Enhanced room-temperature hydrogen storage in super-activated carbons: The role of porosity development by activation

Kaisheng Xia [a],*, Juan Hu [b], Jinhua Jiang [b]

[a] Sustainable Energy Laboratory, Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, PR China
[b] State Key Laboratory of High Performance Ceramics & Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China

ABSTRACT

Efficient hydrogen storage with a high density under near-ambient temperature remains a key technical obstacle for a hydrogen economy. Here we demonstrate the enhanced room-temperature hydrogen storage in super-activated carbon materials, which were prepared by carbon dioxide activation of templated porous carbons. These carbon materials possess high specific surface areas of up to 2829 m^2/g, large pore volumes of up to 2.34 cm^3/g, and hierarchical pore structures consisting of primary micropores with median size in the range of 0.7–1.3 nm and secondary mesopores with the size of 2–4 nm. One of the super-activated carbons exhibits a high hydrogen uptake of 0.95 wt% at 298 K and 80 bar, which is among the highest data reported for the porous carbon materials at room temperature and moderate pressure. The role of porosity development caused by activation in improving the hydrogen storage properties of the carbon materials has been investigated. A close relationship between hydrogen storage capacities and micropore volumes has been found. The microporosity development, especially the rapid increase of narrow pores with the diameters around 1.2 nm, appears to be essential for the enhanced room-temperature hydrogen storage in the super-activated carbons.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen is recognized as a promising energy carrier because it is abundant, renewable, burning pollution-free and containing higher chemical energy than hydrocarbon fuels. However, there are some key technical obstacles to be solved before realizing a hydrogen economy, among which the efficient hydrogen storage presents a huge challenge [1]. Various techniques have been investigated to resolve this problem, in which physisorption of hydrogen in porous materials provides a good option for the fast kinetics, excellent reversibility and high energy efficiency [2]. In the porous materials by the physisorption approach, carbon materials are the most intensively studied candidates because of their lightweight, low cost, excellent stability, high surface area and large pore volume. Considerable attention has been paid to activated carbons, carbon nanotubes (CNT), graphite nanofibers (GNF) and templated carbons as hydrogen storage materials during the past two decades.

Recent studies showed that the cryogenic hydrogen storage capacities of carbon materials are quite promising. Mokaya and coworkers reported a storage capacity of 6.9 wt% at 77 K and 20 bar for a zeolite-like carbon material with 3200 m^2/g specific surface area [3]. Gogotsi et al. described a hydrogen storage density of 4.7 wt% at 77 K and 60 bar of an activated carbide-derived carbon (CDC) with tunable pore size and specific surface area up to 3000 m^2/g [4]. Gao and coworkers prepared a kind of activated carbons which exhibited a high specific surface area up to 3190 m^2/g and demonstrated a large hydrogen uptake of 7.08 wt% at 77 K and 20 bar [5]. These reports clearly indicated that the gravimetric hydrogen storage targets set by US DOE (4.5 and 5.5 wt% by 2010 and 2015 respectively) [1] are actually achievable by using carbon materials. However, due to the weak interaction in physisorption, cryogenic conditions are essential for obtaining these high storage capacities. From the viewpoints of practical application, efficient storage of hydrogen with a high density under near-ambient temperature is more meaningful and imperative.

Several literatures have modeled the hydrogen storage limits on carbon materials at ambient temperature. Alcañiz-Monge et al. calculated a theoretical maximum H$_2$ adsorption in an idealized narrow microporous carbons is around 3.5 wt% for microporous

---

* Corresponding author. Tel.: +86 27 67883808; fax: +86 27 67883431.
   E-mail address: xks_mail@126.com (K. Xia).

activated carbon at room temperature [6]. Kuchta et al. estimated the hydrogen storage limits in carbon-based nanospaces and concluded that porous carbons with pore sizes between 0.8 and 1.1 nm and energies of adsorption equal to or larger than 15 kJ/mol could reach the DOE goals at room temperature [7]. Unfortunately, measured adsorption capacities of various carbon materials at room temperature are rather limited [8–13]. The investigations on single-walled carbon nanotubes (SWNT) and GNF show that less than 0.5 wt% of H_2 can be stored in them at 298 K and 100 bar [8,11]. The studies on super-activated carbons, AX-21 with a surface area of 2513 m^2/g and KUA5 with a surface area of 3183 m^2/g, have shown room temperature storage capacities of 0.68 and 0.78 wt% at 100 bar [9]. Moreover, Cheng and coworkers revisited the hydrogen storage of different types of CNT materials and found the capacity is less than 1.7 wt% under 12 MPa and at room temperature [14]. The difference between the experimental and theoretical values indicates that the structure of carbon materials could be tailored to enhance their hydrogen storage performances at ambient temperature. Inspired by the recent development of templating technique, advances have been achieved by using microporous templated carbons as hydrogen storage media [15–18]. Stadie et al. prepared a zeolite-templated carbon (ZTC) material which displayed a specific surface area of 3600 m^2/g and demonstrated a hydrogen uptake of 1.6 wt% at 298 K and 30 MPa [16]. Park and coworkers described the hydrogen adsorption of metal-organic framework (MOF) derived porous carbons presenting specific surface areas up to 3174 m^2/g and prominence of micropores with diameters 1–2 nm [17,18]. The carbon materials can store up to 0.94 wt% hydrogen at 298 K and 100 bar. Generally, these results suggest that at ambient temperature the hydrogen storage capability for porous carbons is highly dependent on their accessible surface areas, pore size distributions, and microporosities [1,2,12,13].

To improve the accessible surface area and pore structure of a carbon adsorbent, activation is an effective method. Recently, activated carbons prepared by activation of traditional carbons such as amorphous carbon and carbon nanofiber have gained consideration as room-temperature hydrogen storage materials [19–21]. Jiménez et al. prepared a porous carbon by chemical activation of amorphous carbon, which is capable of adsorbing 1.13 wt% hydrogen at 299 K and relatively low pressure of 50 bar [20]. Remarkably, templating technique and activation can also be combined to obtain high surface area carbons and enhanced storage capacities. Our previous studies have shown that activation of templated nanoporous carbons with CO_2 or KOH can generate super-activated carbons possessing ultrahigh specific surface areas (up to 2864 m^2/g) and excellent hydrogen storage performances at 77 K (up to 2.5 and 6.3 wt% under 1 and 20 bar, respectively) [22–25]. Moreover, a variety of super-activated carbons with high surface areas and micropore volumes have recently been prepared by activation of mesoporous silica-templated carbons [26,27], ZTCs [28–30] and carbide-derived carbons (CDC) [4,31]. These super-activated carbons have demonstrated very high hydrogen storage capacities under cryogenic conditions. However, to the best of our knowledge, the hydrogen storage of templated and activated carbons under ambient temperature has rarely been reported in the literature. For this reason, herein we studied the room-temperature hydrogen storage of different super-activated carbon (SAC) materials prepared by activation of three kinds of templated porous carbons. The effects of activation treatment on the textural properties and the hydrogen adsorption performances of the carbon materials have been investigated. Furthermore, we focused on the relationship between the hydrogen storage properties of SACs and their porosity development caused by activation, which may help to understand the underlying mechanisms of hydrogen adsorption in SACs and direct the design of carbon adsorbents for hydrogen storage at ambient conditions.

2. Experimental

2.1. Preparation of SAC materials

SAC materials were prepared by physical activation of templated nanoporous carbons with CO_2. First, templated nanoporous carbons were synthesized via templating technique as described in detail in our previous publications [23–25]. Then, three kinds of nanoporous carbons MC15, MC48 and MC41 were obtained by using mesoporous silicas SBA-15, MCM-48 and MCM-41 as templates, respectively. For the activation, in a typical procedure, the as-prepared nanoporous carbon was placed in the centre of a quartz tube in a tube furnace and heated (5 K/min) to the activation temperature (1223 K) under nitrogen, and then the gas stream was switched to CO_2 (30 cm^3/min). After activation with CO_2 for a certain time, the SAC sample was obtained after cooling to room temperature under nitrogen. The activated MC15 were denoted as SAC15-2, SAC15-4, SAC15-6 and SAC15-8 after activation at 1223 K for 2, 4, 6 and 8 h, respectively. The activated MC48 were labeled as SAC48-2, SAC48-4 and SAC48-6 after activation at 1223 K for 2, 4 and 6 h, respectively. SAC41-4 represented the sample obtained after activation of MC41 at 1223 K for 4 h.

2.2. Characterization

Transmission electron microscopy (TEM) images were taken on a JEOL (JEM-2010) microscope at an acceleration voltage of 200 kV. Nitrogen adsorption–desorption studies were taken at 77 K using a Micromeritics ASAP 2020 system. The specific surface area (S_{BET}) was calculated by the BET method. The total pore volume (V_t) was calculated at relative pressure $p/p_o = 0.98$. The micropore volume (V_{mi}) was determined by applying Dubinin-Radushkevich (DR) analysis. The volume of pores smaller than 1 nm ($V_{<1}$) was determined by the Horvath–Kawazoe (HK) method in the relative pressure range 10^{-6} to 10^{-4}. The volume of pores between 1 and 2 nm (V_{1-2}) was obtained by subtracting $V_{<1}$ from V_{mi}. The meso- and micropore sizes of samples were analyzed by the Barrett-Joyner-Halenda (BJH) and HK methods, respectively.

2.3. Hydrogen storage performance

The hydrogen storage at room temperature was determined by the gravimetric method using a magnetic suspension balance (MSB, Rubotherm) [5,32]. Before loading the sample, a blank measurement was performed to obtain the weight of the empty sample container (m_{sc}) and the volume of the sample container (V_{sc}). For each test, about 0.1 g of sample was loaded in the sample container. The test chamber containing samples was evacuated to remove impurities and water, and then heated (10 K/min) to 573 K for 12 h under vacuum. Subsequently, a buoyancy measurement with high pressure helium (He) gas was carried out to obtain the volume of the sample container and the sample (V_{sc+s}). After that, the sample is evacuated again and the hydrogen adsorption measurement can start. The adsorption measurement was conducted at 298 K by increasing the hydrogen (99.999%) gas pressure from vacuum to 80 bar with a balance time of 2 h at each pressure point. The hydrogen adsorption capacity (W_{AD}) at a given pressure can be calculated by equation (1), in which m_{BAL} is the balance reading, m_{sc+s} is the weight of the sample container loaded with the sample, and ρ_{H2} is the gas density of hydrogen.

$$W_{AD}(\%) = \frac{m_{BAL} - m_{SC+S} + \rho_{H_2} \cdot V_{SC+S}}{m_{SC+S} - m_{SC}} \times 100\% \qquad (1)$$