Review Article

Simulation, Modelling and Design of Hydrogen Storage Materials

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In the current renewable energy scenario, one of the thrust areas is hydrogen generation and storage in an environment-friendly and cost-effective fashion. The primary challenge of efficient generation as well as storage of hydrogen has triggered R&D all over the world. Various routes such as solar photovoltaic, solar thermal, nuclear and bio-inspired routes are being vigorously pursued; the costs are still rather high for the hydrogen economy to be viable for renewable energy. There has been a concerted effort in many Asian countries, to push the frontiers of hydrogen energy for automobile and other applications. From the point of view of fundamental research, Hydrogen storage in solid state is a vibrant research area in materials science. Various types of materials, viz. metal hydrides, complex hydrides, chemical hydrides, and new materials such as functionalized nanostructures have been reported as candidate materials for hydrogen storage. However, their storage efficiencies, desorption kinetics and thermodynamics are yet to be optimized for practical applications. The article presents a broad overview of the current status of these materials issues for efficient storage of hydrogen in solid state. In particular, the focus here is on how first-principles computational approach can be gainfully utilized to design various low-Z complex hydrides (along with their decomposition pathways), as well as functionalized nanostructures (H_2 adsorption and desorption processes). Some of the outstanding issues and challenges will be discussed.

Keywords: Hydrogen Storage; Density Functional; Complex Hydride; Functionalized Nanostructure

1. Introduction

Energy, environment and economy are the most crucial global issues for our sustainable future. While energy is the most vital requirement for the progress of our civilization, it is ironic that this progress is what puts maximum load on our natural resources which are getting depleted in an alarmingly narrow window of time. One thing is amply clear that the way we produce and use energy today is not sustainable, and a new direction is needed. Our current global energy need is about 15 Tera Watt and about 85% is being provided by fossil fuels (Smalley, 2005; Abbott, 2010). Apart from the fact that these high density energy sources are not renewable, they are also associated with emission of carbon and greenhouse gases that have an irreversible effect on environment. Even if we had an unlimited supply of fossil fuels, burning them sends greenhouse gases into the atmosphere, trapping the sun's heat and contributing to global warming (*The Inconvenient Truth*, 2006). The world's energy need is expected to grow by 33% during the next 10 years. The only way to tackle this situation is to use renewable energy sources that are continually replenished by nature, for e.g. (a) solar energy (b) hydro energy (c) bio energy (d) geothermal energy (e) ocean energy (f) wind energy and (g) hydrogen energy. The recommendations for sustainable energy future chalked out by the 18-member Inter-Academy Council Board (*Lighting the Way*, 2007) aptly summarize the road map for energy sources that are abundant secure, renewable, clean, and cost-effective.

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Hydrogen is the universe's most abundant element, exhibits the highest heating value per mass of chemical fuels, and it is pollution-free as water is the only by-product during its combustion. It is this 'clean tag' of non-CO_2-emitting energy carrier, that arguably puts hydrogen as the most potential candidate as the 'fuel of the future' (Jain, 2009)! The question being posed "Is hydrogen-based economy our ultimate destination?" has been posed and addressed in several reports and publications during the last decade (Basic research needs for the hydrogen economy, 2003;The hydrogen economy: Opportunities, costs, barriers and R&D needs, 2003; Fueling the Future: On the road to the hydrogen economy, 2005; Crabtree *et al*., 2004; 2008).There are numerous hurdles associated with its production, storage and transportation that need to be overcome before it can compete with other conventional sources of energy (leaving aside political issues that invariably get linked with energy). Among these, hydrogen storage is considered to be the biggest challenge in a new hydrogen economy.

As Peter Eklund of Penn State Hydrogen Program explained (*National Hydrogen Energy Road Map*, 2002)"When it comes to energy density, gasoline blows hydrogen away. While hydrogen packs more energy per pound than gasoline — roughly three times more — it fills four times the space". Some prototype hydrogen-powered vehicles solve the problem by using compressed gas in high-pressure tanks. Other hydrogen-powered cars such as the newest BMW model, store hydrogen as a liquid in super-cooled tanks nestled near the driver's seat. Cooling the hydrogen increases its density, but a tremendous amount of energy is required both to keep the tanks cold and, when needed, to turn the liquid back into a gas that can be delivered to an engine or fuel cell. Thus safety, space and cost remain significant concerns in gaseous or liquid storage, for which we have more or less reached the technological limit. In view of this, the most promising alternative is solid state storage of hydrogen, and to find out the right candidate is a challenge faced by materials scientists.In addition to the high gravimetric and volumetric density requirement, an ideal storage medium should be able to operate under ambient thermodynamic conditions and exhibit fast hydrogen kinetics. The solid state storage of hydrogen is regarded as the best choice, and the families of materials that are being explored for efficient hydrogen storage are light metal hydrides, amides, alanates, ammonia boranes, composite materials, metalorganic frame works, porous hydrates, etc. (Bhattacharya and Das, 2013)

Hydrogen bonds in various chemical complexes are known to be strong bonds, for e.g., in CH_4 molecule, the binding energy of H is ~4eV which lies in the regime of chemisorption. On the other extreme, bonding of hydrogen to C and BN nanostructures is weak (~0.1eV, i.e. physisorption range) and very little hydrogen can be stored under ambient conditions in these materials (Walker, 2008). It is possible to *'weaken'* the bonds in the former class, or *'strengthen'* the bonds in the latter class in such a way that the binding energy of H lies in the *'right window'* between physisorption and chemisorption (Jena, 2011), as will be discussed in more detail in Section 3 of this article. First-principles electronic structure can be gainfully utilized for *'tailoring'* such behaviour and thereby designing a suitable material for efficient storage of molecular hydrogen. For example, light metal hydrides are envisioned as novel class of materials that can show a major shift towards more favourable thermodynamics, kinetics and reversibility of the hydriding reaction by tailoring its particle size, physical confinement, and doping with suitable materials (Bhattacharya and Das, 2013; Shevlin and Guo, 2013). On the other hand, doping of nanostructured materials with suitable metal atoms can fundamentally change the nature of hydrogen bonding and hence provide a lightweight material capable of meeting the requirements of an ideal hydrogen storage material (Bhattacharya *et al*., 2009a). Thus first-principles simulation and design of materials with a desired combination of properties for hydrogen storage can be very much rewarding in this technologically important domain of solid state hydrogen storage.

In this article, we restrict ourselves to the materials' issues for efficient storage of hydrogen in solid state. More specifically, we shall discuss how first-principles computational approach can be

gainfully used to predict the H_2 adsorption and desorption processes in metal nanoclusters, in complex hydrides (along with their decomposition pathways), as well as in functionalized nanostructures. We start with a brief outline of the theoretical-cum-computational tool that isused to handle this problem of hydrogen storage.

2. Theoretical-cum-Computational Approach

Efficient storage of hydrogen essentially required optimum adsorption as well as desorption, i.e. 'going in' and 'coming out' of the storage medium. Microscopically, this essentially means that we have to tune the binding energy of hydrogen with the material within the desired window, as discussed earlier. For that, one has to use quantum mechanical calculations taking into account the motion of electrons in the presence of ionic core. This is a many-body problem, which is intractable to solve, and therefore we take resource to some simplifying but reasonable approximations such as Born-Oppenheimer (BO) approximation, self-consistent field (SCF) approximation, local density approximation (LDA), tight binding (TB) approximation, etc. that are well-documented in the literature (Das, 2003). In the SCF approximation, the electrons interact in the mean field of the other electrons and ions. Thus, the many-body problem reduces to an effective two-body problem consisting of electron-ion and electron-electron interactions. Calculations are usually performed within the so-called density functional theory (DFT), where the exchange correlation potential is treated via some mean field approximation and the problem of solving an inhomogeneous many-electron system is reduced to that of solving an effective one electron Schroedinger equation with an effective potential (Jones and Gunnarsson, 1989; Das, 2002). Such an effective single-particle approach has been embraced by materials scientists, mainly because it provides a reliable computational tool yielding *material-specific quantitative results* with desirable accuracy for the ground state (cohesive, electronic, magnetic, etc.) properties of a large variety of systems. First-principles DFT calculations, based on LDA (local density approximation) and its improved variants such as GGA (generalized gradient approximation) have reached

an unprecedented level of accuracy and reliability such that one can not only explain but also predict material properties and phenomena. Although LDA has its own limitations in treating excited state properties such as semiconductor band-gap and strongly correlated phenomena, it is still the unchallenged workhorse for investigating the physics of materials. Attempts have been made to salvage some of these limitations via better functionals, as aptly described by John Perdew through his famous 'Jacob's Ladder' (Perdew *et al.*, 2009). However, for rigorous treatment of strongly correlated electron systems, one has to invoke many-body techniques such as quasiparticle GW approach (Hedin, 1965; Hedin and Lundqvist, 1969) or the Quantum Monte Carlo (QMC) method (Mitas, 1996; Foulkes*et al.*, 2001).

The most widely used first principles electronic structure method for materials with fixed geometry are based on either plane wave based pseudo potential methods or on localized basis set methods. From the ground state total energy, one can estimate the force acting on the atoms that is essential to do molecular dynamics. For first-principles simulation and design of hydrogen storage materials, we have used state-of-the-art DFT-based methods with plane wave basis set viz., VASP (Hafner, 2007; Kresse and Hafner, 1993; Kresse and Furthmuller, 1996) with PAW potentials (Blöchl, 1994; Kresse and Joubert, 1999) for extended systems and with localized atomic orbital or Gaussian basis set viz., DMol3 (Delley, 2000)or GAUSSIAN03 (Frisch *et al*., 2004) or GAMESS (Schmidt *et al.*, 1993) for molecular or cluster systems. In all our calculations, the ions are steadily relaxed towards equilibrium until the Hellmann-Feynman forces are converged to less than 10^{-3} eV/Å. Available experimental structural data have been used as input for some of the hydrides whenever they are available. An important breakthrough was the recipe proposed by Car and Parrinello (1985) for *ab initio* MD simulation within the framework of DFT. Such dynamical simulation enables one to determine the so-called "energy landscape", i.e. how the energy of a system evolves with the position of the atoms, to monitor the making and breaking of chemical bonds, for example, desorption of hydrogen molecule from a host material as a function of temperature. The

calculations carried out for studying the above mentioned materials and phenomena can be broadly classified into the following three categories: (a) ground state geometry, electronic structure and activation barrier estimation (using the so-called nudge elastic band method (Sheppard *et al.*, 2008) for different possible configurations, (b) transition state calculations and reaction pathways and (c) *ab initio* molecular dynamics with Nose thermostat for estimating desorption kinetics.

3. Materials for Hydrogen Storage

We now discuss the various ways for efficient storage of molecular hydrogen in solid state (Walker, 2008; Schlapbach and Zuttel, 2001; Zuttel, 2003), for which a fundamental understanding of how hydrogen interacts with materials is of utmost importance (Jena, 2011). High storage capacity, satisfactory kinetics, and optimal thermodynamics are some of the essential criteria for a potential hydrogen storage material. Most of the metals in the periodic table, their alloys or inter-metallic compounds react with hydrogen to form metal hydrides. The bonding between hydrogen and the metal can range from covalent to ionic, as well as multi-centered bonds and metallic bonding (Schlapbach and Zuttel, 2001; Zuttel, 2003). In fact, some metal hydrides can store hydrogen with a density higher than that of liquid hydrogen. It is exciting as well as challenging to probe the possibility of storing hydrogen in a more compact and safer way than pressurized gas and cryogenic liquid. A classic textbook example is palladium hydride (PdH_x) that can retain a substantial quantity of hydrogen within its crystal lattice. At room temperature and atmospheric pressure, palladium can adsorb up to 900 times its own volume of hydrogen in a reversible process. However, Pd is a heavy metal and hence does not yield good gravimetric efficiency, apart from the fact that it is quite costly. Same argument holds for some of the promising intermetallic hydride such as $LaNi_5$. Perovskite hydrides of ABH_3 structure (A is a monovalent alkali metal such as K, Sr, Cs, or Rb, while B is a divalent alkaline earth metal such as Ca or Mg), in particular, Mg-based compounds have received particular attention because of their lightweight and low cost production (Banerjee *et al.*, 2009), as will be discussed in Section 3.1.

Next, we discuss complex hydrides formed by a combination of metals or metalloids, where hydrogen atoms are bonded covalently to a metal or metalloid atom to form an anion. This anion is then bonded ionically to a metal cation present, to form a complex metal hydride (Schlapbach and Zuttel, 2001; Zuttel, 2003). In general, complex metal hydrides have the formula $A_xM_yH_z$, where "A" is an alkali metal or alkaline earth metal cation or cation-complex, and "M" is a metal or metalloid. Well-known examples feature anions of hydrogenated group 3 elements, in particular, boron and aluminium. Borohydrides such as $LiBH_4$andalanates, such as $NaAlH_4$ are among the most widely studied. The variety in complex metal hydrides is very large. The possibility of forming complex metal hydrides using lightweight elements opens a promising route to achieve very high hydrogen content by weight, for e.g., $LiBH_4$ contains 18 wt% hydrogen. Accordingly, there is an increasing interest to explore complex metal hydride systems and their subsequent optimization for practical use. Combining several complex hydrides into one storage system might improve the storage characteristics, but the complexity of reaction mechanisms requires further fundamental research on such materials. Further details are available in some recent reviews on complex hydrides (Orimo *et al*, 2007). While complex hydrides involving light metals show impressive gravimetric efficiencies, the desorption temperature of H_2 turns out to be rather high. Lithium imides, for example, constitute one such promising material showing reversible hydrogenation when reacted with LiH (Chen *et al.*, 2002). Attempts have been made to bring down the desorption temperature close to room temperature by suitable alloying with Ca or Mg (Bhattacharya *et al.*, 2008a; Bhattacharya, 2011) which essentially weakens the effective bonding between the metal M^+ cation and the complex $(NH_2)^-$ anion. This will be discussed in further detail in Section 3.1.Alanates, borates, and amidoboranes are the other families of complex hydrides that are being extensively studied both experimentally and theoretically.

Apart from complex hydrides, there are other kinds of materials that have been investigated for

hydrogen storage, for e.g., carbon-based materials activated with nano-catalysts (Struzhkin, 2007), clathrate hydrates (Panella, 2007), and metal-organic complexes (Dillon and Heben, 2001). Nano-structured cages with curvature such as single-walled carbon nanotubes, boron nitride nanotubes (BNNT), or B-C-N composite nanotubes and buckyball-like clusters of C or BN are among the most widely investigated nano-materials for hydrogen storage (Barman *et al.*, 2008; Bhattacharya *et al.*, 2008a, b; 2009b; 2010). The presence of a highly specific surface area is promising for physical and chemical optimization of such materials. The storage takes place as hydrogen molecules are adsorbed on the surface of the solids. The possibility of storing hydrogen in molecular form is advantageous over chemical storage in atomic form, which requires dissociation of the hydrogen bond and the formation of a hydride. In order to understand and exploit these materials for H-storage, it is crucial to know the way hydrogen interacts with the surface or the bulk. There are mainly three ways in which hydrogen can be adsorbed on a material (Jena, 2011).

(a) *Physisorption*, where hydrogen remains in molecular state (H_2) and gets bound on the surface rather weakly (B.E. ~10-100 meV)

(b) *Chemisroption*, where H_2 dissociates into H atoms that migrate and gets strongly bound to the material (B.E. ~2-4 eV range)

(c) *Molecular chemisorption*, where H-H bonding gets weakened, but not broken (still H_2 molecular state is retained) and the strength of the binding is intermediate between physisorption and chemisorption.

It is this third form of the quasi-molecular bonding that is most suitable for optimal absorption and desorption of hydrogen. The basic quasi-molecular interaction and bonding of hydrogen can be explained via what is known as Kubas interaction (Kubas *et al*, 1984; Kubas, 1988; 2007; 2009) i.e., donation of charge from H_2 molecule to the unfilled d-orbitals of the transition metal ™ atoms and back-donation from the transition metal ™ atom to the anti-bonding orbital of H_2 molecule. Kubas interaction has been exploited for designing transition metal decorated

nano materials (Sun *et al.*, 2005; Chandrakumar and Ghosh, 2008; Hoang and Antonelli, 2009), metal organic frameworks (MOF) (Dixit *et al.*, 2009), spillover catalysts (Singh *et al.*, 2009) and other kinds of materials for H-storage. However, it has limitations in explaining the bonding in alkaline earth metal complexes and alkali metal doped nanostructures (Bhattacharya *et al.*, 2012). In case of metal clusters, the way hydrogen interacts is fundamentally different from bulk and the reactivity and adsorption behaviour change drastically with the addition and subtraction of a few metal atoms (Niu *et al.*, 1992; Giri *et al.*, 2011).

In the following subsections, we shall attempt to illustrate how first principles simulation helps addressing some specific issues in designing materials for efficient storage of hydrogen. We consider materials that we have worked on in our laboratory.

3.1 Simple Metal Hydride: A Case Study of Magnesium Hydride

Bulk hydrides of light weight alkaline earth metals such as MgH_2, contain a large amount (~7.7 wt%) of hydrogen (Imamura *et al.*, 2005; Zaluska *et al.*, 1999). However, the chemically strong metal-hydrogen bonding causes a significantly high hydrogen desorption enthalpy (~0.8 eV/H_2 molecule) (Shevlin and Guo, 2013), thereby resulting in an unfavourable hydrogen desorption temperature of ~300ºC (Liu *et al*, 2013). Due to this fact, their usage for the practical hydrogen storage application has been retarded. There are already efforts to circumvent these constraints by different processes. Nanostructuring via ball milling process (Liang *et al.*, 1999; Orimo *et al.*, 2007) has been found to be a viable route to ameliorate the adsorption and desorption kinetics of hydrogen and thereby to reduce the hydrogen desorption temperature by tuning the Mg-H bond strength. This happens due to the higher diffusivity of hydrogen and higher surface to volume ratios of the nanoclusters. Eventually, a computational analysis on MgH_2 nanoclusters of different sizes (Shevlin and Guo, 2013) reported that nanostructuring of MgH_2 leads to the improvement of the dehydrogenation characteristics only for smaller size Mg_nH_{2n} (n = 1-4) nanoclusters.

This is due to the fact that the majority of the earlier studies have been concentrated on the atomic hydrogen adsorption into the Mg nanoclusters. The H-H bond dissociation energy (~4.52 eV) of H_2 molecules enhance the desorption enthalpy of the atomic hydrogen adsorbed in these nanoclusters. Hence, an attempt has been made to explore the possibility of interaction of hydrogen in molecular form with neutral as well as cationic Mg nanoclusters (Banerjee *et al.,* 2015) and thereby, overcome the limitations of bulk MgH_2. Detailed study on the origin of $Mg-H_2$ and Mg^+-H_2 bonding using molecular electrostatic potential (MESP) (Truhlar, 1981) based charge analysis and energy decomposition analysis (EDA) (Su and Li, 2009) reveals that the polarization of H_2 molecules on the surface of these nanoclusters plays an effective role in binding of the H_2 molecules to these nanoclusters. The results show that incorporation of dispersion correction in these weakly interacting systems is essential to accurately estimate the $Mg-H_2$ bond strength. Banerjee *et al.* (2015) illustrated how dispersion corrected interaction energy of the attached H_2 molecules (~0.1 eV/H_2 molecule) lie in the right energy window required for efficient hydrogen storage. The estimated desorption temperature of ~100^{0}C establishes the suitability of these hydrogen ornamented neutral and charged Mg nanocluster systems for practical hydrogen storage application.

3.2 Complex Hydride: A Case Study of Lithium Imide

First we take up a low-Z complex hydride viz. lithium imide. It was demonstrated by Ping Chen *et al.* (2002) how lithium amide ($LiNH_2$) reacts with lithium hydride (LiH) to yield lithium imide (Li_2NH) or lithium nitride (Li_3N) and molecular hydrogen.

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH$$

The forward reaction results in desorption, while the reverse reaction results in absorption. The reaction is exothermic with ΔH ~-96 kJ/mol H_2, while the gravimetric efficiency turns out to be ~10 wt%. This dehydrogenation reaction leading to release of hydrogen is reversible, which is an additional attractive feature. Li atoms are ionized as Li^+ cations, while

$[NH_2]^-$ forms a complex anion and it is the strength of the interaction between Li^+ and $[NH_2]^-$ that dictates the enthalpy of reactions and hence the desorption kinetics of H_2. One way to do this is to alloy the binary hydride with some divalent alkaline earth metal such as Ca or Mg (Bhattacharya *et al.*, 2008a; Bhattacharya, 2011) and these ternary complex hydrides have been synthesized in recent years (Wu *et al.*, 2007).

The electronic structures of each of the constituents of the equations stated above, and its Ca/Mg-doped counterparts, as well as the heats of reactions (exothermic) have been estimated from first principle DFT calculations (Bhattacharya *et al.*, 2008a; Bhattacharya, 2011). The average N-H bond lengths, hydrogen removal energies and the enthalpy of formation of $Li_2Ca(NH)_2$ and $Li_2Mg(NH)_2$ have been estimated and the results compared with the same quantities estimated for the pure Li imides and amides. The enthalpy of formation is the most fundamental and important quantity for hydrogen storage materials, which can be estimated from the difference between the energies before and after the hydriding reaction. The enthalpy change in a reaction at 0 K was calculated from the difference between the total energies of the products and the reactants, as calculated by DFT for their respective bulk geometries. We investigated the thermodynamics of hydrogen release from the mixture of $Li_2Ca(NH)_2$ and LiH, which allows us to draw comparisons with the thermodynamics of hydrogen release from the other Li-N-based compounds, viz., parent imides and amides along with $Li_2Ca(NH)_2$ with LiH. Table 1 summarizes our results for the specific exothermic chemical reactions that take place for H_2 desorption in different binary and ternary hydrides. We observe that ΔH decreases from 108.8 KJ/mol-H_2 in Li-imide to 102.6 KJ/mol-H_2 and to 82.8 KJ/mol-H_2 for Ca and Mg ternary imides, respectively. The corresponding ΔH value estimated by Araujo *et al.* (2007) is 118 KJ/mol-H_2 for Li_2NH assuming *Pnma* space group; and for $Li_2Mg(NH)_2$, it is 84 KJ/mol-H_2. It is interesting to note that ΔE_H reduces by ~5.5% for the ternary Ca-imide. The H removal energy correspondingly decreases by about 5.5% with a concomitant increase in the N-H bond length by about

Table 1: Estimated bond-lengths, reaction enthalpies (ΔH) and hydrogen removal energies (ΔE_H) for undoped and doped Li-imides (Bhattacharya *et al.*, 2008a)

System	Structure space group (formula unit)	Chemical reaction	Reaction enthalpy (ΔH) KJ/mole H_2	ΔE_H KJ/mol H_2	Average N-H bond length in Å
LiNH$_2$	Tetragonal *I-4* (4f.u)	$LiNH_2 + LiH \rightleftharpoons Li_2NH + H_2$	68.9	268	1.03
Li2NH	Orthorhombic *Ima2* (8f.u)	$Li_2NH + LiH \rightleftharpoons Li_3N + H_2$	108.8	192	1.04
Li$_2$Ca(NH)$_2$	Trigonal *P-3m1* (3f.u)	$3Li_2Ca(NH)_2 + 2LiH \rightleftharpoons 4Li_2NH + Ca_3N_2 + 2H_2$	102.6	181	1.05
Li$_2$Mg(NH)$_2$	Orthorhombic *Iba2* (16f.u)	$3Li_2Mg(NH)_2 + 2LiH \rightleftharpoons 4Li_2NH + Mg_3N_2 + 2H_2$	82.8	183	1.05

0.01 Å for the ternary Ca imide system (Bhattacharya *et al.*, 2008a; Bhattacharya, 2011), indicating weakening of the N-H bond. The enthalpy of reaction $\Delta H = T\Delta S$ for pure lithium imide decreases on ternary addition. Assuming the entropy change ΔS to remain more or less constant during the reactions, the dehydrogenation temperature T is expected to come down to a desirable range.

3.3 Chemical Hydride: A Case Study on Mono-ammoniated Li-Amidoborane

Next, we take up ammonia-borane (NH_3BH_3) or in short, AB-complexes that have emerged as attractive candidates for solid state hydrogen-storage materials because of their high percentage of available hydrogen (19.6 wt%). However, relatively poor kinetics and high temperature of dehydrogenation as well as release of volatile contaminants such as borazine are posing big challenges for practical application of AB (Staubitz *et al.*, 2010; Chua *et al.*, 2011). When one H atom in AB is replaced by an alkali or alkaline earth metal (M), a new class of materials called metal-amidoboranes (MAB) is formed, which in turn can be used for efficient storage of molecular hydrogen (Wu *et al.*, 2008; Shevlin *et al.*, 2011). These materials were highlighted as some of the best potential hydrogen-storage materials in the 2008 DOE Hydrogen Program annual progress report. For example, LiAB and NaAB provide high storage capacity of 10.9 wt% and 7.5 wt%, respectively (Xiong *et al.*, 2008) at easily accessible temperatures without the unwanted release of borazine. $LiNH_2BH_3$ is environmentally harmless and stable in solid-state at ambient temperature and normal pressure. The bonds get distorted as compared to those in pristine ammonia-borane, as seen from the ball-and-stick model optimized geometries and corresponding bond-lengths (Bhattacharya and Das, 2013). However, in order to improve the operating properties of these materials such as rapid H_2 release near room temperature, it is vital to understand the underlying mechanism in the release of H_2.

Recent experimental and computational studies have shown that NH_3 reacts with LiAB to yield H_2 and the dehydrogenation takes place in three different stages (Bhattacharya *et al.*, 2012), each time resulting in an intermediate meta stable product (adduct). We have found a transition state where the hydric B-H bond in the [NH_2BH_3] unit interacts with the protic N-H bond of NH_3, which in turn leads to H_2 release from the system as a first dehydrogenation process. The reaction pathway with the minimum activation barrier has been estimated using transition state calculations (Bhattacharya *et al.*, 2012; Bhattacharya and Das, 2013). Similarly, we have determined using our first principles approach, the second and the third dehydrogenation processes that result in relatively high activation barriers and H_2-removal energies (Table 2), while the metastable products left behind are respectively, Li(NH)NH$_2$BH and Li(NH)NBH, the final product matching with the available experimental results (Bhattacharya *et al.*, 2012).

We explored using our computational approach, the possibility of forming a higher order cluster, especially after the first dehydrogenation when the

Table 2: Activation barriers and hydrogen removal energies for 1ˢᵗ, 2ⁿᵈ and 3ʳᵈ dehydrogenation energies of monoammonated LiAB (Bhattacharya *et al.*, 2012).

Dehydrogenation	Activation barrier (KJ/mol H_2)		H_2-removal energy in eV/H_2	
Monomer of LiAB+NH_3				
First	78		0.16	
Second	105		0.27	
Third	353		1.3	
[LiNH$_2$-BH$_2$-NH$_2$]$_3$				
Second [1]	No Barrier		0.14	
Second [2]	No Barrier		0.20	Average ~0.25
Second [3]	No Barrier		0.40	
Third [1]	230	Average ~236	0.14	Average ~0.67
Third [2]	236		0.20	
Third [3]	243		0.40	

metastable product LiNH$_2$——BH$_2$NH$_2$ is reached. For the subsequent (i.e. after 1ˢᵗ) dehydrogenation reactions, we have studied the stability of [LiNH$_2$-BH$_2$-NH$_2$]$_n$ clusters with *n* varying from 2 to 6. Our results reveal that as the cluster size goes up from monomer to dimer to trimer (*n* = 3), the relative stability keeps on increasing (i.e. more negative) and tends to saturate for $n \geq 6$. The detailed reactions and their pathways are provided in Bhattacharya *et al.* (2012). It is this reduction in the activation barrier as a function of increasing cluster size that provides an explanation for the dehydrogenation mechanism in the monoammoniated LiAB system.

4. Nano-structured Materials

As discussed in Section 3, the binding energy of hydrogen molecules to curved nano-structures such as buckyballs or nanotubes are rather low, i.e. in the physisorption range, which needs to be increased. Also the hydrogen coverage densities need to be enhanced. The usual approach to these problems is decorating these nano-structures with suitable metals.

Considering the gravimetric hydrogen density issue, it is only the lightweight metals that are potentially interesting for decoration. The challenge is to find metals that can bind to nanotubes or bucky balls strong enough so that they remain as immobilized on the surface, and resist metal clustering. The density of the metals covering the surface is also important and needs to be adjusted to an optimum value, that is, it should be high enough to capture as much hydrogen as possible, but low enough to preserve the hydrogen gravimetric density by not influencing the total system weight to a great extend. The interaction between the hydrogen molecules and metal atoms deposited on a surface can be electrostatic, chemisorption or of Kubas type (Dillon and Heben, 2001; Barman *et al.*, 2008; Bhattacharya *et al.*, 2008b; 2009b; 2010; Kubas *et al.*, 1984; Kubas, 1988; 2007; 2009).

In the last decade, graphitic materials with planar structures (Patchkovskii *et al.*, 2005; Bhattacharya *et al.*, 2009a) have been investigated for H-storage. Theoretical calculations show that graphene layers spaced 6 and 7 Angstroms apart, store hydrogen at room temperature and 100 bars (Patchkovskii *et al.*, 2005). However, this is only possible if the interplanar distances can be fixed at an appropriate value that maximizes the stored hydrogen content. Spacer molecules can be used for this purpose, although an ideal one has not been reported yet. For graphene to become a strong contender inpractical hydrogen storage, thermo-dynamical issues need to be resolved as well. The interaction of hydrogen molecules with the layers needs to be increased in order to enable operating under moderate temperature and pressure conditions. In addition, extending the storage densities to more than monolayer hydrogen coverage would be interesting. Recently, there have been numerous studies in this field. While this is still futuristic, single-walled as well as multi-walled carbon nanotubes (CNT) and their isoelectronic counterparts viz. boron nitride nanotubes (BN-NT) are being considered (Dillon *et al.*, 1997; Sun *et al.*, 2005; Gundiah *et al.*, 2002) for storing hydrogen, although they have their own advantages and shortcomings. This will be discussed in the next section.

4.1 Hydrogen Storage in CNT, BNNT and Beyond

In spite of high expectations, the early experiments on carbon nanotubes are not so encouraging for storing hydrogen because of their sub-critical storage capacities (Gundiah *et al.*, 2002; Kajiura *et al.*, 2003). A recent theoretical study indicates that high hydrogen content in the pure carbon nanotubes cannot be achieved through physical sorption (Blasé *et al.*, 1994). Yildirim and Ciraci (2005) have shown from their first principles calculations that functionalizing the CNT with suitable transition metal atoms could lead to high capacity hydrogen storage (~8 wt%) along with the possibility of some interesting hydrogen desorption of the system. However, tendency of a normal CNT to get oxidized around 600ºC is an impediment for the usage of TM-functionalized CNT for high capacity hydrogen storage.

Owing to these shortcomings of carbon nanotube, efforts have been shifted towards non-carbonic materials composed of light elements such as B and N. B-N nanostructures are analogous to their carbon counterparts and offer many advantages. For example, B-N nanotubes are stable up to 900°C. In addition to their heat resistance in air and structural stability, B-N nanotubes are semiconducting with wide band gaps (5.5 eV) that are nearly independent of tube diameter or helicity. Several groups have studied the hydrogen uptake and reversibility issues of B-N nanostructures (Ma *et al.*, 2002; Oku *et al.*, 2004a, b; Oku and Narita, 2004; Narita and Oku, 2002). However, if we look at the practical implementation of these kinds of structures for hydrogen storage, these have limited success. This is because of (a) the stability of most of these cage-like B-N nano-structures at room temperature (Sun *et al.*, 2005) and (b) the abnormally high hydrogen-desorption temperature from the B-N nanotubes for its extra thermal stability (Ma *et al.*, 2002). Is it possible to exploit the thermal stability of BN nanotube, together with the advantages of Ti-functionalized CNT? We have reported (Bhattacharya *et al.*, 2009a) the designing of a Ti-functionalized B-C-N nano-composite, viz., BC_4N nanotube, as a possible H-storage material. $B_xC_yN_z$ nanostructures have been studied both experimentally and theoretically (Sen *et*

al., 1998; Weng-Sieh *et al.*, 1995). Recently, BC_4N nanotubes have been experimentally synthesized (Raidongia *et al.*, 2008) and found to be semiconducting in nature with very high thermal stability. The local structural unit of BN_3 and NB_3 linked with B-N bonds are responsible for the extra stability, as compared to its host carbon nanotube. While the host carbon nanotube is metallic, the substitutional doping of B and N with a large enough concentration (33%) turns it into a semiconductor. The synthesis, characterization and various properties of BC_4N nanotubes are described in detail by Raidongia *et al.* (2008). What we have done is to explore how to functionalize it for storage of molecular hydrogen (Bhattacharya *et al.*, 2008b). We have addressed several open questions, for e.g.: (1) Does transition metal prefer to stay in exohedral or endohedral position of the nanotube? (2) What is the energy barrier for the transition metal to enter into or escape from the nanotube? (3) What happens when more transition metals are decorated in different hexagonal faces of the nanotube? (4) How does the binding energy of H_2 change during addition of more H_2 in the TM-doped BC_4N nanotube both in exohedral and endohedral positions? (5) As more H_2 is stored, what are the changes in the geometry and electronic structures of the nanotube? (6) Lastly, from the hydrogen storage point of view, what is the effect of temperature on the stability of this kind of B-C-N composite nanotube? We have carried out detailed first-principles investigations to address these questions for this novel BC_4N nanotube, and suggested the means of improving the storage efficiency.

5. Concluding Remarks

In this restricted review, we have discussed how density functional based first-principles simulation has been used to design efficient hydrogen storage materials. While complex hydrides have been subjected to extensive investigation, functionalized nanostructures are becoming the focus of attention. Optimizing the gravimetric efficiency, dehydrogenation temperature and fast kinetics pose a real challenge to the materials scientists. The coming decade is going to witness some breakthrough in this direction. .

As an epilogue, I would like to add that while the developing countries in Asia are sincerely trying to achieve some breakthrough in hydrogen economy; in the western world, particularly in the United States, the euphoria on hydrogen seems be on low ebb. This may be because of several reasons such as the finding of huge gas reserves and other political reasons. However, the Asian initiative on hydrogen storage is looking forward to an optimistic goal in the foreseeable future.

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