CARBON 80 (2014) 82–90

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Investigation of morphology and hydrogen adsorption capacity of disordered carbons

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ARTICLE INFO

Article history:
Received 1 April 2014
Accepted 15 August 2014
Available online 22 August 2014

ABSTRACT

Small angle neutron scattering (SANS), scanning transmission electron microscopy (STEM) and gas adsorption, were applied to study the morphology and hydrogen adsorption properties of a wood-based ultramicroporous carbon (UMC) and a poly(furfuryl alcohol) derived carbon (PFAC). The polydispersed spherical model and the Guinier analysis of the scattering profiles were applied to obtain morphological parameters such as average pore size and pore size distribution of the two carbons; the results agreed reasonably well with independent gas sorption measurements and structural analysis by electron microscopy. The density of hydrogen physisorbed in these two carbons at room temperature and at moderate pressures was investigated by *in situ* SANS measurements. The experimental data, analyzed using a modified Kalliat model for decoupling scattering contributions from pores of different sizes, indicate that the molecular hydrogen acquires high densities preferentially in pores of subnanometer size at all measured pressures. These results support existing quantum mechanical and thermodynamical models that have predicted that the narrowest pores enhance the adsorption due to the overlapping of the potential fields from both wall sides in the slit-like pores. The structural information at a nanometer level gained via this work could guide the new development of porous-carbon based materials for hydrogen storage.

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1. Introduction

Limited fossil fuel reserves have spurred tremendous interest in developing new processes for supplying the world's energy needs [1]. Fuel cell technologies are one of the strongest candidates to replace gasoline and coals, hence mitigating concerns about pollution, global warming and exhausting of nonrenewable energy sources [2]. For fuel cell technology, hydrogen is the most attractive energy carrier due to its energy density and non-pollution feature (i.e, it can be produced from renewable sources) [3]. However, there are several key technical barriers that have to be tackled before the hydrogen fuel cell vehicles can be widely commercialized. One of those challenges is to achieve an efficient, economical and safe mechanism for on-board H_2 storage [4–6]. Several years ago, the US Department of Energy (DOE) proposed a set of technical targets for on-board storage system, however, to date, no approaches or materials have been found to satisfy all of the requirements regarding efficiency, weight, cost, and safety for transportation [5,7]. Current research activities

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http://dx.doi.org/10.1016/j.carbon.2014.08.041
0008-6223/Published by Elsevier Ltd.

continue to concentrate on finding the materials that have high storage capacities with fast storage/release rate at or near ambient temperature and moderate pressures. Materials store H_2 either by chemisorption or physisorption mechanisms. Hydrogen physisorption in porous materials offers some advantages over chemisorption, namely, fast adsorption kinetics, no need of energy for releasing hydrogen and high H_2 uptake at low temperature and moderate pressures. Amongst porous materials, activated carbons is one of the most promising candidates because of their high accessible surface area and pore volume, low bulk density, tunable pore size, low cost and easy preparation [8,9].

The hydrogen storage capacity of porous carbons relies greatly on the morphological features of the carbonaceous materials [9–13]. The features include structure regularity, surface area, average pore size and total volume of pores, especially micropores (<20 Å), pore connectivity and accessibility for hydrogen. These textural properties together with adsorption enthalpy depending on adsorbent–adsorbate interactions determine the total amount of adsorbed hydrogen. In the past decade, researchers have been working to understand how these parameters impact the adsorption by means of a variety of characterization techniques and computer simulations [14–17]. Average pore size has been found to be a rather important parameter determining the performance of physisorption-based materials. Both experiments and simulation have suggested that pore widths between 5 Å and 7 Å are ideal for hydrogen adsorption due to the overlap of potential fields from each wall of the pores [10,12,18]. However, a carbon material with perfectly uniform pore size does not exist in nature; further improvement of materials for solid hydrogen storage requires information about the total accessible micropore volume and surface area, along with knowledge on how the pores with different sizes connect in the materials and how they behave under hydrogen pressure. Unfortunately, the latter information generally cannot be provided by regular characterizing techniques.

In the present study, *in situ* small angle neutron scattering (SANS) was coupled with gas adsorption and electron microscopy in order to probe the pore structure of two carbons: an ultramicroporous carbon (UMC), obtained through chemical activation of wood, and a poly(furfuryl alcohol) derived carbon (PFAC), obtained by physical activation of the carbonized polymer. Previous studies have shown that UMC exhibits four times higher H_2 uptake than PFAC at 25 °C and 20 bar (0.8 wt% vs 0.2 wt%), which is surprisingly high given that UMC possesses only twice the surface area and total pore volume of PFAC based on gas adsorption results [19–21]. We expect that the insights on the internal pore structure and the densities of confined hydrogen in these materials probed using SANS can help us better understand their different adsorption performances. SANS is a well-established noninvasive technique used to study the hierarchical pore geometry in porous media [22–25]. Using contrast matching method, SANS can provide not only direct and accurate information on the pore size distribution and specific surface area, but also information about the accessibility of the pores to the adsorbate fluids [23,24]. In addition, *in situ* SANS is especially suited to study H_2 adsorbed in porous carbons because the negative neutron scattering length of hydrogen provides increased contrast between the adsorbed phase and the solid matrix with increased pressure. The goal of this work is to correlate the hydrogen storage capacity with the morphological structure of activated carbons, to provide new insights into the complex structure-property relationship governing gas adsorption in porous carbons, and therefore guide the synthesis of future materials.

2. Experimental

2.1. Materials and gas adsorption characterization methods

Two porous carbon materials were used in this study. PFAC is a poly(furfuryl alcohol)-derived carbon synthesized after a modified Burket procedure [26] and physically activated using CO_2 at 850 °C, to achieve a 50% burn-off by weight. UMC is an ultramicroporous carbon made available by MeadWestvaco Corporation (Charleston, SC). It was obtained through phosphoric acid activation of wood followed by secondary activation with KOH [27]. Physical properties of these two porous carbons were characterized by gas adsorption of CO_2 at 273 K and N_2 at 77 K using a Quantachrome Autosorb 1 C instrument with ASiQwin 2.0 data processing software. CO_2 adsorption data were analyzed using the non-local density functional theory (DFT) approximation for slit shaped pores, to obtain the size distribution of open pores in the ultramicropore range ($\leqslant$0.7 nm). N_2 adsorption data were analyzed using the quenched surface DFT model assuming a slit/cylindrical pore geometry, to obtain the size distribution of open pores in the supermicropore (0.7–2 nm) and mesopore (2–50 nm) ranges. The results of the two methods were merged in a unique pore size distribution. A summary of physical properties determined by gas adsorption is presented in Table 1. The hydrogen adsorption capacities of these two materials have been studied extensively and reported elsewhere [20,21]; a summary graph of their H_2 uptake capacities at 25 °C and

Table 1 – Pore surface areas and pore volumes of carbons under vacuum from different methods.

	BET[a] surface area (m^2/g)	Results from adsorption using the QSDFT analysis (for pores <30 Å)			Results from scattering using PDSP model (for pores <30 Å)		
		Pore surface area (m^2/g)	Pore volume (cc/g)	Volume to area ratio (Å)	Pore surface area (m^2/g)	Pore volume (cc/g)	Volume to area ratio (Å)
PFAC	1530	1160	0.42	3.6	2798	0.59	2.1
UMC	2540	1510	0.61	4.0	3644	0.79	2.2

[a] The BET surface area is calculated using the Brunauer–Emmett–Teller equation.

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