Available online at www.sciencedirect.com

SciVerse ScienceDirect

Analysis of adsorption equilibrium of hydrogen on graphene sheets

Qingrong Zheng [a,*], Xuewen Ji [b,**], Shuai Gao [a], Xiaohua Wang [a]

[a] Institute of Marine Engineering, Jimei University, No. 176 Shigu Road, Jimei, Xiamen, Fujian 361021, PR China
[b] Shenzhen Dovelet Sensors Technology Co., Ltd, Shenzhen 518057, PR China

ARTICLE INFO

ABSTRACT

The adsorption equilibrium of hydrogen on graphene sheets (GS) was studied based on a sample of GS with S_{BET} = 300 m^2/g at the temperatures of 77.15 K–293.15 K and the pressures of 0 MPa–6 MPa. In the meantime, the adsorptions (Excess adsorption measurements) of hydrogen on granular coconut shell SAC-02 activated carbon (S_{BET} = 2074 m^2/g) and carbon nanofiber (CNFs, S_{BET} = 205 m^2/g) were investigated at the pressures of 0–8 MPa and the temperature of 77.15 K. The outcomes from experiments were used to determine the parameters in Toth equation by way of Non-linear fit. The absolute adsorption amounts of hydrogen on the GS, which were calculated from the equation, were used to calculate the isosteric heat of hydrogen adsorption by use of adsorption isosteres.

It shows that, under the experimental conditions, the excess adsorption amount of hydrogen on the GS increases monotonically and correlatively as pressure increases, and the mean relative deviation between the experimental data and those predicted from Toth equation is less than 1%. The result also shows that the storage density of hydrogen on the GS is 1.75 wt% and 0.168 gH$_2$/L at pressure 5.4 MPa and temperature 77.15 K, which is lower than that of hydrogen on the activated carbon but is higher than that of hydrogen on the CNFs. The isosteric heat of hydrogen adsorption on the GS falls within 5.14 kJ/mol–6.37 kJ/mol, which is comparable to that of hydrogen adsorption on the activated carbon. It suggests that interaction between hydrogen molecules and the graphene layer is stronger than that between hydrogen and carbon surface, and the hydrogen storage capacity of GS is closely related to its physical properties.

1. Introduction

Physisorption is a promising method for storing hydrogen because the adsorbed hydrogen can be easily released at lower pressure. The adsorbents such as zeolites, carbon materials as well as metal-organic frameworks (MOFs) have therefore been intensively investigated [1]. However, the outcomes show that without setting the temperature to cryogenic region the amount of physically adsorbed hydrogen can not meet the economic targets set out by United States' Department of Energy (DOE) and International Association of Energy (IAE). How to improve the interaction between hydrogen molecules and adsorbent surface becomes a hot topic in this area [1–3].

* Corresponding author. Tel.: +86 592 6183533; fax: +86 592 6180332.
** Corresponding author.
E-mail addresses: qrzheng816@sina.com (Q. Zheng), djw@dynanonic.com (X. Ji).

The recent research suggests that graphene materials, the new member in carbon materials, have potentials for achieving the targeted energy storage capacity due to their unique planar nanostructure and a wide range of unusual properties [4]. Graphene is composed of a monolayer of carbon atoms packed into a dense honeycomb crystal structure. This structure makes it possible to significantly enhance its physical adsorption capacity of hydrogen molecules by modifying the physical construction data and properties of the functional groups [4–6]. However, the graphene-based adsorbents that have been tested so far are of low specific surface area and low micro-porous volume and it is probably the main reason to produce a poor hydrogen storage capacity [7–10]. Theoretically the guidelines for development of graphene-based adsorbent lie on the understanding of adsorption behavior of hydrogen molecules upon the GS. The graphene is a well-defined two dimensional crystal materials and it can be regarded as the elementary structure of carbon-based materials. The interaction exerted on hydrogen molecules from the GS is stronger than that from carbon layers [11]. Therefore in addition to the specific surface area, micro-porous porosity and the contribution of the functional group upon the adsorbent surface, how to maintain a low storage temperature and the modification of interaction mechanism of hydrogen molecules could be a way to increase the storage capacity.

Furthermore, as set out by DOE, the economic delivery temperature of the storage system is within 233.15 K–358.15 K. But in this temperature range, the storage densities of physisorption of hydrogen on currently adsorbents are far below the DOE 2015 targets (5.5 wt%, 40 gH_2/L). Modification of the composition and structure of the adsorbent is therefore necessary. In general, a lower temperature is beneficial to physisorption but inhibits the contributions from other interaction mechanisms. A hydrogen storage system on adsorption should be equipped with a mechanism to achieve and maintain the maximum interaction between hydrogen molecules and adsorbent surface in the system. In other words, it is important to fully understand the temperature dependent behavior of hydrogen molecules confined within the GS.

An enhanced interaction between adsorbate and adsorbent produces a higher adsorption enthalpy and accordingly a greater thermal effect, which needs to be effectively managed by appropriate heat transfer measures [12–14]. The variation of the adsorption enthalpy is usually determined by adsorption isosteres on excess amounts from Clausius–Clapeyron equation. However the result may be ambiguous if isotherms of excess amounts pass the maximums or are measured over a wide temperature range [15,16]. In terms of practical applications, it is the absolute adsorption amount that has a clear physical meaning in designing an adsorption storage system. As the experimental data represents excess amounts, it is necessary to develop an accurate method to transform the excess amount into absolute amount. According to the Gibbs definition of the adsorption [17], the transformation can easily be achieved where the adsorbed density of the adsorbate is certain. But this will be difficult if the adsorption is in supercritical region in that the state of the adsorbed phase is unclear. Approximations such as the superheated liquid [18], quasi-liquid and compressed gas have been proposed to describe the adsorbed phase of supercritical gases [19], but these approaches are based on the limited experimental data. Hence, an approach, which can directly calculate the absolute adsorption amount without any assumption on the state of the adsorbed phase, is another hot topic.

This paper is to explore the factors affecting the physisorption capacity of hydrogen on the GS experimentally and theoretically. Firstly, the GS sample whose structure has been investigated was selected, and hydrogen adsorptions over a range of 77.15 K–293.15 K in temperature and 0–6 MPa in pressure were accurately measured and recorded. Secondly, the parameters of Toth equation were determined by non-linear fit of the adsorption data. Finally, absolute adsorption amounts were determined by use of the modified Toth equation and the adsorption isosteres of the absolute amount were plotted to calculate the isosteric heat of hydrogen adsorption on the GS.

2. Experiment

2.1. Preparation of graphene

Graphite powders with an average particle size of 65 μm were from Shanghai Fuyouqin Trading Co. Ltd. The modified Hummer method was used to oxidize the graphite for synthesizing graphite oxide (GO) [20], this GO was then undergone thermal exfoliation by rapidly heating to achieve thermally expanded GO. The resulting thermally expanded GO was firstly cooled in a gas flow of hydrogen and argon, then stirred for about 1 h in ammonia solution. The sample out off ammonia was washed with de-ionized water and then dried at 373.15 K for 12 h. The GS sample for experiment was finally obtained from centrifugal separation.

2.2. Structural characterization

The sample was investigated for its microstructure and morphology by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The SEM image in Fig. 1(a) reveals that the GS has a pocket-like morphology with wrinkled paper structure, and the HRTEM image in Fig. 1(b) and (c) shows that the sample is consisted of a single layer or multiple layers of graphene. There are wrinkles on the edge of each layer and the layers are linked by transparent membranes. By comparison of the scale in Fig. 1(c) to the thickness of a chemically derived single-layer graphene [21], the thickness of layer in the used GS sample is approximately 1 nm and it is composed of 1–3 layers of graphene sheets.

Fig. 2(a) is a N_2 adsorption isotherm of GS at 77.15 K which was derived from the experiment by use of Micromeritics ASAP 2020. The results from BET plot and the pore size distribution (PSD) by Non-local density functional theory (NDFT) calculation are respectively shown in Fig. 2(b) and Table 1. In comparison with coconut shell SAC-02 activated carbon and carbon nanofiber (CNFs), The GS has significantly bigger pores and its pore sizes are more concentrated around 4.71 nm. However the BET surface area of the GS is higher than CNFs' but much lower than that of coconut shell SAC-02 activated carbon.