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Cryogenic hydrogen uptake of high surface area porous carbon materials activated by potassium hydroxide

Hongliang Guo, Qiuming Gao*

State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Graduate School, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 20050, People's Republic of China

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ABSTRACT

A porous carbon material with specific surface area of 894 m²/g and pore volume of 0.47 cm³/g has been easily synthesized by pyrolysis of a gel containing nickel chloride. Transmission electron microscopy reveals a texture of evenly spreading spherical mesopores and well dispersed micropores. Potassium hydroxide treatment results in a surface area and pore volume of the pristine materials of up to 2930 m²/g and 1.52 cm³/g, respectively. Cryogenic hydrogen uptake capacities were measured and the highest capacity of 6.24 wt% was obtained at 77 K under 2 MPa.

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1. Introduction

Non-renewable resources account for over 50% of the primary energy supply, and fossil fuels are believed to last no longer than a few decades [1]. It is urgent to exploit renewable resources to maintain the development of human society. Global warming is also believed by many to be due to the emission of carbon dioxide (CO₂) induced by burning of the fossil fuels. Hydrogen has been recognized as an ideal energy carrier, because it is clean and the most abundant element on the Earth [2]. Besides, it can be easily produced from renewable energy sources and contains higher chemical energy per mass than the hydrocarbon fuels. The U.S. Department of Energy (DOE), in collaboration with automotive industry partners, has established specific technical targets for on-board hydrogen systems [3]. However, efficient hydrogen storage and transportation have been the major concerns for the hydrogen

economy. Dillon et al. [4] first reported the hydrogen storage in carbon nanotubes (CNTs). After that, much more efforts have been focused on the hydrogen storage performance of the CNTs [5,6]. Further investigation has showed that the CNTs only possessed relatively low hydrogen storage capacities (<0.2 wt%) regardless of their synthesis routes and purities [7]. Porous carbons, especially microporous carbons, may be good hydrogen storage materials due to their advanced characteristics of high surface area and large micropore volume. However, the interaction between the adsorbents and non-polar hydrogen molecules depends on the dispersion forces, which are usually weak for the carbon materials [1]. Alcaniz-Monge et al. reported that the theoretical maximum H₂ adsorption is around 3.5 wt% in an idealized narrow microporous carbon at room temperature [8]. Jiang et al. prepared hollow nitrogen-containing carbon spheres which exhibit a storage capacity of 2.21 wt% at room temperature under

* Corresponding author. Tel.: +86 21 52412513; fax: +86 21 52413122.

E-mail address: qmgao@mail.sic.ac.cn (Q. Gao).

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8 MPa [9]. Hence, it is difficult for the hydrogen physisorption on the porous carbons to meet the U.S. DOE target at room temperature.

In recent years, scientists tried to put on hydrogen adsorption at a cryogenic temperature. Ma et al. [10] reported the hydrogen adsorption behavior of the pristine single-layer graphene sheets in a powder form. Only 0.4 wt% hydrogen are adsorbed at 77 K under 100 kPa. Meisner et al. successfully prepared nanoporous carbon particles with unimodal, bimodal and highly porous foam-like pore structures from a simple solution of sucrose and silica precursors through an aerosol-assisted one-step synthesis method. The nanoporous carbon particles with surface areas of about 2000 m²/g could adsorb more than 4.0 wt% hydrogen at 77 K under >2 MPa; but only adsorbed 0.25 wt% at room temperature under 5 MPa [11]. Yang et al. prepared ordered porous carbon materials templated by zeolite 13X, Y and β via chemical vapor deposition. A high hydrogen uptake of 6.9 wt% was obtained at 77 K under 2 MPa [12–14]. Cheng et al. reported a facile preparation of biomass waste-derived microporous carbons which could adsorb 5.05 wt% hydrogen at 77 K under 1 MPa [15]. Very recently, our group reported the high hydrogen uptake of 7.08 wt% at 77 K under 2 MPa for the porous carbon with a large surface area of 3190 m² g⁻¹ achieved by KOH activation [16]. Accordingly, the carbon materials with large specific surface area and considerable micropore volume may actually adsorb hydrogen to a large extent at liquid nitrogen temperature [17,18]. In order to strengthen the interaction between carbon matrix and hydrogen molecules, several approaches were conducted to get the surface of carbon materials polarized by incorporating heteroatoms into the graphene layers [19,20]. In addition, pore size should be tuned because the adsorption of hydrogen onto carbon matrix may be enhanced by overlap of the potential fields exerted from the two opposite walls of a pore. Casa-Lillo et al. [21] found that the optimum pore size is the case that may hold two layers of adsorbed hydrogen (i.e. pore size about 0.6 nm) for hydrogen adsorption in the porous carbons. Gogotsi et al. [22] also investigated the importance of pore size in high-pressure hydrogen storage by porous carbons, finding that the pores with sizes larger than 1.5 nm contribute little to hydrogen storage and the effect of pore size was stronger than that of the surface chemistry on the hydrogen uptake.

Carbon dioxide and potassium hydroxide (KOH) activations are regarded as effective methods to synthesize highly porous carbons. Xia et al. [17,23] studied the activation of mesoporous carbons by CO₂ and they found that the activation can create micropores on the mesopore walls, which dramatically enlarge the specific surface areas, and the hydrogen uptake capacities are over 2 wt% at 77 K under 0.1 MPa. KOH has been used as an activating agent for producing activated carbons with a large surface area [24] from various precursors, including anthracite, natural cellulose and CNTs, etc., [25–28].

In this study, we prepared a kind of highly porous carbons with large specific surface areas by pyrolyzing gels and further KOH activation. The pyrolyzed gels consist of micropores and the usage of KOH is helpful to increase the surface area and the micropore volume to a large extent. The effects of preparation parameters on the surface area and pore volume were

investigated, and their hydrogen storage properties were tested at 77 K.

2. Experimental

2.1. Preparation of the porous carbon materials

Porous carbon materials were derived from a gel which contained citric acid and boric acid. The gel was prepared as follows: 3.85 g of boric acid (AR-grade) and 7.02 g of citric acid (AR) were dissolved in 50 mL of distilled water at 85 °C. 9.0 g of nickel chloride was dissolved into the solution subsequently. The concentrated ammonia solution (25%, AR-grade) was added dropwisely into the solution to adjust the pH value which was kept within the range of 2–3. The temperature of the solution was elevated to 110 °C to remove the excess water. The green ropy gels were obtained after evaporation. Then, the gel was heated to 200 °C and hold for 2 h, and then it was kept at 900 °C for 4 h under nitrogen flow to complete the pyrolysis and carbonization. The residual nickel was removed by etching in 2 M hydrochloric acid. The carbon materials were ultimately obtained after filtration, washed with deionized water and dried overnight.

KOH activation was carried out under N₂ flow by heating a physical mixture of KOH and the porous carbon and the products were denoted as APC-n (APC means activated porous carbon and n equals to the mass ratio of KOH/carbon). The mass ratios of the KOH/carbon were set at 1 and 3; accordingly, the activated samples were denoted as APC-1 and APC-3, respectively. APC-0 represents the non-activated sample. And APC* is a nickel/porous carbon composite from which APC-0 can be obtained after the HCl etching. The activation process was carried out by heating up to 750 °C with a ramp of 1.5 °C/min and hold at that temperature for 1 h. After that, the samples were washed with 2 M hydrochloric acid. The APC materials were collected after filtered and dried. The yields of these activation products are about 20–40%.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2250V diffractometer with Cu K α radiation source (40 kV and 40 mA). Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS, Microlab 310F with a dual anode X-ray source) was conducted to determine the form of carbon. Nitrogen adsorption/desorption measurements were performed in Micromeritics ASAP 2020M instrument at 77 K. The micropore volume and size distribution were calculated by the Dubinin–Radushkevich (DR) equation and Horvath–Kawazoe (HK) method [29,30], respectively. The total pore volume was calculated at a relative pressure $p/p_0 = 0.98$. By subtracting micropore volume from the total pore volume, the mesopore volume can be obtained.

Hydrogen uptake capacities were tested gravimetrically and volumetrically. High-purity hydrogen (99.999%) was used for the measurements. Volumetric approach was performed on the Micromeritics ASAP 2020M instrument. The sample was

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