Thermodynamical model for hydrogen storage capacity in carbon nanostructures

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ABSTRACT

A simple thermodynamical model taking into account non-ideality and inhomogeneity of absorbed hydrogen molecular gas has been proposed to calculate hydrogen storage capacity in carbon nanostructures as a function of temperature and pressure. The model utilizing the effective interaction potential of the hydrogen molecule with the atoms of the considered material, is based on the experimental equation of state and a local density approximation for molecular hydrogen. We have applied the model for the search of the optimal geometry for hydrogen storage of such promising carbon materials as a set of graphene layers and bundles of carbon nanotubes. We demonstrate that the hydrogen storage capacity depends on the geometry of material and discuss the origin of this effect.
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Introduction

The search for effective hydrogen storage is still an utmost issue for both experimental and theoretical investigations [1]. In spite of a few discouraging experimental data on some nanostructured carbons, carbon-based materials are still considered as an essential component of a novel promising nanostructure material [2–5]. Though some progress has been achieved in experimental studies, the results are often not in chime, which is caused by the methods of measuring [2]. The theoretical studies depend on models, and there is no robust understanding of the sorption mechanism yet.

The adsorption of hydrogen on the surface can be of two types: physisorption of hydrogen molecules or chemisorption of hydrogen atoms. As we are only interested in the reversible

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hydrogen sorption process, we limit ourselves to physisorption mechanism only. In this case the interaction of a hydrogen molecule with nanostructured carbon (i.e. H_2–C interaction) is basically of the van der Waals type.

The storage capacity can be defined as a sum of the capacity due to adsorption on the solid surface and the volumetric capacity due to compression in the void space [4]. The physical explanation of the adsorption by the existing experimental data is often based on a simple empirical model of Langmuir monolayer adsorption on a surface [6,7]. It should be noted that the storage capacity is often explained only by adsorption itself.

It has been demonstrated recently [8–15] that by designing a proper geometrical confinement, one can achieve more effective carbon-based storage. In Ref. [12] it is shown that tunable storage media (i.e. materials whose storage geometry can be changed or tuned) provides a potential for improving hydrogen capacity. In this paper we demonstrate that the same effect can be accomplished with a bundle of nanotubes, either by changing the distance between them or by choosing an appropriate diameter. The alternative point of view [6] is that the geometric structure does not influence the amount of absorbed hydrogen, which is defined solely by the specific surface area of a nanostructured carbon sample. Moreover, it has been claimed [7] that in a simple empirical model of monolayer adsorption the upper limit of the adsorbed hydrogen is 3.0 mass%, if only one side of the surface is used and 5.76 mass% for both sides. However, the "natural" nanostructured carbon material for which the model was applied is characterized by a relatively dense packing of nanotubes or graphite platelets in carbon fibers with the intertube (interlayer) distance of 0.33 nm. At this distance the H_2–C potential is repulsive (positive), hydrogen molecules are pushed out, and the storage capacity is smaller than for uniform hydrogen gas. Such effects are not accounted for by the model. The model is also not applicable to the cases of nanotubes with small (less than 0.3 nm) or large diameters when the gravimetric storage goes to zero or 100%, respectively, or to the small and very large distances between graphite sheets. Our calculations show that the hydrogen storage capacity in this method is generally overestimated.

Several other theoretical models are suggested for calculations of the hydrogen capacity of nanostructure materials. Most of them are based on Monte Carlo molecular simulations, which are numerically rather expensive [16,11,17,18] and ignore quantum effects. The influence of quantum effects on hydrogen storage capacity was investigated in Refs. [12,19] but the results were inconclusive. However, it has been established that locally the hydrogen molecular density differs from that in the simple monolayer model. Other models use the density functional theory [20,21] (DFT) for the density of molecular hydrogen or a combination of DFT and Monte Carlo (MC) approaches [5].

In the literature, there is a discussion of other important factors that affect hydrogen storage capacity. Among them the most important is the effect of pores on gas adsorption [22–27]. For example, using a quantum-thermodynamic model Cabria et al. [23] studied the influence of pore shape and size on hydrogen storage. The authors showed that at ambient temperature (300 K) and elevated pressure (10 MPa)

slitpores (planar pores) of optimal size (at which pores have the maximum storage capacity) have larger storage capacity than cylindrical and spherical ones, independently of the type of hydrogen–carbon surface interaction potentials (Lennard-Jones, Moller–Plesset, and DFT). However, at low pressure (0.1 MPa) and at 300 K, spherical pores have higher storage capacity [23]. Remarkably, the optimal size of planar pores at high pressure (10 MPa) and ambient temperature lies in the range of 5.8–7.5 Å, which agrees well with our results (6 Å at 300 K and 50 bar, see later). Recent extensive molecular dynamics (MD) simulations for nanoporous carbon extended this range up to 10 Å for planar and curved pores [25]. Interestingly, the experimental and theoretical work by Burress et al. [26] has demonstrated that the bimodal pore size distribution in nanoporous carbon has peaks at 7 Å and >10 Å with binding energies of 9 kJ/mol and 5 kJ/mol, respectively. It turned out that the curvature of the pore region also affects the hydrogen storage capacity. Lee et al. [27] have showed that a concave surface enhances gas–pore interaction, while a convex one reduces it.

In practice, one could increase accessible surface area and ultramicropore volume multifold, resulting in enhanced hydrogen storage by a factor of 2–4.5 [28], by using a chemical activation process for carbon-based materials. Alternative way is to create controllable pore size distribution, which was done by Almasoudi and Mokaya with templated zeolite-like carbons [29]. One of the main factors for pore distribution is the temperature of synthesis. Bimodal pore distribution (with sub- and supra-nanometer peaks) of KOH- activated carbon can also be controlled by the weight ratio KOH:C [30]. Zhao et al. [31] even argue that the weight ratio is the only significant parameter while temperature plays a negligible role.

The hydrogen storage capacity maximum for pure carbon at room temperature, ~2 wt.%, is observed at P = 100 bar [22,32]. It can be enhanced if one succeeds in increasing the hydrogen-material interaction up to 15–25 kJ/mol. For that one has to modify chemically the carbon matrix or design a nanostructured carbon materials. In the first case, the carbon substrate is doped by such elements as boron, phosphorus, nitrogen, alkali or alkali-earth metals, transition metals, etc [33–37]. A more sophisticated way is to decorate pure or doped carbon atoms by metal atoms which have higher interaction with hydrogen molecule and provide with a larger active surface area [34,38]. Theoretically, this can increase the hydrogen storage capacity up to 12–14 wt.%.

Kuchta et al. recently constructed a model (based on grand canonical MC simulations using LJ potentials with Feynman–Hibbs quantum correction) which lead the authors to a new hypothetical carbon structure with high-surface-area, which they called open carbon frameworks (OCF) [39,40]. The OCF consists of unbound or bound fragments of graphene sheets. High hydrogen storage capacity of these structures is caused by enhanced hydrogen adsorption on the abundant edges of the fragments. Carbon nanotubes (CNTs) also remain a promising candidate for hydrogen storage. Storage capacity of CNTs varies in the range of 0.01–20 wt.% [41]. Factors causing such variety (thus, affecting storage) are chemical modification, tube diameters and their packing, governed by pressure and temperature in the synthesis process.