Reversible Hydrogen Storage Using Nanocomposites

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Abstract: In the field of energy storage, recently investigated nanocomposites show promise in terms of high hydrogen uptake and release with enhancement in the reaction kinetics. Among several, carbonaceous nanovariants like carbon nanotubes (CNTs), fullerenes, and graphitic nanofibers reveal reversible hydrogen sorption characteristics at 77 K, due to their van der Waals interaction. The spillover mechanism combining Pd nanoparticles on the host metal-organic framework (MOF) show room temperature uptake of hydrogen. Metal or complex hydrides either in the nanocomposite form and its subset, nanocatalyst dispersed alloy phases illustrate the concept of nanoengineering and nanoconfinement of particles with tailor-made properties for reversible hydrogen storage. Another class of materials comprising polymeric nanostructures such as conducting polyaniline and their functionalized nanocomposites are versatile hydrogen storage materials because of their unique size, high specific surface-area, pore-volume, and bulk properties. The salient features of nanocomposite materials for reversible hydrogen storage are reviewed and discussed.

Keywords: nanocomposite materials; carbon nanotubes; nanocatalyst; nanoparticles; ball-milling; hydrogen storage system; complex hydrides; sorption kinetics

1. Introduction

The increased deployment of fossil fuels produces an exorbitant amount of greenhouse gases such as CO₂ [1–3], which has already caused an increase in the Earth’s temperature and will continue to do so unless CO₂ emissions are significantly curtailed. In addition to the occurrence of global warming due to combustion of fossil-based fuels, there is wide agreement that these fossil fuels are running out [4], therefore increasing the urgency of finding new energy alternatives. One such alternative, especially for use in mobile applications, is hydrogen [5,6]. Hydrogen is an ideal fuel, particularly for transportation because it has the highest energy density per mass (149 MJ·g⁻¹) among the known fuel sources, and it is a safe, environmentally friendly fuel source that can be easily transformed to useful work without releasing harmful emissions. If burned in internal combustion engines (ICE), hydrogen can be combusted at high compression ratios, which leads to improved engine efficiencies, and substantially reduced pollutants compared to fossil fuels [7–9]. A better alternative to utilize hydrogen in mobile platforms is to burn it catalytically with oxygen using fuel cells to
obtain desired work output. This catalytic conversion of hydrogen and oxygen to work produces primarily heat and water vapor as byproducts [10]. Hydrogen storage is a vital component between hydrogen production and utilization, for a full-fledged hydrogen economy as shown in Figure 1 [11–14]. Hydrogen economy will be realized only when the hydrogen production, transportation/distribution, storage, and utilization (see Figure 1) are streamlined [15–17].

**Figure 1.** Storing hydrogen in the molecular or atomic form is a challenging task and equally important like producing it from clean sources and utilizing for stationary and vehicular applications (reproduced with permission from [18], Cambridge University Press, 2008).

Hydrogen storage system is an essential part of any fuel cell or hydrogen-ICE automobile [19,20]. The roadblocks for the widespread commercialization of the hydrogen powered automobile are the development of safe and reliable hydrogen storage and transportation systems. The required properties of hydrogen storage systems for automotive applications are low cost, high volumetric and gravimetric storage capacity, favorable cycling kinetics, and near ambient operation temperature. Improving these properties requires better understanding of the fundamental physicochemical processes of solid–gas reactions at the nanoscale.

There are four major approaches to storing hydrogen: (i) compressed-gaseous, (ii) liquefied, (iii) solid-state (on-board regenerable), and (iv) chemical (off-board regenerable) [21]. Compressed-gaseous and liquefied hydrogen storage systems are considered as physical hydrogen storage methods. Both of these methods are mature and compressed-gaseous hydrogen storage is the only method employed in commercially available fuel-cell vehicles such as Honda Clarity, Toyota Mirai, and Hyundai Nexo. The main disadvantages of compressed-gaseous hydrogen storage are a high energy penalty for compression, which consumes 15% of total internal energy of hydrogen for pressures up to 350 bar, and high cost carbon-fiber wound cylinders to withstand pressures up to 700 bar [22]. Storing hydrogen at such a large pressure is acceptable to users as long as the safety is demonstrated, which is a considerable challenge. Liquefied hydrogen is the other major form of physical hydrogen storage. It provides a compact medium for on-board storage [23], but again, the energy penalty for liquefaction is quite high (liquefaction process consumes around 30% of total internal energy of hydrogen) and it is impossible to prevent the loss of hydrogen through boil-off during long dormancy periods [24]. Liquefied hydrogen tanks operate at atmospheric pressures, and they are perfectly insulated to minimize heat transfer to hydrogen at 20 K from surroundings. There is a promising hybrid physical–chemical storage method called cryo-compressed hydrogen storage [25]. In this method, high storage capacity, on par with liquefied hydrogen, can be achieved at a lower energy penalty because hydrogen is cooled to 77 K as opposed to 20 K required for liquefaction and hydrogen is compressed to pressures around 100 bar, which is significantly lower than the compressed-gaseous hydrogen storage. Another advantage of this physical
storage method is to extend the dormancy period almost indefinitely. However, high surface area porous materials are required to store hydrogen inside a tank. The third method, solid-state storage, relies on storing hydrogen inside a host material, and the main promise of this method is the ability to refill hydrogen on-board. Significant research efforts have been devoted to this area during the last two decades to improve storage capacity, kinetics, reversibility, and safety of these materials. There are mainly two sub-categories of solid-state storage; (a) chemical storage via metal/complex hydrides and (b) physisorption based high surface area materials such as metal organic frameworks (MOFs). The last method is chemical storage in liquid organic compounds such as methanol, and in boron-nitrogen based compounds such as ammonia-borane. These materials are off board regenerable adding complexity and cost to hydrogen storage and distribution infrastructure. Though each storage method possesses desirable characteristics, no single method provides the volumetric and gravimetric storage capacities, cost, and safety requirements for transportation. The third and most researched method of hydrogen storage is by using metal hydrides. The chemical bonding between the metal and hydrogen is weakened by adjusting the temperature and pressure parameters so the hydrogen is released from the metal-hydrogen (M–H) systems. Metal hydrides, though investigated for decades, still not qualified as a reliable method for hydrogen storage. The hydrogen sorption kinetics are often very slow with low usable capacity (<2 wt.%). Various hydrogen storage methods are presented and discussed by Züttel [19].

The most critical challenges for improving hydrogen storage technologies are increasing their gravimetric and volumetric storage capacity while reducing their cost [19]. For a full tank charging, the mileage range of hydrogen fueled hybrid vehicles are in par with the gasoline-based vehicles (for example, Toyota Mirai can get 312 miles with a full tank, Honda Clarity fuel-cells claims 360 miles range, and Hyundai Nexo of the 380 miles range), however the lack of hydrogen filling stations, the transportation, and distributions looks critical [26]. The energy required to get hydrogen in and out of storage is an issue for reversible solid-state materials storage systems. In addition, the energy associated with compression and liquefaction must be factored in when considering compressed and liquid hydrogen storage technologies. The durability of some hydrogen storage systems is inadequate. Materials and components are needed that allow hydrogen storage systems with a lifetime in excess of 1500 refueling cycles. Refueling times are currently too long as for as the solid-state chemical hydrides are concerned. There is a need to develop hydrogen storage systems with refueling times of less than five minutes over the lifetime of the system (Table 1). Overall, the economic and technical challenges in developing all of the hydrogen storage technologies mentioned above demand new approaches and methodologies.

| Storage Parameter                                | 2020 | 2025 |
|-------------------------------------------------|------|------|
| Gravimetric Hydrogen Storage Capacity (kg H₂·kg⁻¹ material) | 0.045 | 0.055 |
| Volumetric Hydrogen Storage Capacity (kg H₂·L⁻¹ material) | 0.030 | 0.040 |
| Hydrogen Delivery Temperature (°C)              | −40/85 | −40/85 |
| System Fill Time (min; for 5 kg of H₂)           | 3–5  | 3–5  |
| Cycle Life (1/4 Tank to Full; non-dim)           | 1500 | 1500 |

Different hydrogen storage systems namely metal hydrides, complex hydrides, chemical hydrides, high surface area porous materials (metal organic frameworks and similar), and nanovariants [27–32] have been investigated for hydrogen storage applications. However, none of these materials fulfill all the hydrogen storage criteria set by US Department of Energy (DOE) such as (1) high hydrogen content; (2) favorable thermodynamics to achieve system fill-time less than 5 min; (3) operation below 85 °C and above −40 °C for hydrogen delivery; and (5) cyclic reversibility (1500 cycles) at ambient temperatures.
Carbon based materials, on the other hand, possess salient properties that make them interesting for storing hydrogen. Due to the abundance of carbon and the simplicity by which one can produce various forms of it, such as carbon nanotubes, carbon nanofibers, nanobells, or graphite [33,34], there is virtually an unlimited amount of materials that can be investigated for hydrogen storage. One of the most important advantages of carbon-based materials is that they do not need to be kept in an inert atmosphere. It was initially thought that carbon materials are environmentally friendly and benign to humans, however, recent reports on the health risks of carbon nanotubes needs considerable attention [35,36]. Graphite nanofibers, in its herringbone structure, have been shown to store hydrogen [37], though the exact structure required to store the hydrogen is still being investigated. Hydrogen storage in carbon nanotubes [38], carbon nanobells [39], carbon nanofibers [40], and especially doped carbon nanotubes [41,42] have shown reversible hydrogen storage at 77 K. Carbon based materials possess another important feature, namely a hydrogen binding energy between 10 and 50 kJmol⁻¹. This is an ideal value for the binding of hydrogen, since a material with weak bonding of molecular hydrogen with binding energy <10 kJmol⁻¹ is not a suitable candidate material, as the hydrogen can be readily and accidentally released. Materials that have high energy hydrogen bonds, such as chemical hydrides (400 kJmol⁻¹) or metal hydrides (50–100 kJmol⁻¹), can store a large amount of hydrogen, but they will require an excessive energy, either as heat or pressure difference, to store or release the hydrogen. The carbon structures that possess this binding energy namely graphene, carbon nanotubes, and fullerenes. This enhanced physisorption, “spillover”, and “Kubas” binding represent the ideal hydrogen bonds. In this review, among the different storage options, we have compared and contrast the salient features and underlying applications of nanostructured variants for the reversible hydrogen storage.

In this review article, the most notable solid-state hydrogen storage materials and their nanocomposites are discussed in detail. The structure of the present review is as follows. In Section 2, we have introduced the definition of nanocomposites and their key features for reversible hydrogen storage. In Section 2.1 MgH₂ nanoparticles and catalytically doped MgH₂ nanocrystalline forms for lowering the decomposition temperatures is discussed. Section 2.2 focuses on Mg₂FeH₆ and the role of Fe in reversible hydrogen storage, additionally this section explains the effects of Ti doping on kinetics at moderate temperatures. Nanoengineering of LiBH₄/MgH₂ complex hydrides via different synthesis schemes are discussed in Section 2.3. A new class of complex hydrides, Zn(BH₄)₂, where nano-Ni doping reduces the di-borane gas formation is discussed in Section 2.4. Section 2.5 elaborates the salient features of carbon nanovariants, such as carbon nanotubes, and graphitic nanofibers for enhancing the physisorption of molecular hydrogen under sub-ambient temperatures. The new class of polymeric nanofibers obtained from electrospinning processes and their cyclic de-/hydrogenation are discussed in Section 2.6. Finally, recent development in metal organic frameworks is outlined in Section 2.7.

2. Nanocomposite Materials for Hydrogen Storage

Nanocomposite materials are the combination of two or more elements, phases, or compounds in which at least one of these constituents has features at the nanoscale. Nanocomposites make it possible to achieve superior material properties due to nanoscale interactions such as nanoconfinement and spillover enhancement. Nanocomposite materials such as nanoparticles hold promise in hydrogen storage because of their unique features such as high specific surface area [43,44]. Nanostructured and nanoscale materials strongly influence the kinetics of hydrogen sorption due to their high surface area [45]. However, nanoparticle agglomeration due to repeated cooling/heating and contraction/expansion during cycling might result in degraded performance over time. Nevertheless, the nanoscale systems enable controlling the property of materials beyond what is possible in their bulk counterparts. Additionally, these nanoscale materials lead to the design and development of light weight hydrogen storage systems with affordable characteristics for an on-board application. Some of the prominent nanoparticulate systems for hydrogen storage are discussed in the following subsections.
2.1. MgH₂

Bulk magnesium hydride, MgH₂, shows promising hydrogen storage capacity of 7.6 wt.% at temperatures above 300 °C and at a hydrogen pressure of 1 atm [46–48]. However, MgH₂ have limited practical applications because of slow kinetics and high temperatures (>200 °C) required for de-/hydrogenation reactions. [49]. In bulk MgH₂, high activation energy (162 kJ·mol⁻¹) is required for the dissociation of hydrogen molecule to its atoms. Mechanical pulverization/milling of bulk MgH₂ creates micro/nanocrystalline phases, the surface to volume ratio increases, which leads to lower activation energy of desorption, 144 kJ·mol⁻¹, hence on-set temperature for hydrogen dissociation also decreases. Further reduction of the activation energy, as low as 71 kJ·mol⁻¹ [21], can be achieved by nanocatalyst doping of micro/nanocrystalline MgH₂.

Figures 2 and 3 demonstrate the thermogravimetric (TGA) and differential scanning calorimetric (DSC) curves of hydrogen decomposition from bulk MgH₂, micro/nanocrystalline MgH₂ and nano-Ni doped micro/nanocrystalline MgH₂. The bulk MgH₂ shows a sharp weight loss due to hydrogen release in the endothermic reactions at around 410 °C. The TGA (Figure 2) of micro/nanocrystalline MgH₂ obtained by 9 and 12 h ball milling exhibit weight loss at reduced temperatures of 345 and 340 °C, respectively; whereas the DSC (Figure 3) of 10.5 h ball milled MgH₂ shows two endothermic transition at 390 and 375 °C. For the 10 mol% nano-Ni catalyzed micro/nanocrystalline MgH₂, thermal decomposition temperature is further reduced to 245 °C (Figure 2), which is at least 170 °C lower than the bulk counterpart. The DSC experiments were carried out for the different concentrations of nano-Ni in micro/nanocrystalline MgH₂ as depicted in Figure 3. For the low 1 mol% nano-Ni concentration, there is a wide endothermic transition that occurs due to decomposition of hydrogen from micro/nanocrystalline MgH₂ at around 295 °C, however for higher concentrations, 2–4 mol%, a sharp endothermic peak is predominant at a temperature around 230 °C. Therefore, by comparing both TGA and DSC results (Figures 2 and 3), one can derive the conclusion that at least 45–70 °C reduction in temperature is possible by mechanical pulverization of bulk MgH₂, and further 100–140 °C reduction in hydrogen decomposition temperature was observed for mechanically pulverized MgH₂ doped with metal nanocatalysts, nano-Ni. The enthalpy of hydrogen decomposition from MgH₂ metal hydrides were calculated and tabulated in Table 2.

| Sample                  | T_{dec} (°C) | ΔH_{dec} (kJ mol⁻¹ H₂) |
|-------------------------|--------------|------------------------|
| Commercial MgH₂         | 415          | 55.98 ± 0.50           |
| MgH₂ (MC)               | 375          | 46.35 ± 0.50           |
| MgH₂ (MC)-nano-Ni       | 225          | 36.50 ± 0.50           |

The structural characterization of the bulk, micro/nanocrystalline and nanocatalyst doped MgH₂ was carried out using X-ray diffraction (XRD) and is shown in Figure 4. The Bragg reflection of bulk MgH₂ shows sharp crystalline peaks. However, in the micro/nanocrystalline MgH₂, the crystallite size is reduced to the nano dimension (5 times reduced X-ray intensity in terms of counts) as observed from broadening of full width at half maximum (FWHM) of the crystalline peaks. No additional peaks corresponding to MgO or any other impurities were observed in the ball milled samples. For the nanocatalyst doped MgH₂, a small inflection peak at an angle of 45° represents the nano-Ni.

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Figure 2. Thermogravimetric hydrogen release profiles of bulk MgH$_2$, ball milled (BM) micro/nanocrystalline MgH$_2$ and nano-Ni catalyst doped micro/nanocrystalline MgH$_2$.

Figure 3. Differential scanning calorimetric (DSC) profiles of commercial MgH$_2$, 10.5 h ball milled (BM) micro/nanocrystalline MgH$_2$, and micro/nanocrystalline MgH$_2$ doped with nano-Ni catalysts at different mole concentrations and ball milled for additional 15 min.

The scanning electron microscopy (SEM) images of bulk and micro/nanocrystalline MgH$_2$ given in Figure 5 aligns with reduced crystallite size inferred from XRD profiles. As for the sharp XRD peaks of bulk MgH$_2$ (Figure 4) corresponds to the crystallite size of at least 200 nm as obtained from the SEM microstructure (Figure 5, left). Similarly, the reduction in the XRD peak intensity of bulk MgH$_2$ phase and the corresponding FWHM broadening correlates the smaller sizes of the MgH$_2$ grains at least an order of magnitude lesser, for example 27 nm as derived from the Figure 5, right image.
Therefore, the reduction in thermal decomposition (up to 70–100 °C) of molecular hydrogen to atomic hydrogen as demonstrated in Figures 2 and 3 were very well supported by the X-ray and SEM analysis of both bulk and nanocrystalline MgH₂.

Figure 4. X-ray diffraction spectra of bulk commercial MgH₂, micro/nanocrystalline MgH₂ by mechanical pulverization of MgH₂ for at least 15 h and mechanically pulverized MgH₂ subsequently doped with metal nanoparticle such as nano-Ni with 0.1 mol%.

Figure 5. SEM of (left) commercial bulk MgH₂ and (right) micro/nanocrystalline MgH₂ prepared via mechanical pulverization for at least 10 h.
2.2. \( \text{Mg}_2\text{FeH}_6 \) Complex Hydride

The nanocatalysts (e.g., nano-Ni) lead to lower hydrogen decomposition temperature characteristics of micro/nanocrystalline MgH\(_2\) as demonstrated in the previous section. In this section, a novel transition metal complex hydride involving the combination of MgH\(_2\) and Fe ball milled under hydrogen ambient thus exhibit reversible hydrogen storage capacity by volume, 150 kg·m\(^{-3}\) [50], which is greater than the liquid hydrogen storage capacity [51] at cryogenic temperature. Moreover, these Mg\(_2\)FeH\(_6\) complex hydride possesses a storage capacity by weight basis, 5.0 wt.% at 400 °C, which is very comparable to plain MgH\(_2\) capacity of 7.6 wt.%.

The Mg\(_2\)FeH\(_6\) hydrides having \([\text{FeH}_6]^4-\) complex anion sites that are octahedrally coordinated the central Mg atoms in an octahedral crystal lattice [52]. In a similar way, the MgH\(_2\) will react with other transition metals such as Co and Ni to form ternary and quaternary structures, such as Mg\(_2\)CoH\(_5\) and Mg\(_2\)NiH\(_4\) thus leads to obtain reversible hydrogen storage systems [53]. The reaction kinetics of the above Mg-based transition metal complexes can be improved by reacting MgH\(_2\) in the nanoform with nano Fe, nano Co, or nano Ni [46,54]. It has been very recently shown that the combination of nano Fe and nano Ti transition metals with the carbon nanovariant such as carbon nanotube on the MgH\(_2\) exhibited faster hydrogen dissociation and effective hydrogen atom transport between the MgH\(_2\) grains [55,56].

Unlike Mg\(_2\)Ni intermetallic equilibrium phase for efficient reversible hydrogen storage (Mg\(_2\)NiH\(_4\)) at low temperature (<300 °C), the Mg\(_2\)Fe does not exist as an intermetallic stable compound phase. However, under hydrogen gas pressure Mg/MgH\(_2\) and Fe creates a stable Mg\(_2\)FeH\(_6\) complex hydride [50] per the following chemical reactions,

\[
2\text{Mg} + \text{Fe} + 3\text{H}_2 \leftrightarrow \text{Mg}_2\text{FeH}_6
\]

\[
2\text{MgH}_2 + \text{Fe} + \text{H}_2 \leftrightarrow \text{Mg}_2\text{FeH}_6
\]

The synthesis of nanocomplex hydride Mg\(_2\)FeH\(_6\) was done in solid-state milling process based on the above reactions with either Mg or MgH\(_2\) as precursor with the appropriate crystallite size. The hydrogen gas pressure is adjusted to optimize the milling parameters such as the time duration, ball to powder ratio, etc., to obtain a single phase Mg\(_2\)FeH\(_6\). The X-ray diffraction patterns of the bulk materials before and after milling are depicted in Figure 6. The bulk Mg and Fe show sharp crystalline Bragg reflection before ball milling, whereas, the nanocrystalline Mg\(_2\)FeH\(_6\) phase forms after ball milling processes as revealed from the widening of the XRD peak around 44°.

The DSC profiles of Mg\(_2\)FeH\(_6\) in its bulk and nanocrystalline forms are shown in Figure 7. The bulk Mg\(_2\)FeH\(_6\) shows an endothermic transition due to hydrogen decomposition at peak temperature of 380 °C and a shoulder inflection transition at 310 °C reflects the secondary phase decomposition. In comparison to the bulk, the nanocrystalline samples showed a sharp endothermic transition temperature at a lower peak temperature of 280 °C; additionally, on-set temperature of 200 °C is also clear from Figure 7 Mg\(_2\)FeH\(_6\) behaves very similar to nano-Ni doped micro/nanocrystalline MgH\(_2\) examined in the previous section.
Figure 6. XRD patterns of the transition metal complex hydride before and after milling.

Figure 7. DSC curves of Mg$_2$FeH$_6$ in its bulk and nanocrystalline forms.

The hydrogen absorption kinetics experiments were carried out on Mg$_2$FeH$_6$ in its bulk, nanocrystalline and nano-TiF$_3$ doped forms as shown in Figure 8. The nano-TiF$_3$ doping of nanocrystalline Mg$_2$FeH$_6$ outperformed in terms of fast absorption when compared to the bulk and nanocrystalline counterparts. This may be due to the catalytic dissociation of hydrogen molecules to hydrogen atoms at lower temperature in addition to the higher specific surface area of the base Mg$_2$FeH$_6$ complex hydride. The hydrogen absorption kinetics increased multifold and in the 10th cycle, the kinetics exhibited were
rapid such that within 10 s at least 90% of hydrogen was absorbed by the candidate material as shown in Figure 9. The addition of nano-TiF3 greatly improved hydrogen uptake kinetics, but it did not enhance the overall hydrogen storage capacity.

Figure 8. Hydrogen absorption kinetics of Mg$_2$FeH$_6$ at 250 °C in its three different forms such as bulk, nanocrystalline, and 2 mol%TiF$_3$ nanocatalyst doped.

Figure 9. The hydrogenation kinetics of Ti-doped nanocrystalline Mg$_2$FeH$_6$; the rate of hydrogen absorption increases with runs (mass of material: 1.5 g and desorption temperature: 250 °C).
2.3. Nanoengineered Complex Hydrides (LiBH₄/MgH₂)

The dramatic enhancement of kinetics of MgH₂ has also been explored through a reaction with small amounts of LiBH₄ [57]. Though the MgH₂ admixing increases the equilibrium plateau pressure of LiNH₂ [58] or LiBH₄ [59], nanoengineering of the ingredient hydrides are not widely reported. Nanocrystallinity of the ingredient hydrides and nanocatalytic doping are the two innovative methodologies that have been proposed to explore their impacts on the overall hydrogen storage behavior of complex hydrides. The mechanochemical milling discussed previously helps for the particles pulverization, in this case, MgH₂ crystallites downsize into micro or nanocrystalline phases and thus leads to a lowering the activation energy required for dehydrogenation [60]. The activation energies of the hydrogenation for bulk MgH₂, mechanically milled MgH₂ and nanocatalyst doped MgH₂ are schematically shown in Figure 10a.

Figure 10. (a) Conceptual model and (b) flowchart for the reaction pathway schemes of the plain, nanocrystalline, and nanocatalysts doped nanocrystalline LiBH₄/MgH₂ cluster.

Figure 10a also demonstrates the effect of nanocatalyst doping on the hydrogenation and dehydrogenation behavior of MgH₂. The transition metal nanoparticle clusters during the mechano-chemical processing disperse uniformly within the micro/nanocrystalline grains of MgH₂ and serve as nuclei for H₂ molecular dissociation. An optimum level of the nanocluster catalyst density, for surface coverage, can be determined by finding the rate limiting steps for maximum storage capacity via volumetric measurements. Three different reaction pathway mechanisms can be evaluated for the nanocatalyst doped nanocrystalline complex hydride system. The flow chart shown in Figure 10b gives the reaction pathway mechanisms used to optimize the effective catalyst addition for improving the sorption characteristics.

The reversible hydrogen sorption characteristics of the nanocrystalline complex hydrides are shown in Figure 11. An extended plateau region at which the maximum reversible hydrogen content is clearly seen from this figure. Moreover, the hydrogen capacity and the plateau pressure increase with a temperature up to 375 °C.
Figure 10. (a) Conceptual model and (b) flowchart for the reaction pathway schemes of the plain, nanocrystalline, and nanocatalysts doped nanocrystalline LiBH4/MgH2 cluster.

The reversible hydrogen sorption characteristics of the nanocrystalline complex hydrides are shown in Figure 11. An extended plateau region at which the maximum reversible hydrogen content is clearly seen from this figure. Moreover, the hydrogen capacity and the plateau pressure increase with a temperature up to 375 °C.

2.4. Nanocatalyst Doping in Complex Borohydrides

For an on-board hydrogen vehicular application, a proton exchange membrane (PEM) based fuel cell that can operate with available hydrogen that is obtained from the reversible hydrogen storage materials needs to be explored. One such reversible hydrogen storage system is the complex metal hydrides that are weightless due to light metal/carbon/organics and store a large amount of pure hydrogen [12,61,62]. A series of complex hydrides have been explored in the past decade, such as sodium aluminum hydrides [63,64], lithium amides [65,66], and magnesium or lithium borohydrides [67–69], and their combinations [70,71]. Two important limitations such as bulk thermodynamic effects and surface assisted kinetic constraints [7,71] are to be solved from the first principles in order to greatly implement these complex hydrides for practical applications. The low temperature dissociation of hydrogen and its reversible absorption behavior with a capacity >5.0 wt.% can be achieved by doping these complex materials with few mole concentrations of mono- or bi-metallic nanoparticles as catalysts. The short reaction pathways, greater gas–solid interactions, rapid diffusion kinetics, efficient transport of atomic hydrogen between the grains of the complex matrix, superb surface, and interfacial interactions are some of the features offered by the nanostructured catalytic particles.

Figure 12 demonstrates the thermal analysis of the novel complex hydride, Zn(BH₄)₂ systems undoped and doped with nanocatalyst (Nano-Ni). The Zn(BH₄)₂, is prepared from the mechano-chemical treatment of (Na(Li)BH₄ + ½ ZnCl₂), exhibits an endothermic DSC peak due to melting at 80 °C and a weight loss occurring at 120 °C because of hydrogen decomposition at this temperature. Preliminary experiments were conducted by adding different nanocatalyst (nano-Ni) to the complex hydride in systematic mole fractions from 1 to 4 mol%. It is clearly discernible from Figure 12 that nanocatalyst doping enables the reduction in the melting transition and decomposition temperature. A concentration of the 3 mol% nanocatalyst was found to be optimum for the gravimetric weight loss due to thermal decomposition at low temperature. At these low temperatures, the nanocatalyzed Zn(BH₄)₂ exhibited a reduction in the amount of borane (BₓHᵧ) gases released by a factor of 20 as compared to the undoped sample (Figure 13). From the series of catalysts investigated, we found that nano-Ni shows excellent H₂ decomposition behavior (kinetics and overall hydrogen storage capacity) due to their unique size distribution, high specific surface area, and microstructural characteristics.
2.5. Carbon based Nanovariants

The physisorption of hydrogen are phenomenally superior in carbon nanovariant types of materials such as Buckminster Fullerenes, single of multiwalled carbon nanotubes, nanofibers, nanoshells, nanobells etc., because of their unique characteristics such as a high surface to volume ratio, highly porous microstructure, lighter weight, and low heat or thermodynamic values. Though the thermodynamic effects and surface assisted kinetic constraints are to be solved from the first principles in order to greatly implement these complex hydrides for practical applications. The low weight, weightless due to light metal/carbon/organics and store a large amount of storage materials needs to be explored. One such reversible hydrogen storage system is the complex hydrides.

For an on-board hydrogen vehicular application, a proton exchange membrane fuel cell (PEMFC) would be the most efficient fuel cell system which can work efficiently with a hydrogen fuel. Hydrogen is the most preferred fuel for vehicular applications due to its high energy density and low emissions. Hydrogen is stored as a compressed gas in tanks or as a cryogenic liquid. However, these storage methods are bulky and require high pressure tanks or cryogenic refrigeration systems. Therefore, there is a need for alternative hydrogen storage methods that are efficient, safe, and can be easily incorporated into existing fuel cell systems. One such method is the use of metal hydrides.

The reaction pathways, greater gas–solid interactions, and overall hydrogen storage capacity) due to their unique characteristics such as a high surface to volume ratio, materials such as Buckminster Fullerenes, single or multiwalled carbon nanotubes, nanofibers, nanoshells, nanobells etc., because of their unique characteristics such as a high surface to volume ratio, highly porous microstructure, lighter weight, and low heat or thermodynamic values. Though the thermodynamic effects and surface assisted kinetic constraints are to be solved from the first principles in order to greatly implement these complex hydrides for practical applications. The low weight, weightless due to light metal/carbon/organics and store a large amount of storage materials needs to be explored.
highly porous microstructure, lighter weight, and low heat or thermodynamic values. Though there were some discrepancies in terms of hydrogen storage that was reported for these carbon nanovariants, the physical understanding and mechanistic approach of the hydrogen-solid surface interaction is emerging. The physical adsorption occurs while interacting molecular hydrogen on the surface of the nanovariant material because of weak van der Walls forces of attraction. Additionally, the highest occupied molecular orbital of carbon atom overlaps with the occupied electronic wave function of the hydrogen electron. The chemisorption on the other hand related to overcoming the activation energy barrier in the process of dissociation of hydrogen reversibly. The major difference between the physisorption and chemisorption of hydrogen is that for the physisorbed process, one or less than one hydrogen atom is coordinated with at least two carbon atoms, whereas the chemisorbed process, at least two hydrogen atoms coordinated with one carbon atom [72–74]. The binding energy required for the physisorbed hydrogen is on the order of 0.1 eV, while the chemisorbed hydrogen requires greater than 2–3 eV.

Carbon nanotubes, an allotrope of carbon played a vital role in hydrogen storage [75] and this first study created waves in preparing such nanovariants experimentally and understanding them in the theoretical framework. Densifying hydrogen on both the surface and bulk of the carbon nanostructures has proven to be an ideal solution than the compressed hydrogen in gas cylinders. A storage density of at least 10% could be stored in single wall carbon nanotubes [76] and was demonstrated using thermal programed desorption at NREL, USA. Fullerenes, on the other hand, are a new form of carbon with close-caged molecular structure, which were first reported by Smalley in 1985 [77]. It is a potential hydrogen storage material based on the ability to react with hydrogen via hydrogenation of carbon–carbon double bonds. Theory predicts that a maximum of 60 hydrogen atoms can be attached to both the inside (endo) and outside (exo) of the fullerene spherical surface. Thus, a stable C_{60}H_{60} isomer can be formed with a theoretical hydrogen content of 7.7 wt.%. It seems that the fullerene hydride reaction is reversible at high temperatures. The 100% conversion of C_{60}H_{60} indicates that 30 mol of H\textsubscript{2} gas will be released from each mole of fullerene hydride compound. However, this reaction requires a temperature of about 823-873 K [78]. Solid C\textsubscript{60} has an FCC lattice at room temperature and a molecular density of 1.69 g cm\textsuperscript{-3}. The molecules can rotate due to the weak molecular interaction. fullerene is an allotrope of carbon. Fullerene molecules have five-fold and six-fold symmetries, whose vertexes contain carbon atoms. Fullerene, C_{60} is the smallest, highly symmetric and an equilibrium structure for gas storage applications.

2.6. Polymeric Nanostructures

Polymeric nanocomposite materials consist primarily of polyaniline, a conducting polymer, which has conductivity on the order of 1 Siemens/cm [79]. The chemical makeup of polyaniline in its emeraldine form has anions, which allow hydrogen ions to bond to the material very well. Due to its porosity, the surface area of the conducting polymeric matrix material will allow for additional hydrogen binding in the form of physisorption. The polymer nanostructures are widely studied for their interesting physical and chemical properties [80–83] and are deployed for practical applications [84–86]. Conducting polyaniline is a type of polymer that could be prepared in powder, gel, or other suitable forms and have employed them for storing hydrogen at varying densities [87,88]. The physical adsorption mechanism of hydrogen both on the surface and into the bulk structure of the polyaniline is widely studied by several researchers [89–92]. Similar to carbon nanotubular [75,93] and nanofibrillar [94] structures, polyaniline could be prepared in nanoforms for increasing their surface area for maximizing the hydrogen adsorption [95] and other physicochemical applications such as chemical/biochemical sensors [96], actuators [97], and high speed memory devices [98].

In the chemical oxidative polymer condensation process of aniline, one can easily produce the fibrous nanostructures that could form with a few nanometers thickness and a micrometer length. These nanofibers are in the real sense grown on the granular particles of polyaniline solution. There may be a number of preparation techniques such as interfacial polymerization and chemical templating that
can readily generate the polyaniline nanofibers that are of great control structures, and process mechanisms. Based on this highly controlled template synthesis process, various polyaniline nanostructures have been produced in recent times, [99] and their structural morphology and other properties have been optimized [100]. The electrospinning is another useful and potential technique by which we have prepared our polyaniline nanofibers [101,102] whose morphology is shown in Figure 14. The reversible hydrogen uptake at room temperature was performed on these polyaniline nanofibers and is demonstrated in Figure 15. Since the molecular hydrogen binding energies need to be adjusted by understanding the mechanistic behavior of these polyaniline nanofibers, the reversible hydrogen storage characteristics is an ongoing research and development.

**Figure 14.** SEM images showing the surface morphology of electrospun polyaniline nanofibers.

**Figure 15.** Hydrogen sorption cycle-life of electrospun polyaniline nanofiber at 100 °C. A1–A4: Absorption in four consecutive run and D1–D3: desorption after every hydrogen absorption for three consecutive runs.

Doping with carbon nanotubes and fullerenes, as well as catalyst materials enable the formation of chemical and physical bonds at the materials interface. By combining different carbon nanovariant
structures, a new hydrogen storage system can be manufactured that exceeds the performance of the existing materials and facilitates commercialization of hydrogen storage systems. These new catalyst doped hydrogen storage materials can be described as porous nanocomposites of a conducting polymer with modified fullerene compounds and carbon nanotubes, as well as kinetics enhancing catalyst materials. The combination of the high surface area of carbon nanotubes and modified fullerenes [103] with the tunable redox behavior of the conducting polymer potentially offers enhanced performance as a reversible hydrogen storage system.

2.7. Metal Organic Frameworks (MOF)

There is a pressing need for the discovery and development of new reversible materials. One new area that may be promising is that of high surface area hydrogen sorbents based on microporous metal-organic frameworks (MOFs). Such materials are synthetic, crystalline, and microporous and are composed of metal/oxide groups linked together by organic struts. Hydrogen storage capacity at 77 K (−195 °C) has been reported as high as 10 wt.% [104] via an adsorptive mechanism, with a room temperature capacity of approximately 1 wt.% [105]. However, due to the highly porous nature of these materials, the volumetric capacity at a room temperature remains a significant issue. Besides, their significant potential for applications such as novel storage media for natural gas and hydrogen, the MOFs suffer from very high structural instability when exposed to atmospheric moisture [106].

3. Conclusions

Nanostructured materials exhibit excellent properties for hydrogen storage due to desired and tunable specific surface area along with many others. These functional smart nanosystems offer superior properties for the physical and chemical reactions, such as surface interactions, adsorption on the active surface while maximizing the bulk absorption, fast reaction kinetics, low temperature hydrogenation and dehydrogenation, hydrogen atom dissociation on the nanocatalytic surface, and molecular diffusion via the active polymeric chain. The huge surface to volume ratio, and an exclusive hydrogen adsorbing properties of nanophase materials can facilitate the dissociation of gaseous hydrogen effectively. Similarly, the small volume of individual nanoparticles can produce short diffusion paths to the materials’ interiors, therefore enhances the hydrogen atomic transport between the granular composites. The use of nanosized catalytic doping agents provides a higher dispersion of the catalytically active species and thus participates in higher mass transfer reactions. Nanocomposites based on polyaniline nanofibers and further functionalized with carbon nanotubes possess a unique microstructure for hydrogen storage for on-board vehicular applications.

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