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Molecular hydrogen storage in fullerenes — A dispersion-corrected density functional theory study

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ABSTRACT

H_2 physisorption within curved carbon nanomaterials for potential fuel storage on board vehicles is studied using dispersion-corrected Density Functional Theory. Full C_n ($n = 20$, 60, 180, 540, 960) fullerenes were considered along with single-walled carbon nanotubes ((3,3), (5,5), (9,9)) and graphene to investigate the effects of curvature, confinement, platinum and non-metal (B, N, O) dopants, $C_{fullerene}$–H_2 and H_2–H_2 distances, H_2 orientation on $C_{fullerene}$–H_2 interactions. The study mainly focuses on H_2 stored within the fullerene with some investigation into external H_2. A significant attractive $C_{fullerene}$–H_2 interaction energy of −28 kJ/mol is observed for H_2 in curved carbon nanomaterials where H_2 molecules are located ca. 2.9 Å from carbon atoms in a highly confined system. Dopants have the potential to increase the favourability of $C_{fullerene}$–H_2 interactions when multiple H_2 molecules are present by affecting the orientation of H_2 molecules within the carbon nanomaterial. This paper presents analysis of several carbon nanosystems and then proposes possible materials for H_2 storage on board vehicles.

Introduction

The Earth's fossil fuel reserves are depleting quickly and their use creates significant environmental problems. Optimization of alternative fuels is key to sustainable energy usage. Hydrogen gas is a strong contender to replace gasoline in automobiles due to the increasing efficiency and uses of hydrogen fuel cells (FCs). Hydrogen FCs are preferred to combustion engines because they produce energy efficiently with minimal pollution through the combination of H_2 with O_2 to produce H_2O. Since their use in NASA's Gemini space program in the 1960's hydrogen FCs have entered the regular consumer market in a variety of automobiles. The most common fuel cells, PEMFCs (polymer electrolyte membrane FCs or proton exchange membrane FCs), use a proton exchange membrane to transfer the protons produced by H_2 splitting then combine with oxygen to form H_2O, and electrons, which are used to power the vehicle [1].

Hydrogen fuel cells have been extensively researched for the past six decades because hydrogen gas is a strong candidate to replace gasoline in automobiles. At 143.0 MJ/kg, H_2 has

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the highest energy density of common fuels by weight (ca. three times larger than gasoline). Unfortunately, it will not be commercially viable until reliable storage methods are developed. Storage of hydrogen is challenging because, at 0.0108 MJ/L, gaseous H_2 has the lowest energy density by volume (over 3000 times smaller than gasoline) and it is highly diffuse and buoyant [1]. Therefore, compact and efficient storage techniques must be developed.

Traditionally, hydrogen storage techniques are evaluated by analysis of the gravimentric density (GD) and volumetric density (VD) of the storage system. The GD is the weight percentage of hydrogen relative to the total weight of the system (hydrogen + storage medium). The VD is the mass of hydrogen stored per unit volume of the system. The US Department of Energy (DoE) has released 2015, 2017 and ultimate targets for H_2 storage. These targets address GD, VD and the ideal temperatures for H_2 sorption and release [2]. The DoE GD and temperature targets are shown in Fig. 1 along with the placement of current H_2 storage methods.

As shown in Fig. 1, at present the ammonia borane (AB) family of chemical hydrides are the only hydrogen storage methods that meet the DoE targets. However, these materials present challenges because the hydrogen is stored through the formation of chemical bonds so on board chemical reactions are required to release H_2. This can be done through thermal dehydrogenation when AB is in the solid state or solvolysis (hydrolysis or methanolysis) when in solution. Thermal dehydrogenation typically requires high temperatures and a large energy input. Therefore, AB hydrides can only be used if catalysts are added to assist in dehydrogenation. However, the use of catalysts produces problems of cost, deactivation and control of reaction kinetics [3]. Therefore, alternative storage methods are still under investigation.

The ideal storage media should be lightweight (to meet the GD requirements), inexpensive, and store a high density of H_2 by physisorption (to meet VD goals and limit the energy required to released H_2). Carbon nanostructures are a potential cheap, abundant, and lightweight storage system that has become increasingly prominent in the last few decades. Initial work began with carbon nanotubes (CNTs) in the late 1990s and has since expanded to include a wide variety of sp^2-hybridized carbon structures including graphene and spherical fullerenes [4–8]. Fullerenes have a theoretical maximum storage capacity of 58 hydrogen atoms in C_{60} (7.5 wt%) at 0 K. This produces a metastable structure with an internal pressure of 1.3 Mbar. The practical storage capacity will be lower, but storage in fullerenes is still promising [9].

There are two main approaches to hydrogen storage on large area carbon nanomaterials. The first, hydrogen chemisorption, considers hydrogen chemisorbed on an expansive carbon surface to create C–H terminations through covalent bonds. The most extreme possibility is graphane, an extended 2-dimension hydrocarbon derived from chemisorption of hydrogen at every available position on graphene, leading to a GD of 8.3 wt%. Unfortunately, thermal annealing, a complex and high-energy processes, is required to add and remove hydrogen from this system so it is not commercially viable [10–12]. In general, hydrogen storage by chemisorption experiences the same issues observed with ammonia boranes with difficult and energetically expensive processes required to release H_2 on board a vehicle. In particular, both adsorption and desorption of hydrogen on carbon nanomaterials have energetic barriers greater than 100 kJ/mol [13].

The other method of hydrogen storage on carbon nanomaterials is via physisorption, in which H_2 is weakly attracted to the carbon surface by van der Waals forces. The strength of

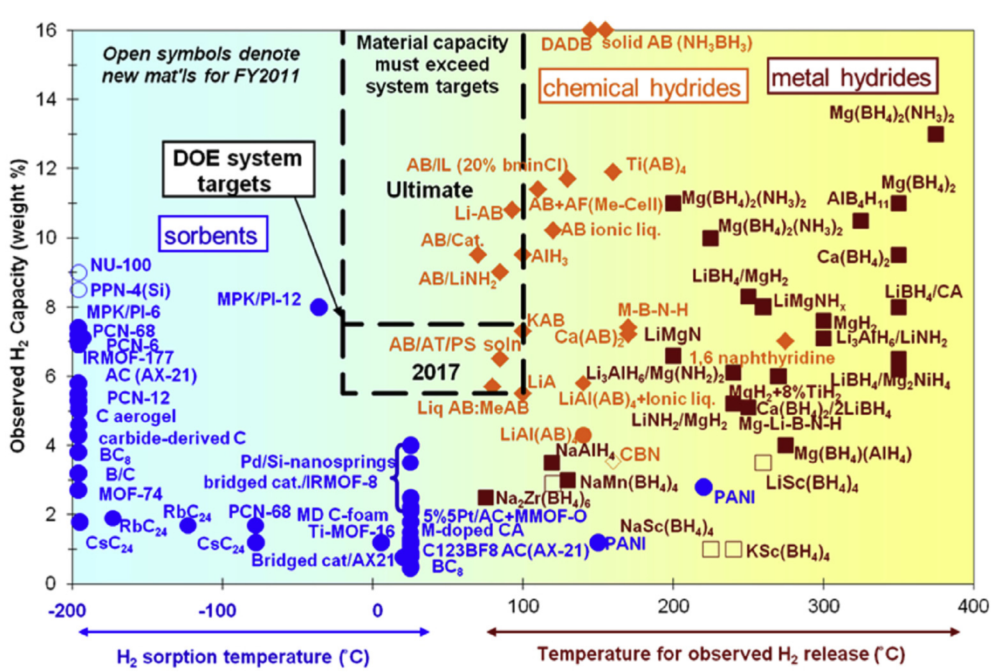

Fig. 1 – US Department of Energy targets for gravimetric capacities and temperatures for H_2 sorption and release (2017 and ultimate) shown beside abilities of current storage methods. Reprinted with permission from S. Satyapal, US Department of Energy.