

Advanced carbon materials for gas storage and space cryocoolers applications

Materiales carbonosos avanzados para el almacenamiento de gases y aplicaciones espaciales

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Abstract

Performance of advanced carbon materials in two applications, storage of H₂ and space cryocoolers are reported, concluding that carbon material properties must be designed for the adsorption of the corresponding gas (H₂ and He) at high pressures and different temperatures. Results shown here remark the importance of optimizing the porous texture (mainly the micropore volume and the micropore size distribution) and density of the materials for achieving high capacities in gravimetric basis, and volumetric, respectively (in all cases the adsorbent is confined in a limited volume).

Resumen

El comportamiento de materiales carbonosos avanzados en dos aplicaciones (almacenamiento de hidrógeno y aplicación espacial) ha puesto de manifiesto que las propiedades de los materiales carbonosos se deben diseñar para la adsorción del correspondiente gas (H₂ and He) a alta presión y diferentes temperaturas. Los resultados remarcan la importancia de optimizar la textura porosa (principalmente volumen de microporos y distribución de tamaño de la microporosidad) y densidad de los materiales para alcanzar altos valores de capacidades en base gravimétrica, y volumétrica, respectivamente, (en todos los casos, el adsorbente está confinado en un volumen restringido).

1. Introduction

H₂ could be used as a substitute of fuel oil in the vehicles, but the main drawback of its use is their storage in the vehicular fuel tank. H₂ can be stored as an adsorbed phase in porous materials filling the storage vessel. The search for a suitable porous material, in terms of further improving the storage volumetric energy density and lowering the adsorbent cost to the end use, is currently an active area of research. The Department of Energy of the United States (DOE) has established different targets for H₂ storage systems, including the minimum "gravimetric" and "volumetric" capacities and the reversibility of the charging/discharging processes. Thus, to cover the same range than commercially available cars, the DOE storage target for hydrogen is set at 9 wt. % of stored hydrogen and a volumetric density of 0.081 kg H₂/L [1]. The more recently calculated values for "Light-Duty vehicles" reduce the targets down to 5.5 wt.% of H₂ and 0.040 kg H₂/L [2]. In Europe, the targets are less restrictive and in the European Hydrogen and Fuel Cell Strategic Research Agenda and Deployment Strategy, S. Barret pointed out an energy density value of 1.1 kW h/L, that is equivalent to a volumetric hydrogen storage capacity of about 0.033 kg H₂/L [3].

A new and very singular application of activated carbons (ACs) is its use in an adsorption compressor. The European Space Agency is developing a space interferometer that requires a cooling system cooling to around 4.5 K. Such a cooling system must be mechanically vibration-free so as not to disturb the sensitive optical system [4]. A sorption cooler is a favourite option because, having no moving parts, it is essentially vibration-free. The key component of such sorption cooler is the sorption compressor, which is based on a solid that adsorbs a large amount of gas and, by subsequent electrical heating, creates a high pressure inside the closed vessel. In this sense the University of Twente, the University of Alicante and the Dutch Space were working to develop a breadboard 4.5 Kelvin sorption cooler for the European Space Agency (ESA) [5,6]. It uses an AC because of its high adsorption capacity. Of course, the selection of the adsorption material is a key point, since the performance of the sorption compressor is very much influenced by the characteristics of the material used. For both applications, sorption cooler and hydrogen storage application, the porous texture (micropore volume, micropore size distribution) and the density of the carbon materials were demonstrated to be crucial parameters to optimize the performance [5,7].

2. Hydrogen storage on Activated Carbons

As mentioned in the introduction, the hydrogen storage systems not only have to achieve the target in gravimetric basis but also in a volumetric one. From an application point of view it is much more relevant to compare storage data on a volume-specific rather than on a weight-specific storage capacity basis, because hydrogen storage would be carried out in a material filled vessel. Thus, the packing density of the materials is crucial, and in general, for porous carbons, decreases with the porosity development [8-11].

Using the values of packing density, hydrogen adsorption capacities at 77 K and up to 4 MPa in volumetric basis were estimated for a series of activated carbons (ACs), prepared by KOH activation of an anthracite, and activated carbon monoliths (ACMs). These values are presented in Figure 1 versus the micropore volume, together with the hydrogen adsorption capacities in gravimetric basis. It is clearly seen that the hydrogen adsorption capacity in gravimetric basis (wt.%) at 77 K and at pressures up to 4 MPa follows a good correlation with the total micropore volume, obtaining the highest value for the sample with the highest micropore volume. On the other hand, for the data in volumetric basis (g/l) it can be seen that the maximum hydrogen adsorption does not correspond to the sample with the highest

micropore volume. The maximum in volumetric basis corresponds to samples with a relatively high porosity and packing density. Thus, according to these results, in order to get a maximum hydrogen adsorption capacity in volumetric basis we should choose an activated carbon with a good balance between porosity development and packing density or, in other words, an activated carbon presenting, simultaneously, high micropore volume and high packing density. This Figure contains also the values obtained with an ACM, which presents high porosity and also high density. The maximum value obtained for this material is 29.7 g/l.

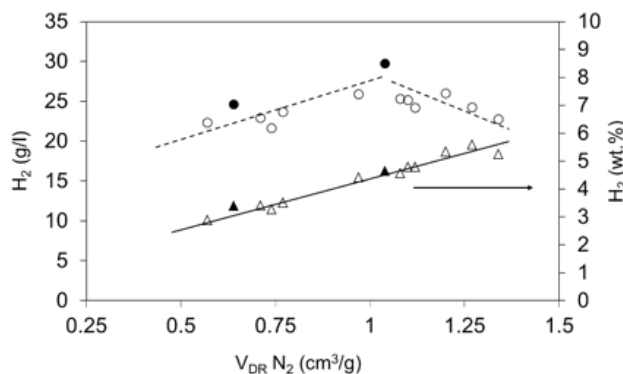


Fig. 1. Amount of hydrogen adsorbed at 77 K and 4 MPa (in volumetric and gravimetric basis) versus the total micropore volume. Empty symbols correspond to powder ACs and full symbols to ACMs

Fig.1. Cantidad de hidrógeno adsorbida a 77 K y 4 MPa (en base volumétrica y gravimétrica) frente al volumen de microporos totales. Símbolos vacíos corresponden a carbones activados en polvo y símbolos llenos a monolitos de carbón activados

The results presented so far both in gravimetric and volumetric basis, correspond to the adsorption excess of hydrogen on different solids at different temperatures and pressures. However, a more important parameter from an application point of view, which is rarely found in the literature, is the total storage capacity. The storage capacity in a specified volume filled with a physisorption-based hydrogen carrier is the sum of the capacity due to adsorption on the solid surface and the volumetric capacity due to compression in the void space [12]. The void space per unit volume (V_s) was assessed using the packing density (r_p) and the skeleton density (r_s) of adsorbent ($V_s = 1 - r_p/r_s$). The packing density of the materials was measured as described elsewhere [9,13,14]. The skeleton density of the activated carbons was determined by the helium expansion method. Figure 2 includes the total hydrogen storage capacity of a super activated carbon at 298 K and at 77 K on the basis of a 1 l container. This Figure also includes the amount of hydrogen stored just by compression and the adsorption excess data, based on the weight of carbon in the 1 l container (the packing density of activated carbon is 0.5 g/cm³). It can be seen that storage of hydrogen at room temperature and 77 K achieves considerable enhancement due to both adsorption and compression. The total storage capacity of a 1 l container filled with carbon powder is 16.7 g H₂ at 19.5 MPa and 298 K and 38.8 g H₂ at 4 MPa and 77 K. In the case of the best sample prepared obtained in our laboratory in terms of volumetric values (the activated carbon monolith), the total storage capacity of a 1 l container filled with this material is 39.3 g H₂ at 4 MPa and 77 K. Interestingly,

this value of volumetric hydrogen storage capacity is almost 1.2 times higher than the European target for on-board hydrogen storage systems (33 g H₂/L). Considering the good results obtained with these materials, our effort now focuses on optimizing monoliths preparation and properties.

If the weight percentage of total H₂ stored on the powder activated carbon at 298 K is assessed from the hydrogen adsorption isotherms measured up to 50 MPa, the values obtained are 3.2 wt.% and 6.8 wt.% at 20 MPa and 50 MPa, respectively. Very high pressures (50 MPa) are required to approach to the DOE target at room temperature with a KOH-activated carbon. On the other hand, at 77 K, this sample gave very interesting values of H₂ stored at a quite low pressure (4MPa), 8.0 wt.%.

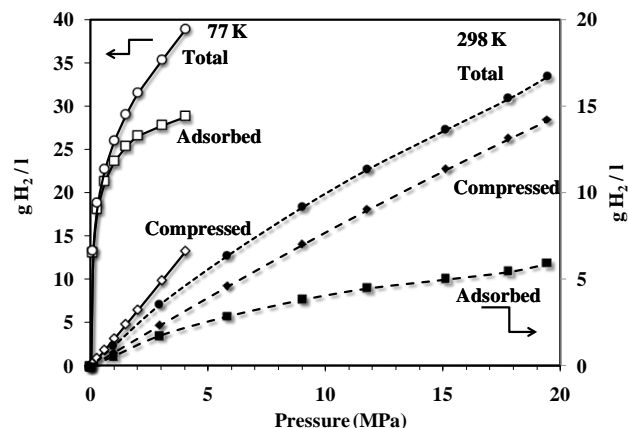


Fig. 2. Total hydrogen storage capacity of a superactivated carbon (prepared by KOH activation) on the basis of a 1 l container at 298 K (right Y-axis) and 77 K (left Y-axis).

Fig. 2. Capacidad de almacenamiento de hidrógeno total de un carbón superactivado (preparado por activación con KOH) en un depósito de 1 litro a 298 K (eje Y derecho) y 77 K (eje Y izquierdo).

It can be observed that the preparation of a series of KOH-activated carbons with a wide variety of properties has allowed us to select very good materials for different hydrogen adsorption conditions, remarking the importance of developing materials with suitable porosity for this application. All these results confirm that ACs are promising candidates for hydrogen storage for on-board vehicles.

3. Space Cricoolers

As mentioned in the Introduction, the European Space Agency (ESA) is developing a cooling system (cooling to around 4.5 K). To reach such low temperature, a two-stage vibration-free sorption He/H₂ cooler has to be designed with a suitable AC [15]. In this section, an example corresponding to the development of such an adsorbent is presented. The detailed results of the study have been published elsewhere [5-7].

A sorption cooler has two parts: (i) a cold stage; and (ii) a sorption compressor. A sorption compressor can be described as a thermodynamic engine that transfers thermal energy to the compressed gas in a system without moving parts. Its operation is based on the principle that large amounts of gas can be adsorbed on certain solids such as highly porous ACs. The amount of gas adsorbed is a function of temperature and pressure. If a pressure container is filled with an adsorbent and gas is adsorbed at low temperature

and pressure, then high pressure can be produced inside the closed vessel by an increase in the adsorbent temperature. Subsequently, a controlled gas flow out of the vessel can be maintained at high pressure by a further increase in temperature until most of the gas is desorbed.

ACs are obviously very interesting candidates for this application. They have to satisfy three essential requirements: (i) a large adsorption capacity per mass of adsorbent; (ii) a minimum void volume; and (iii) very good mechanical properties.

In order to optimise AC properties for this application, studies with samples prepared from different raw materials (anthracite and bituminous coals) and using different activation processes (KOH, NaOH and CO_2 as activating agent) were carried out. To predict their adsorption performance, helium adsorption isotherms at different temperatures ((from 20 K up to 150 K) and high pressures (up to 3.5 MPa) were measured as explained elsewhere [7]. As an example, Figure 3 shows these isotherms corresponding to an AC prepared by anthracite activation. According to the conditions needed in the compressor stage, we are interested in obtaining a material with a maximum helium adsorption capacity at 2 bar (0.2 MPa) and 50 K (adsorption stage) and a minimum adsorption capacity at 13 bar (1.3 MPa) and 120 K (desorption stage). Moreover, the density of the material should be maximized. Then, the selected AC was combined with a binder to prepare an ACM with suitable mechanical properties for machining. The best adsorption capacity were obtained with an activated carbon monolith with relatively high development of porosity and, most importantly, with high narrow micropore volume assessed by CO_2 adsorption at 273 K. This material also presents quite high density (0.7 g/cm^3). A very high activation degree of the material is not desired because the density of the material becomes low. In addition to the porous texture characterization and helium adsorption isotherms for the ACs, the ACM was submitted to a complementary mechanical characterization that included the following tests: maximum compression strength and strain, vibration, pressure drop and thermal expansion [7].

Interestingly, the procedure and binder used to prepare the ACM was very successful because: (i) it does not considerably modify the adsorption/desorption properties of the AC used; (ii) it causes a significant increase in the density of the material ($(0.70 \text{ g/cm}^3$ for the monolith ACM vs. 0.46 g/cm^3 for the AC); (iii) it allows for the formation of a dense monolith, easy to machine, maintaining good adsorption characteristics, having good mechanical properties and; (iv) presenting a low pressure drop and a low thermal expansion [7]. As a result, the ACM prepared achieved the target performance properties for being used in a sorption compressor.

A sorption cooler was built in the project using the ACM prepared from our study. Such cooler delivered 4.5 mW at 4.5 K with a long-term temperature stability of 1 mK and an input power of 2 W. It operated continuously for a period of 2.5 months and did not show any sign of performance degradation, performing well within all the specifications imposed by ESA. A more extensive discussion of tests on the developed breadboard cooler is given elsewhere [5].

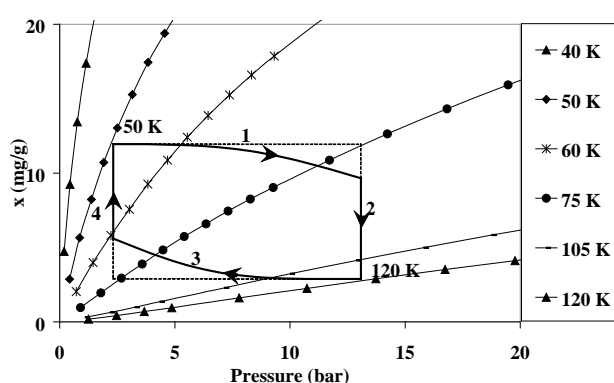


Fig. 3. Helium adsorption isotherms at different temperatures corresponding to an activated carbon prepared by KOH activation of an anthracite. The numbers 1, 2, 3 and 4 correspond to each step of a complete cycle of a cell.

Fig. 3 Isothermas de adsorción de Helio a diferentes temperaturas correspondientes a un carbón activado preparado por activación química de una antracita. Los números 1,2, 3 y 4 corresponden a cada paso de un ciclo completo de una celda.

4. Conclusions

Key properties of nanoporous carbon materials (i.e. micropore volume, micropore size distribution) can be tailored by KOH activation of carbon precursors. Examples of the performance of this type of advanced carbon materials in gas storage (hydrogen) and space cryocoolers have been included. It is demonstrated that, for these applications, it is crucial developing materials with simultaneously both, high volume of narrow microporosity and high density. Thus, Activated Carbon Monoliths (ACM) with optimized properties were designed, prepared and tested, obtaining promising materials for these advanced applications.

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