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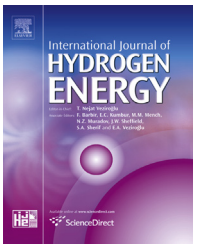

# Liquid-like hydrogen in the micropores of commercial activated carbons

*Francesco Demetrio Minuto* [a,*], *Alfonso Policicchio* [a,b], *Alfredo Aloise* [c], *Raffaele Giuseppe Agostino* [a,b]

[a] *Dipartimento di Fisica, Università della Calabria, Via Ponte P. Bucci, Cubo 31C, 87036 Arcavacata di Rende (CS), Italy*

[b] *CNISM – Consiglio Nazionale Interuniversitario di Scienze Fisiche della Materia, Via della Vasca Navale, 84, 00146 Roma, Italy*

[c] *Dipartimento Ingegneria per l'Ambiente e il Territorio e Ingegneria Chimica, Università della Calabria, Via Ponte P. Bucci, Cubo 42A, 87036 Arcavacata di Rende (CS), Italy*

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ABSTRACT

The hydrogen adsorption properties of commercial activated carbon (aC) samples, in particular Nuchar SA-1500, Filtercarb GCC 8x30 and Filtercarb PHA, are evaluated at different temperatures (77 K, 196 K and ambient temperature) and pressure up to 80 bar. A comprehensive characterization is carried out by means of a volumetric Sieverts-type apparatus for hydrogen adsorption measurements and helium picnometry for the skeletal density evaluation, by nitrogen adsorption measurement for the evaluation of the surface area (BET) and pore size distribution (NLDFT), by Scanning Electron Microscopy (SEM) for morphology. All the adsorption data are evaluated by Langmuir/Tóth isotherm model with a very high accuracy and the enthalpy of adsorption is calculated through the Clausius–Clapeyron equation. Comparison between the different samples is shown. The probed aC samples show interesting hydrogen storage capacity and reversible behavior up to many cycles with and without any thermal treatment in between. Our data point out the crucial role of the microporosity and ultra-microporosity in the adsorption process at low $H_2$ pressures. The surfaces exhibit an average adsorption enthalpy around 6.5 kJ/mol while for the ultra-microporous sites a 14 kJ/mol value is found. The observed trapping behavior at 77 K is attributed to the ultra-microporous morphology of the porous structure in GCC and PHA samples. A further result is the evaluation of the hydrogen molar density in the micropores with size below 10 Å, which is 30 mmol/cm$^3$, a value very close to the liquid hydrogen one. These results could represent an interesting starting point for a real and efficient alternative method to the hydrogen storage using cheap and easy scalable materials.



* *Corresponding author*. Tel.: +39 0984 49 6177; fax: +39 0984 49 4401.
E-mail address: francescodemetrio.minuto@fis.unical.it (F.D. Minuto).

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## Introduction

Adsorption of hydrogen as energy carrier has to pass through solving on-board storage issues which still discourage the widespread of hydrogen economy [1,2]. In the last decade, many efforts were performed in order to find an effective hydrogen storage method. To date, the proposed storage methods for on-board applications are liquefaction, pressurization and storage into solid-material; even if they are potentially suitable, up to now, none of they met all the required specifications simultaneously [3]. However, the one who has the most interesting prospects, for development and improvement, appears the adsorption into porous solid materials, because of the absence of activation energy, fast kinetic of adsorption and desorption, reversibility, non-destruction of material structure [4–6].

The adsorption process, named physisorption, occurs when a gas molecule approaching to surfaces binding-site is weakly linked by van der Waals forces, avoiding molecules dissociation or chemisorption processes [6,7].

By an applicative point of view, finding an adsorbing material that is easily gettable and immediately usable represents a big advantage for the development of the hydrogen economy. Activated carbon (aC), compared to other high specific surface porous materials like zeolites [7,8], porous silica [9,10], metal organic frameworks (MOF) [11–13], shows many advantages in view of large scale on-board applications: abundance and low cost of raw precursor (coal, coconut shells, woods, bamboo, cellulose and others materials at high carbon content), ease synthesis, stabile and tunable pore structure [7,14–21]. Commercial aCs, frequently used as sorbent for separation and purification of gas and liquid [7], exhibit defined meso- (pore width from 2 to 50 nm) and macro-porosity (pore width >50 nm) structure which allow them to select specific molecules [8,22]; but, in principle, they can have also an unknown, but not negligible, microporosity which makes them good hydrogen sorbents.

The structural parameters are very important in adsorption/desorption processes. Normally in fact, the maximum gas adsorption capacity, at a given temperature, depends to the availability of surfaces sites, which are energetic enough to bind the molecule (ad-sites). In the case of hydrogen for example, it is verified that, at liquid nitrogen temperature (77 K) there is a quite linear correlation between the hydrogen uptake and the available surface area (SSA) [23]. Nevertheless an important role is covered by the pore morphology, indeed this relation is disobeyed when the pores diameter are in the same order of magnitude of adsorbed molecule width: an enhancement of the net attractive force occurs, due to the overlap of opposed pore walls potential [6,8,24]. In the case of hydrogen, for example, the best adsorption is observed on microporous (pore width < 20 Å) and ultra-microporous (pore width < 7 Å) [19,25–27]. For all these reasons, great care should be taken into account in the evaluation of the SSA, pore volume and pore diameter. Indeed in order to figure out how the hydrogen adsorption on commercial aCs is correlated to these samples properties, a systematic characterization of structural (SSA, pore volume, pore distribution) and morphological features is performed.

## Materials and methods

### Materials

The commercial aC samples, here investigated, were supplied by MWV (MeadWestvaco) Specialty Chemicals (5255 Virginia Avenue, Charleston, SC, www.mwv.com) and Carbon Italia (Via Emanueli-19020 Vezzano Ligure La Spezia - Italy, www.carbonitalia.com). In particular the Nuchar SA-1500, provided by MWV, is a food grade aC derived from wood and chemically activated, generally used in processes as filtering aid. The Filtercarb GCC 8x30 and the Filtercarb PHA, provided by Carbon Italia and commonly used for water purification, are both physical activated in a controlled atmosphere in presence of steam and temperatures ranging from 800 up to 1000 °C, the former is derived from coconut shell while the latter's mineral origin. Both MWV and Carbon Italia samples show very high specific surface area (SSA) and pronounced micro- and meso-porosity. The values declared by manufactured are 2150 $m^2/g$ for the Nuchar SA-1500 and an average of 1150 $m^2/g$ for the Filtercab samples (see Table 1).

### Methods

*SEM*

Scanning electron images were recorded using a Quanta FEG 400 (FEI) scanning electron microscope (SEM). The SEM images were acquired by using an electron beam of 15 keV. The images provide the typical macro e meso-scale morphology of the samples deposited on carbon tape.

*Nitrogen adsorption measurement*

The porous properties of each sample were examined by nitrogen adsorption isotherms at 77 K, using a Micromeritics ASAP 2020 instrument. Before the analysis, all samples were pretreated in vacuum at 473 K for 12 h.

The $N_2$ adsorption data are elaborated, with the ASAP 2020 v1.05 software, to obtain the BET specific surface area (SSA)

**Table 1 – Samples information summary. From left to right: sample name, acronym, producer, type of activation, declared specific surface area, precursor.**

| AC sample | Acronym | Producer | Activation | Declared SSA ($m^2/g$) | Precursor |
|---|---|---|---|---|---|
| Filtercarb PHA | PHA | Carbonitalia | Physical | 1100–1200 | Mineral origin |
| Filtercarb GCC 8x30 | GCC | Carbonitalia | Physical | 1100–1150 | Coconut shell |
| Nuchar SA-1500 | SA | MWV | Chemical | 2139 | Wood |

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