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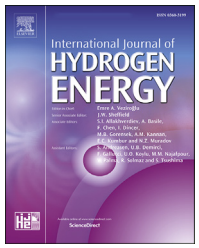

Assessment methodology of promising porous materials for near ambient temperature hydrogen storage applications

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ABSTRACT

With the rapid increasing of the available number of novel porous materials, a straightforward and low-cost testing methodology to assess those suitable for near ambient temperature hydrogen storage applications is needed. In this work, we developed a new assessment methodology to quickly identify those porous materials potentially suitable for near ambient temperature hydrogen storage applications. We introduced the usable capacity map showing why the absolute adsorption capacity at the temperature of 77 K is not a good indicator to compare the material's storage performance. In fact, some porous material that shows low usable capacity at 77 K appear to be better adsorbent at a higher temperature. Moreover, we demonstrated that using quick cyclic adsorption isotherm or TDS is possible to easily individuate those materials that are the most suitable for near ambient temperature applications. Therefore, as a general result, we showed that among the three commercial activated carbon, used here as case study, the one with the higher content of ultramicroporosity is the most promising because the optimum operating temperature shifts towards ambient temperature.

Introduction

Hydrogen (H_2) is a promising energy carrier since its high gravimetric energy density (142 MJ/kg) is three times higher than normal fossil fuels, although at ambient temperature hydrogen has a very low volumetric energy density (0,013 MJ/L at 1 bar) compared to common fossil fuels (~35 MJ/L). The two mature technologies used to increase the volumetric energy density of hydrogen are compression at high pressures and liquefaction, which achieve values of 5,54 MJ/L (at 700 bar, 300 K) and 10 MJ/L (at 1 bar, 20.3 K) [1], respectively. Nevertheless, both technologies have drawbacks related to storage, delivery and end-use systems design [2–5] that are pushing the research on alternative storage principles, including storage of molecular hydrogen in solid materials via

Abbreviations: aC, activated carbon; PDS, pore size distribution; SSA, specific surface area; HV, high vacuum; QMS, quadrupole mass spectrometer; TDS, thermal desorption spectroscopy; SM, supporting material.

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physisorption [6]. Indeed, the hydrogen adsorbed phase, in activated carbon small pores (<1 nm), can reaches energy densities of 8,5 MJ/L (30 mmol/cm^3 at 0.5 bar, 77 K) [7] that is comparable to the other two technologies. Nevertheless, hydrogen storage at liquid nitrogen temperature is considered challenging for many applications that require a working temperature closer to ambient temperature, therefore finding materials with higher operating temperature is an important focus for future research [8,9].

The number of novel porous materials for a variety of different applications is rapidly increasing and many of these materials are already commercially available. The identification of novel materials suitable for near ambient hydrogen storage applications, lacks a straightforward and low-cost testing methodology. At the moment, the traditional way to evaluate the potential for hydrogen storage is the measurement of the material's absolute (or excess) saturation capacity at a temperature of 77 K at relatively moderate pressures (<100 bar) [10]. However, from an applicative point of view, these quantities are misleading because they do not coincide with the amount of deliverable hydrogen (usable capacity) at cryogenic temperature.

In this work we develop a new analysis method of the usable capacity [11–14], to evaluate the material's best operational conditions by means of contour plot maps. We show how these maps can be used to identify easily the best materials for each thermodynamic condition.

Even though usable capacity maps are extremely effective to fully characterize the material's adsorption proprieties, the construction of these maps requires many measurements at different temperatures, which are too time-consuming and costly to be applied to each material. For this reason, we developed two experimental tests to quickly select the most promising materials for storage applications above 77 K by checking preliminary the presence of strong adsorption sites.

In this work, among the different families of high SSA adsorbents, we chose three commercial activated carbons (aC) as a case study for our new assessment methodology because of their easy and inexpensive large-scale production from a wide range of organic raw materials, combined with suitable structural properties, such as chemical stability, lightness, pore size tunability and good thermal conductivity [15,16].

Materials and methods

Materials

The choice of the adsorbents is based on their pore size distribution (PSD), in order to evaluate the effect of the pore morphology on the sample's hydrogen adsorption properties. We focused specifically on three ranges of pore sizes: ultra-micropores (pore size < 7 Å), super-micropores (pore size 7÷20 Å) and mesopores (pore size >20 Å) [17]. The target materials for the present analysis are commercial aC samples: Nuchar SA-1500 (SA), Filtercarb GCC 8 × 30 (GCC) and Filtercarb PHA (PHA); whose hydrogen sorption properties were already reported by Minuto et al. [7].

In Table 1 we recall the sample's structural properties as specific surface area (SSA) and pore volume (PV) fraction in each pore size range. By this classification, the GCC sample represents ultra-microporosity since about 48% of the PV is below 7 Å (0.18 cm^3/g). In contrast, the PHA sample shows a PSD quite equally balanced between ultra-micropores (24%), super-micropores (31%) and mesopores (45%), even though the content of pores below 7 Å is similar to the GCC sample (0.16 cm^3/g). Finally, the SA sample shows the lowest content of ultra-microporosity (0.07 cm^3/g) and its porosity is dominated by pores above 20 Å (94% of the total), thus it represents mesoporous aC.

Methods

Hydrogen isotherm measurements

Hydrogen adsorption measurements are performed by a Sievert's type apparatus PCT-PRO2000 (Setaram) equipped with a microdoser. The fully automatic device performs Helium (He) pycnometry and high-precision hydrogen adsorption/desorption. The sample holder temperature is controlled by using a thermic bath, as liquid nitrogen (77 K) or liquid argon (87 K); alternatively a home-built cryostat it is used to measure in the temperature range 97–117 K, in steps of 10° [11].

The samples are outgassed at 573 K in high vacuum (HV) for 12 h after their loading into the PCT apparatus. Then, the skeletal volume is evaluated by means of He pycnometry up to 5 bar at ambient temperature.

The hydrogen isotherm measurements are performed in two modes: *single* or *cyclic*. In the *cyclic* mode, the apparatus performs a sequence of *single* isotherm measurements keeping the temperature constant during the whole experiment, even during the sample evacuation (30 min) between each isotherm. In both modes, prior the starting of the experiment, the sample is evacuated in high HV at ambient temperature for 12 h. The amounts of used sample are 251.8 mg, 263.7 mg and 177.6 mg for the GCC, PHA and SA, respectively.

Excess and absolute uptake

The excess uptake is defined as the amount of molecules in the system in surplus due to the physisorption process experimentally calculated subtracting the adsorption isotherm of a non-adsorbing material, which measured under

Table 1 – Samples information summary [7].

aC sample	Acronym	N_2 SSA (m^2/g)	pore volumes (cm^3/g) and relative percentage		
			<7 Å	7 ÷ 20 Å	>20 Å
Filtercarb GCC 8 × 30	GCC	816 ± 3	0.18 (48%)	0.13 (36%)	0.06 (16%)
Filtercarb PHA	PHA	1026 ± 8	0.16 (24%)	0.21 (31%)	0.30 (45%)
Nuchar SA-1500	SA	2235 ± 4	0.07 (6%)	0.60 (44%)	0.68 (50%)

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