corrected ideal gas law:

$$wt\%_{adsorbed} = \alpha\frac{bP}{(1+bP)} \qquad (6)$$

$$wt\%_{stored} = \alpha\frac{bP}{(1+bP)} + \beta P \qquad (7)$$

In this model, the α parameter represents the maximal storage capacity due to adsorption phenomena. This maximal capacity is obtained for pressure around 20Bar and corresponds to the limit of the hydrogen physisorption onto activated carbon at 77K.

For the investigated carbon materials, relationships between α and the porosity characteristics of the samples were investigated. It was then pointed out that α is strongly correlated to the BET surface and the micropore volume of the materials. The determination coefficients (R^2) of the linear regressions obtained, available at 77K, were thus as high as 0.98 (Fig. 3 and 4). According to these results, the adsorption capacity of an activated carbon having a specific surface area approaching 2600 m^2/g (which is high but remains a reasonable value) would be 6.0 wt% at 77K. This result agrees with the value advanced by Bénard and Chahine (2001), which was deduced from a molecular modelling approach.

The compression parameter β, is dependent upon the internal and external voidage of the material, and was logically found to be correlated to the bulk density (Figure 4).

At last, beyond 20Bar, the hydrogen storage capacities of the various activated carbons can be predicted according to equation (8) :

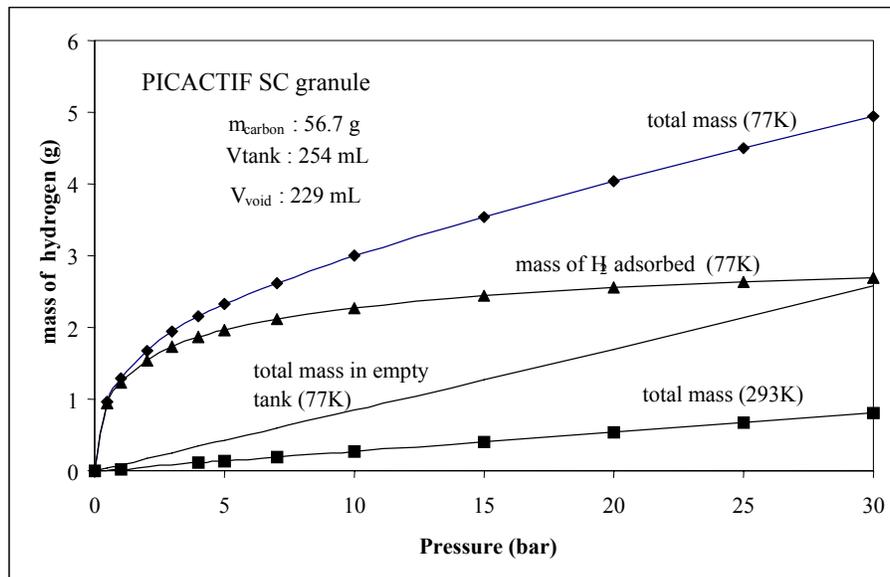$$wt\%_{stored} = 0.0023 \; S_{BET} \; + 61.6 \; \rho_{bulk}^{-1.14} \; P \tag{8}$$

Figure 2. Typical example of the changes in the mass of hydrogen stored and adsorbed in the activated carbon materials with pressure.
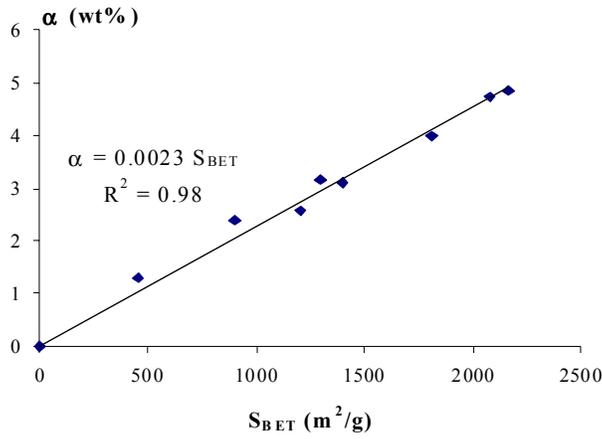
Figure 3. Relation between the maximal hydrogen adsorption capacity of different activated carbons measured at 77K and their BET surface.
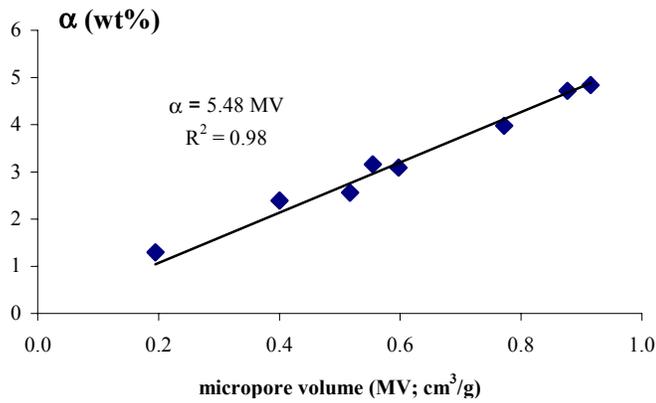

Figure 4. Relation between the maximal hydrogen adsorption capacity of different activated carbons measured at 77K and their micropore volume.
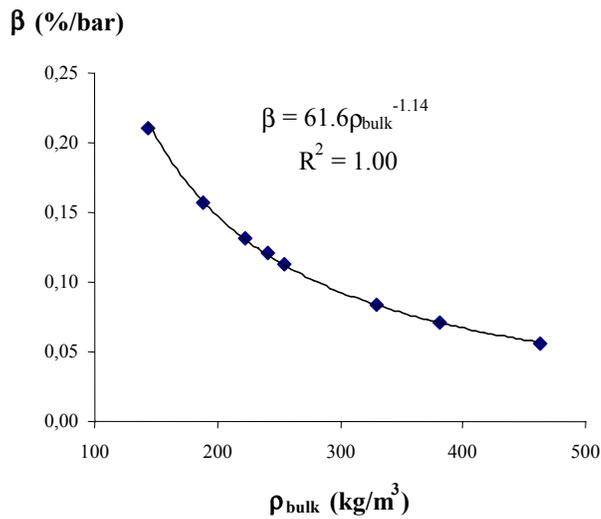

Figure 5. Relation between the compression parameter β and the bulk density of the different carbon materials at 77K.

From the previous model (eq. 8), it appears that the gravimetric hydrogen storage capacity of an activated carbon having a BET surface area of 2600 m^2/g, and a bulk density of 200 kg/m^3 could reach the DOE target 2015 of 9 wt% at 20Bar and 77K. However, taking into account the low bulk density of the activated carbon, the volumetric hydrogen capacity obtained in these conditions remains far from the volumetric 2010 DOE target, as shown in Figure 6.

The key to achieve this target is the use of a densification process which can produce activated carbons with a high bulk density and high surface area. Nonetheless, according to Bénard and Chahine (2001) a densification process increasing the bulk density from 300 to 700kg/m^3 lowers the surface area by roughly 30%. Assuming that a densification process does not modify the microporous properties of the activated carbon (S_{BET} remaining equals to 2600 $m^2.g^{-1}$), the model (eq 8) can be used to assess the influence of the increase in the bulk density of the material on the gravimetric and volumetric storage capacities at 77K and 20Bar (Figure 7). It appears that the gravimetric capacity will decrease with the increase of the bulk density due to the decrease of the material's voidage. Figure 7 shows that both the volumetric and gravimetric DOE targets 2010 can be reached for a densification process leading to a final bulk density around 600 kg/m^3, i.e 2 to 3 times higher than the bulk density of usual activated carbons. However, Figure 8 indicates that the activated carbon densification does not allow to reach the volumetric DOE target 2015 (81kg/m^3) at 20bar.
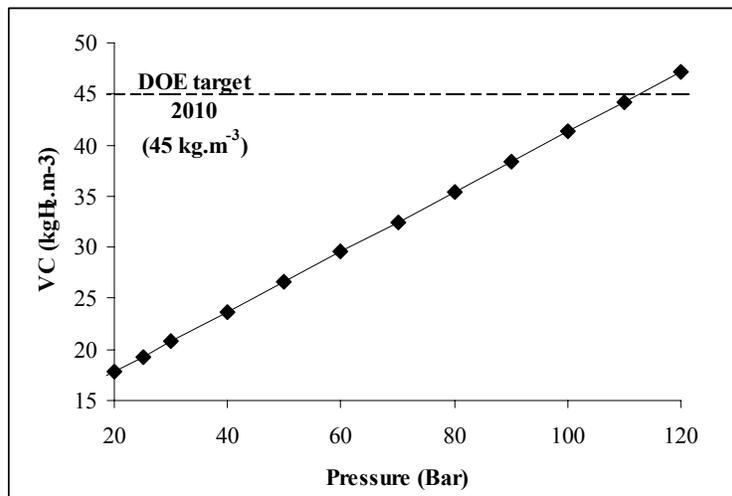

Figure 6. Volumetric storage capacity versus pressure at 77K according to eq (8) and (5) for an activated carbon with following properties: S_{BET}=2600 m^2/g; ρ_{bulk}=200 kg/m^3.
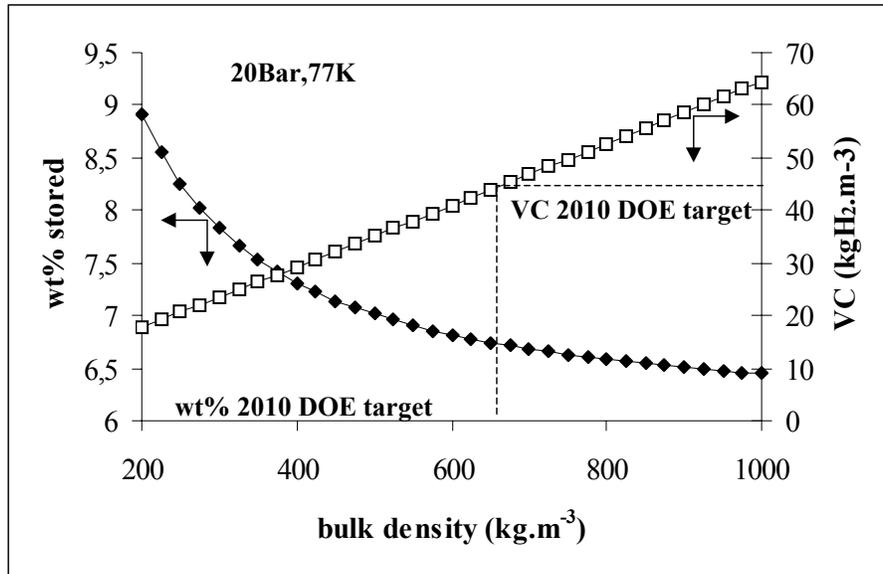
Figure 7. Gravimetric and volumetric hydrogen storage capacities versus bulk density at 77K and 20bar according to eq (8) and (5) for an activated carbon with S_{BET}=2600 m^2/g.

Conclusions

Different activated carbons were investigated for hydrogen storage at 77 and 293K, at pressure up to 30Bar. The storage capacity results from the hydrogen physisorption on the surface of the microporous material and from gas compression within the internal and external voidage of the solid particles. Activated carbons are hopeless at room temperature for hydrogen storage since the part of hydrogen adsorbed is so low that storage occurs mainly by compression. Under cryogenic conditions (77K), the part of adsorbed hydrogen becomes significant and contributes to enhance significantly the storage capacities compared to pure gas compression, especially at pressure under 20Bar. Beyond 20Bar, the increase in the storage capacities with the pressure is mainly due to compression. From the experimental data, a model was developed taking into account both adsorption and compression phenomena at 77K. From the modelling approach, it was shown that the maximal amount of hydrogen that can be physisorbed at 20Bar and 77K onto an activated carbon, depends linearly on the specific surface area (or on the micropore volume). The part of hydrogen stored by compression varies linearly with the pressure and depends on the bulk density of the carbon material ($\rho_{bulk}^{-1.14}$).

From this model the characteristics of an ideal activated carbon enabling to reach the 2015 DOE gravimetric target (9wt%) were derived. An activated carbon having a BET surface as high as 2600 m^2.g^{-1}, and a bulk density of 200kg.m^{-3} could reach this objective since 20 bar, at 77K.

However the low bulk density of such an activated carbon limits the volumetric storage capacity (only 18kg/m^3 at 20Bar, 77K). The key or a successful application of adsorption storage could be the mechanical densification of activated carbons. Thus a densification process leading to a material with a bulk density around 600 kg.m^{-3}, keeping a BET surface of 2600 m^2.g^{-1} could nearly satisfy both the volumetric and gravimetric 2010 targets. However, to reach the volumetric 2015 target far higher pressures (around 200Bar) are required which is prohibitive. In that way, only considerable improvement of the hydrogen adsorption

capacities of the activated carbons could be considered as promising for automotive applications.

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