



Optimization of biomass-based carbon materials for hydrogen storage



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ABSTRACT

Hydrogen is considered as the most promising future fuel, as its combustion generates only water vapor besides energy. However, finding efficient, safe and low cost storage methods is the basic impediment for the adoption of hydrogen as fuel. For this purpose, five biomass-based carbon samples have been successfully prepared through KOH activation procedure. The microstructure of the prepared materials was tuned by varying KOH/precursor weight ratio from 1:1 to 5:1, in order to optimize their hydrogen storage behavior and to clarify the storage mechanism. A careful textural and morphological characterization of the prepared samples (N_2 and CO_2 adsorption, X-ray diffraction, electron microscopy observations) showed that by increasing the activation ratio the nature of the carbons changes from microporous to micro-mesoporous. Thus, an increase in the surface area was observed which enhanced H_2 sorption capacity when high H_2 pressures were adopted. At subatmospheric pressure, the role of active sites for H_2 adsorption, located in the oriented graphene sheets, was clearly elaborated. Finally, the optimal carbon sample has shown a capacity of 6 wt% and 1.22 wt% at $-196^\circ C$ and $25^\circ C$ respectively, and 200 bar. These results make biomass-based carbons promising materials for H_2 storage application.

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1. Introduction

After the first oil crisis in 1973, scientists have looked seriously for alternative renewable resources to exit from the dependency to the fossil fuels, and to reduce the greenhouse gas emissions. However, the most prominent disadvantage of renewable energy sources (RES) is their variability (e.g., lack of wind in aerogenerators, lack of solar radiation for photovoltaics). Hence to overcome this variability energy storage becomes a major issue. Batteries and accumulators have shown the drawback of low capacity and discharge when not connected to the load, high maintenance cost, short life span and a limited numbers of charge–discharge cycles [1]. Internal combustion engines have been used for higher power and longer times. However their use, which emits CO_2 , often consumes fuel also if RES are available, limiting potential fuel saving to only 20% when used in combination with RES systems [2]. Energy storage by means of hydrogen (H_2) could represent the solution capable of guaranteeing long storage times, high capacities and smoothing of intermittent and discontinuous RES. For instance, an hybrid system for solar hydrogen employs photovoltaic technology (PV) to convert direct sunlight energy in

electrical energy, used as input to an electrolyzer (EL) which splits water into hydrogen and oxygen that takes place in fuel cells (FC) [3]. Energy can then be provided to stationary or mobile applications, and several systems have been already built all over the world [4]. H_2 is indeed very good energy vector since it can substitute for fossil fuels without releasing any harmful emissions. The chemical energy per mass (on a gravimetric basis) of H_2 is approximately three times greater than that of other chemical fuels (e.g., on average the equivalent value for liquid hydrocarbons is $43 MJ kg^{-1}$). However, the energy density of H_2 (on a volumetric basis) is very low compared to gasoline and other hydrocarbons. For example, one liter of gasoline ($31.7 MJ/L$, $8.8 kW h/L$) contains approximately six times as much energy as a liter of H_2 compressed to 70 MPa ($4.7 MJ/L$, $1.3 kW h/L$) [5].

Therefore, H_2 storage is a major barrier in the development of an energy economy based on hydrogen. Actually, the classical H_2 storage technologies show some important drawbacks such as low density and high pressures operations for compression [6], boil-off excessive energy consumption for liquefaction [7]. To overcome these issues, researchers have focused their attention on exploring material-based hydrogen storage, due to their ability to increase the density of H_2 under safe operation conditions. These materials are typically categorized according to hydrogen storage mechanism: (i) physisorption of molecular H_2 on microporous surfaces; (ii) chemisorption of atomic H_2 on the lattice framework of metal hydrides. Chemisorption is less attractive due to relatively high

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temperatures required for hydrogenation and release of H₂. Therefore, a lot of attention has been focused during last decades on studies of H₂ physisorption on different adsorbents including metal organic framework (MOF) [8–10], Zeolites [11], and carbon-based materials [12,13]. Compared to crystalline materials (MOFs and Zeolites) carbon-based adsorbents are more advantageous. This is related to their low cost, good chemical, mechanical and thermal stability, easier regeneration, low densities, and wide diversity of bulk and pore structures [14]. Moreover, several carbonaceous adsorbents have shown similar and even better hydrogen sorption capacity compared to MOFs and Zeolites [15–17].

Among them, activated carbons (ACs) have been intensively studied as H₂ storage materials, since it is easy to obtain and their porous structure is more developed than carbon nanotubes and carbon nanofibers. Indeed, recent studies showed that the cryogenic hydrogen storage capacities are quite promising. Yang et al., reported a storage capacity of 6.9 wt% at 77 K and 20 bar for a zeolite-like carbon material [18]. Wang et al. prepared a kind of activated carbons which exhibits high specific surface area and achieved a large hydrogen uptake of 7.08 wt% at 77 K and 20 bar [19]. However, Fierro et al. described a hydrogen storage density of 6 wt% at 77 K and 40 bar for an activated carbon derived from a high-rank mineral coal [20]. The porous texture is the main feature determining the hydrogen adsorption capacity of ACs. Some authors have stated that ACs should have a highly developed internal surface and a large volume of micropores [21] with diameters in the range of 0.6–0.8 nm [22–24] for an efficient performance as a hydrogen storage material at both atmospheric and high pressures. Hence tailoring pore structures of carbon's surface is crucial. Recently, KOH activation of carbonaceous precursor has attracted a great attention as it has often formed porous carbons with high surface areas and pore volume. For example, Sevilla et al. have synthesized nitrogen-doped porous carbons with surface area of up to 3480 m²/g by KOH activation of polypyrrole as carbon source [25]. A H₂ uptake of 2.63 wt% was obtained at 1 bar and –196 °C for these carbons. They also reported the similar H₂ uptake (2.6–2.7 wt%) was obtained for zeolite-templated porous carbons and zirconium carbide derived carbons after chemical activation [26,27]. However, from the view of sustainability, environmental friendliness, and continuous availability, biomass-based materials are more promising carbon sources for porous carbons.

As Mediterranean country, olive cultivation is particularly widespread throughout Tunisia. The mean annual olive oil production for the decade 2004–2014 is 180 thousand tonnes and reached 299 thousand tonnes in 2015 [28]. Therefore, olive pomace with high olive stones content is a very abundant agricultural by-product in Tunisia, and many results obtained made clear that this lignocellulosic precursor is a very adequate raw material to obtain efficient activated carbons [29,30].

All these favorable observations have encouraged the present study, in which ACs are obtained from natural bio-precursor; olive stones, using KOH as an activating agent. The effect of different KOH/precursor weight ratio on the textural properties of the ACs was investigated in detail. Finally, their H₂ sorption properties were investigated in three different international laboratories; using verified automated and lab-made devices which ensure high reproducibility.

2. Experimental

2.1. Activated carbons preparation

Carbon materials were prepared from olive pomace. First, the raw precursor was washed abundantly with hot distilled water to

Table 1
Elemental analysis of olive stones (wt%).

Element	C	H	O	S	N
Tunisian olive stones	47.50	4.36	35.30	0.83	2.02

obtain grains of olive stones sized to about 1–3 mm. Then, dried olive stones were soaked in an aqueous solution of KOH at 85 °C without evaporation for 3 h. The weight ratios of KOH to precursor; R, were from 1:1 to 5:1. Subsequently, activated carbons were produced by heating at 800 °C for 2 h in N₂ flow (100 cm³ min⁻¹) with a heating rate of 5 °C min⁻¹. The activated samples were then washed several times with HCl solution (0.1 M) to remove any organic salts and then washed with distilled water until neutral pH. Finally, the carbons were dried in an oven at 120 °C. The ACs synthesized were denoted as **OB-KOH-x**; where x is the activation weight ratios (1–5). The elemental analysis of the stones is included in Table 1. The high carbon and low sulfur contents make olive stones good starting material for the production of porous active carbons.

2.2. Characterization of the activated carbons

Textural properties characterization of the prepared samples was carried out by the physical adsorption of gases (N₂ at –196 °C and CO₂ at 0 °C) in a pressure range of 0–1 bar. Fully automated equipment was used at the Advanced Materials Group (LMA at Alicante university, Spain), N₂-G-sorb-6 (Gas to Materials Technologies). Previous to the adsorption measurements, the samples were degassed at 250 °C under vacuum for at least 4 h. From N₂ adsorption isotherms, specific surface area S_{BET} (according to the BET equation), total pore volume V_T (calculated from the nitrogen uptake at relative pressure of 0.95), total micropore volume V_{DR-N₂} (by applying the Dubinin Radushkevich, DR, equation) were determined. Whereas, the application of the DR equation to CO₂ isotherms leads to the volume of narrow micropores, V_{DR-CO₂} (up to about 0.7 nm) [31]. Finally, the pore size distributions (PSD) were calculated by Quant Functional Theory (DFT) using Plus Software (provided by Quantachrome Instrument Corporation), considering slit-shaped pores.

The morphology changes during activation were observed by means of scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). SEM analysis was carried out on FEI Helios 600 Nanolab equipment. While, HRTEM analysis was performed by means of JEM 2100, JEOL, Japan.

Elemental analysis of olive stones was carried out using ELTRA elemental analyzers; CS-800 and ONH-2000. Powder X-ray diffraction (XRD) experiment for OB-KOH-1 sample was performed using a Philips X' Pert diffractometer (Co_K α radiation, $\lambda = 1.7903 \text{ \AA}$) equipped with position sensitive detector and monochromator in the diffracted beam. XRD pattern was recorded for 2 θ in the range [5–135°], under operating conditions of 40 kV and 40 mA, at a step of 0.05° and 10 s per step.

2.3. Measurement of hydrogen storage capacities

H₂ storage was measured in three independent laboratories in volumetric devices. In all experiments, high-purity H₂ ($\geq 99.9999\%$) was used for the uptake measurements. H₂ uptakes were calculated in gravimetric basis (wt%).

2.3.1. At –196 °C and up to 1 bar

Determination of H₂ storage at liquid nitrogen temperature and up to 1 bar was carried out at Alicante University (Laboratory of Advanced Materials, Spain). The automated apparatus was the one used for N₂ and CO₂ adsorption measurements. In each adsorption

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