

HYDROGEN STORAGE IN CARBON NANOSTRUCTURES

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Introduction

Conventional ways to store H₂ gas consist of applying high pressure (700 bar) and low temperature (20 K) or both, which is too expensive and inconvenient for routine mobile applications. The two prominent alternatives are chemisorption and physisorption (Grochala et al., 2004; Liu et al., 2005) of hydrogen. Chemisorption, for example in metals, is often hampered by slow loading and/or unloading process due to slow diffusion and a large heat exchange.

Carbon materials like activated carbon (ACs) and ball-milled graphite are already known with their abilities to adsorb various gases. The hydrogen-storage behaviour of carbon materials with high specific surface area, such as AC and AC fibres, has been investigated since the 1980s. A capacity of 3–6 wt % was reproducibly obtained at cryo-temperatures, although at room temperature the capacity is well below 1 wt % (Carpentis et al., 1980; Chahine et al., 1994). Ball-milled (under hydrogen-gas atmosphere) graphite powder shows considerable hydrogen storage capacity partially due to chemisorption; however, the desorption temperature is too high for it to be used in practice (Orimo et al., 1999; Chen et al., 2003; Francke et al., 2005). Hydrogen storage in mesoporous carbons was also reported recently (Pang et al. 2004). Hydrogen uptake investigations have been performed on various carbon materials. Especially carbon nanotubes (CNTs)/nanofibers (CNFs) have been most intensively studied for hydrogen storage in recent years. However, the interaction of H₂ with graphite surfaces, slit pores, (Deng et al. 2004; Kadono et al. 2003) carbon nanotubes, (Dillon et al. 1997; Rzepka et al. 1998; Chen et al. 1998; Wang et al. 1999; Kowalczyk et al. 2007) and nanofibers (Gogotsi et al. 2005) have been reported in the literature, not without controversy (Liu et al. 2005; Elefskii 2004; Nechaev 2006; Ströbel et al. 2006), applying arguments based on both, experimental and theoretical results. Despite the numerous articles and discussions whether carbon materials are suitable for hydrogen storage, the research on that topic is still on the spot of many theoretical and experimental scientists. So far, no general conclusion can be drawn from the above cited reviews on whether carbon is suitable for hydrogen storage. In fact, structural characteristics, synthesis techniques and post-treatment methods may evidently influence on the hydrogen-storage behaviour. However, experimental and theoretical investigations suggest a close relation between the nano-scale structure of the materials and their abilities to absorb hydrogen gas. Two main reasons can be referred as a source of the abovementioned problems. Besides diamond, graphite and C₆₀-solid no other carbon allotrope has a well defined periodic structure. Moreover, it is difficult to manipulate them in the nano scale range.

Method

We employ multi-scale simulation techniques to investigate the properties of the H₂—host system. We use an approximate density-functional scheme with van-der-Waals corrections (Seifert et al. 1996; Zhechkov et al. 2005) to determine the mechanical and structural properties of the nanostructures. Then, we model H₂ interactions with the host using an additive Buckingham potential, with parameters fitted to high-level ab initio calculations (MP2, CCSD(T)) on model systems. We solve the stationary Schrödinger equations for shapeless particle motion, with H₂ mass, on a numerical grid, inside nanostructures with periodic boundary conditions applied. We neglect the internal degrees of freedom of the hydrogen molecule and interactions between the molecules. The result is the energy spectrum \mathcal{E}_i of bound H₂, together with corresponding eigenstates Ψ_i , determined in the ideal gas approximation. The equilibrium constant K_{eq} for hydrogen adsorption is then calculated as a function of temperature T using standard statistical thermodynamic expressions. For details, we refer to the literature (Patchkovskii et al. 2005; Heine et al. 2004). The storage capacities (volumetric and gravimetric) are calculated by correcting the neglected H₂—H₂ interactions using the experimental equation of state (EES) (Mills et al. 1977). The pressure used in EES P_{int} is calculated as $P_{int} = K_{eq} P_{ext}$ where P_{ext} is the pressure outside the material. Thus EES gives us the density of H₂ in the material, and the gravimetric capacity is the ratio between this density and that of the whole system.

Results and Discussion

The strength of the H_2 –host interaction is proportional to the polarisability of the host material. Therefore, carbon nanostructures are among the most promising light storage materials. In a graphene layer as a prototype structure the H_2 –graphene interaction energy is 7 kJ mol^{-1} (Heine et al. 2004). Our simulation shows that it increases the H_2 density by only 60 % ($K_{eq} = 1.6$) at ambient temperature – hardly useful for practical applications. In contrast, a graphene bilayer with optimised interlayer distance shows a remarkable potential to store hydrogen, having $K_{eq} \geq 50$ at room temperature (Figure 1).

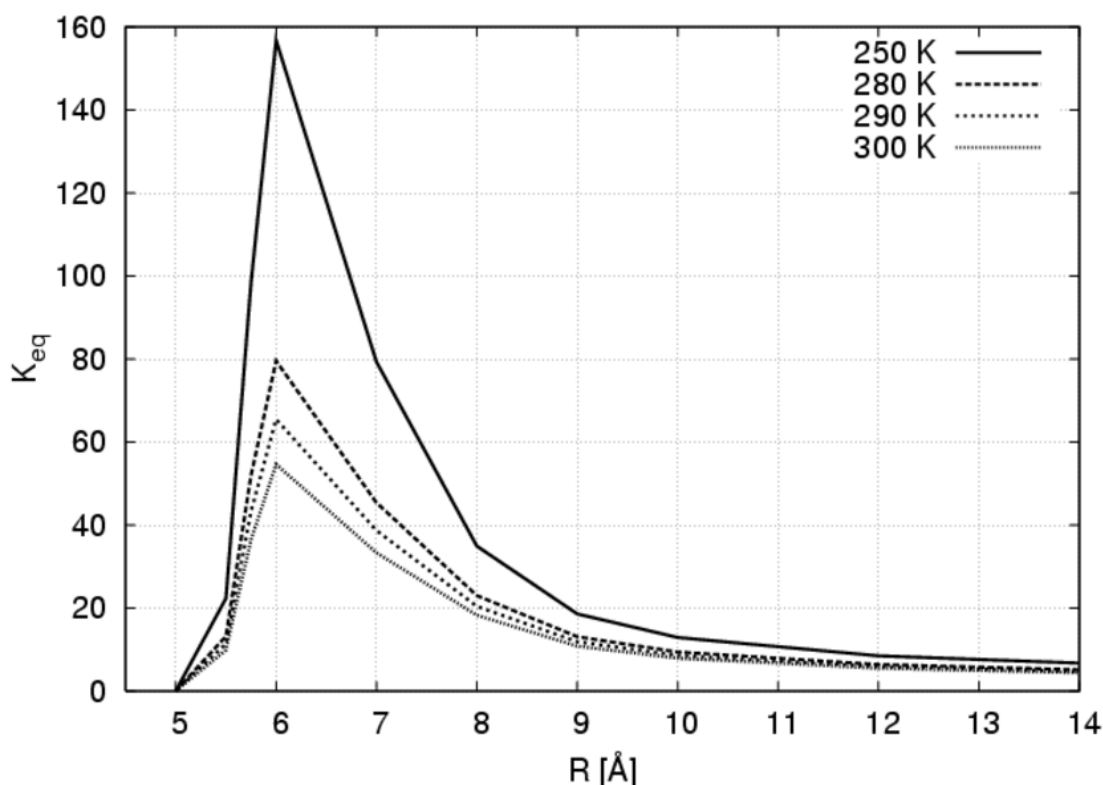


Figure 1. Equilibrium constant plotted against the width of the pore for different temperatures (see the legend on the plot).

We found, in agreement with recent experiments (Gogotsi et al. 2005), that optimal slit pores have a width of $\approx 0.7 \text{ nm}$ (Patchkovskii et al. 2005). However, it is not sufficient to provide carbon material with optimal structural properties as there might be better adsorbats than H_2 . The likely contaminant gases (N_2 , O_2 , CO_2) are more polarisable than H_2 , and bind much stronger to the nanostructure. For the most abundant atmospheric gas, N_2 , we calculated the nitrogen–graphene binding energy to 16 kJ mol^{-1} (Zhechkov, Heine, Seifert 2005), which is as much as twice stronger than the hydrogen–graphene interaction. The optimal storage material design should not only maximize the H_2 abundance, but also be resistant to 'poisoning' by other molecules. One possibility for a slit pore design is the intercalation of graphite, for example with C_{60} fullerenes (C_{60} -intercalated graphite, CIG). Such material was recently reported by Gupta and coworkers (Figure 2) (Gupta et al. 2004).

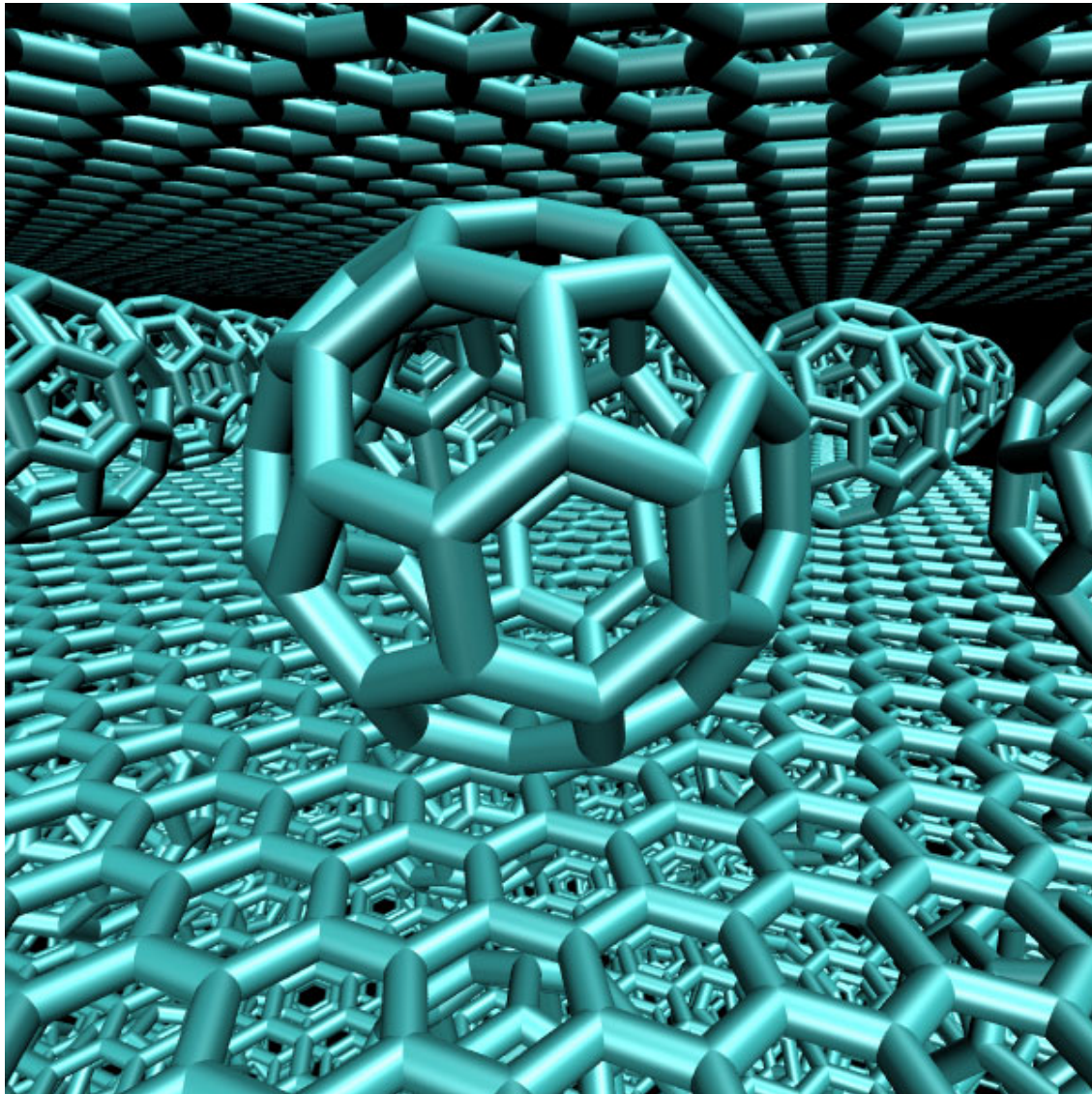


Figure 2. Structure of C_{60} intercalated between graphene platelets.

Our calculations confirm the experimentally observed structure and the energies of this new carbon phase. The fullerenes simultaneously spread the graphene layers and enhance the H_2 – host interaction, leading to a reasonably possible hydrogen storage medium. Our simulations indicate that at a moderate temperature (250 K) and pressure (10 MPa), this material could host enough hydrogen gas to approach the Department of Energy of the USA target for mobile applications (≈ 6 wt.%). Additionally, as a consequence of the pore sizes of the material, the N_2 contaminants should be trapped between the fullerene cages and have only superficial penetration into the material. The nano-scale design of the H_2 storage media has crucial importance on the storage capacities. This can be demonstrated by investigating other candidates with well-defined pore sizes, high mechanical stability and low density, such as honeycomb graphite (Figure 3) (Kuc et al. 2006).

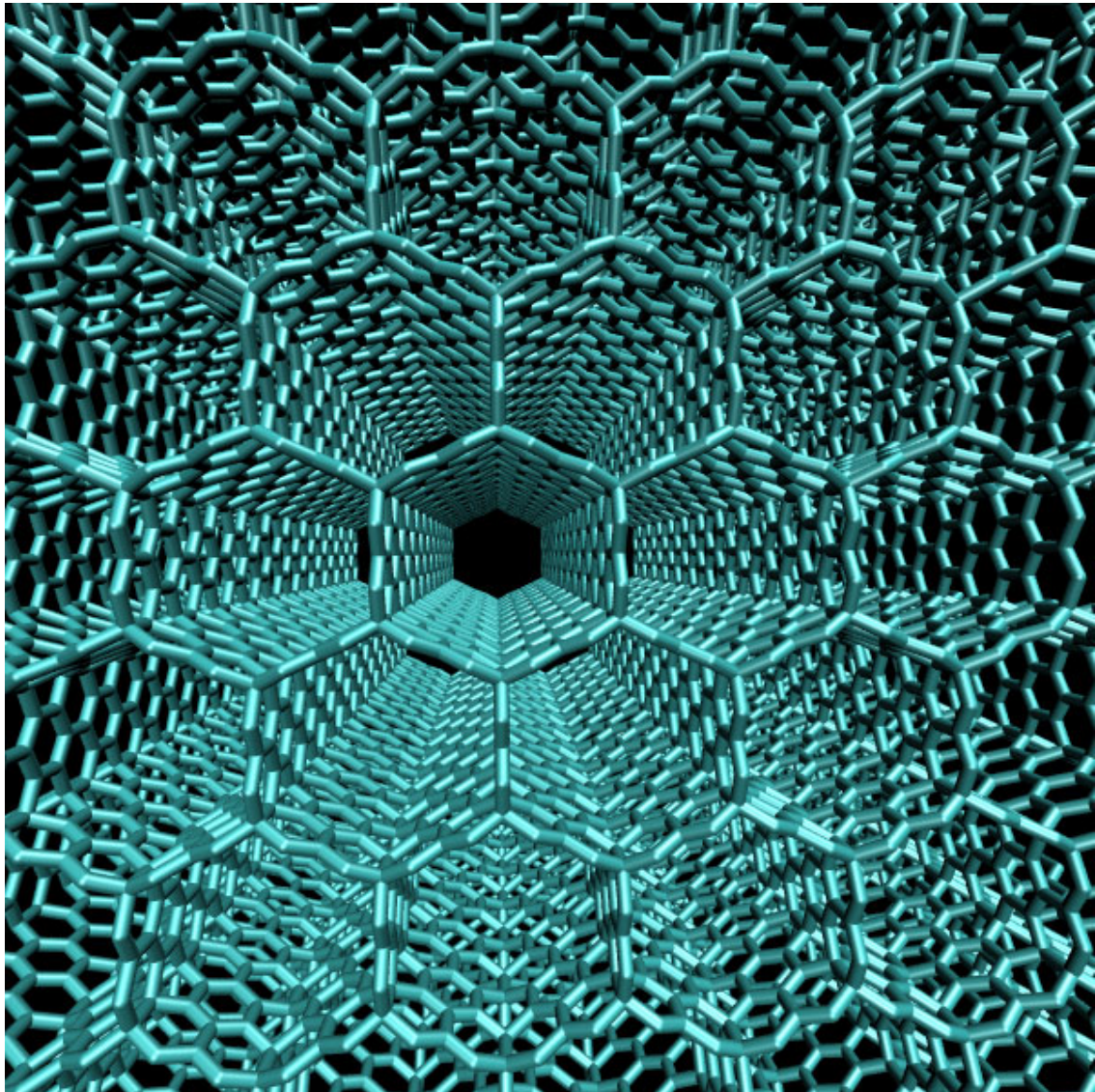


Figure 3. Structure of carbon foam (honeycomb graphite).

Our simulation shows that varying the pore size in the range from 3 to 11 Å the gravimetric capacities of the carbon foams do not change considerably. However, the volumetric capacities do (see Fig. 4)

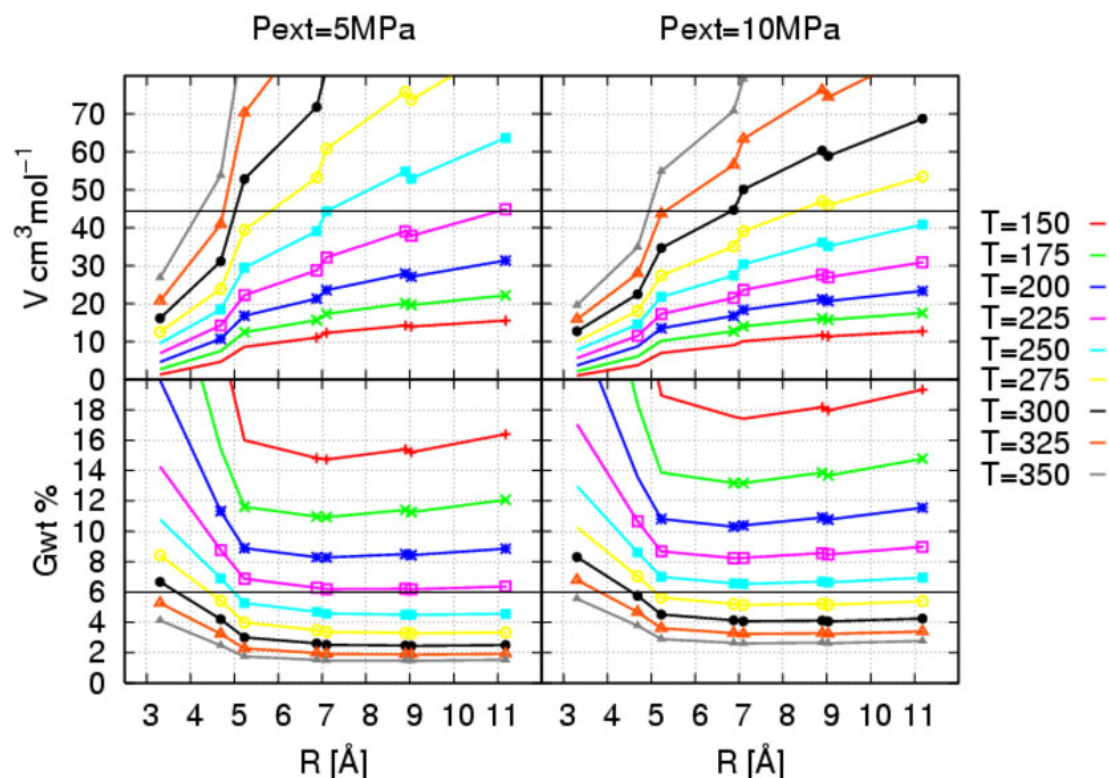


Figure 4. Volumetric (Top) and gravimetric (Bottom) storage capacities for carbon foams with radius R are given for various temperatures (see the legend). Left and right columns give the values respectively for pressures at 5 and 10 MPa. The symbols on the curves denote that the approximation is within the limits (pressure and temperature) of the real gas equation of state (Mills et al. 1977). The targets (DOE targets) for automotive applications (Gwt) 6.0 %, (V) 44.4 cm^3/mol are indicated as horizontal lines.

Hence, despite the reasonable gravimetric capacity for the materials with larger pore sizes the energy density may decrease dramatically. A very important conclusion is that properties as high surface or high gravimetric storage capacities are not sufficient to prove a material as hydrogen storage media. Therefore, in order to avoid ambiguities, the storage and structural properties (gravimetric, volumetric, surface area etc.) of the media should not be discussed separately.

Conclusion

Well-defined carbon nanostructures are suitable materials for the design of hydrogen storage devices. Target storage capacities of the U.S. Department of energy (4.5% gravimetric, volumetric 0.039 $\text{kg H}_2/\text{L}$, 2007) may be reachable at moderate pressures and temperatures. The weak, attractive interaction of the host material with the hydrogen gas allows reversible loading cycles with low heat exchange with the environment. Well-defined pore sizes avoid material poisoning with larger molecules present in the atmosphere. New carbon materials, as honeycomb graphite structures so far show very promising results. Due to their mechanical and structural properties they are very good candidates for future automotive applications.

Acknowledgements

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Hydrogen storage basically implies the reduction of the enormous volume of the hydrogen gas; 1 kg of hydrogen at ambient temperature and atmospheric pressure takes a volume of 11 m³. In order to increase the hydrogen density in a storage system, work must either be applied to compress hydrogen, or the temperature has to be decreased below the critical temperature, or finally, the repulsion has to be reduced by the interaction of hydrogen with another material. The second important criterion for a hydrogen storage system is the reversibility of the hydrogen uptake and release. Most papers reporting theoretical studies on hydrogen absorption in carbon nanostructures focus on the physisorption of H₂ on carbon using the grand canonical Monte Carlo simulation. Creation of devices for hydrogen storage is urged by the fact that energetically efficient and environmentally clean types of fuel draw more and more attention for some well known reasons at present, especially in the countries with a high level of urbanization. It will suffice to mention that 80% of gaseous pollutants are connected with the automobile transport. One of the most promising types of fuel both from the ecological perspective and from the point of view of power capacity is hydrogen. New materials on the basis of nanostructured carbon are capable of absorbing and keeping considerable quantities of hydrogen. CNT also belong to these materials. They are some graphite layers folded into a one-layer or multi-layer tube.