Comparative study of Hydrogen Storage Efficiency and Thermal Effects of Metal Hydrides vs. Carbon Materials

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ABSTRACT:

Storage of hydrogen is one of the key challenges in developing hydrogen economy. Conventional storage methods such as high-pressure gas or cryogenic liquid hydrogen can not fulfill the set future storage goals. Storage in solid fuel form by chemically or physically combined within materials has potential advantages over other storage methods. There is enduring research both on modifying and optimizing the known solid store materials. In the present paper, recent developments of metal hydrides and carbon based materials based on storage capacity, operating conditions and thermal effects are comparatively reported. The reported work will provide guidance to planned future programs.

KEYWORDS : Hydrogen storage, Metal Hydrides, Carbon Materials, Operating Temperature and Pressure

Nomenclature

\(BCC\) Body Centred Cubic
\(BET\) Brunauer-Emmett-Teller
\(GNF\) Graphite Nanofiber
\(SSA\) Specific Surface Area
\(SWCNT\) Single Walled Carbon Nanotubes

1. Introduction

Hydrogen is the ideal candidate as an energy carrier for both mobile and stationary applications while averting adverse effects on the environment, and reducing dependence on imported oil for countries without natural resources. Hydrogen storage is clearly one of the key challenges in developing hydrogen economy world wide. Hydrogen can be stored as (i) pressurized gas, (ii) cryogenic liquid or (iii) solid fuels as chemical or physical combination with materials, such as metal hydrides, complex hydrides and carbon materials. Each of these options possesses attractive attributes for hydrogen storage [1].

Hydrogen storage as chemical compounds or adsorbed species have definite advantages from the safety perspective, however, some form of conversion or energy input is required to release the hydrogen for use.

An optimum hydrogen-store material is required to have the following properties; high hydrogen capacity per unit mass and unit volume which determines the amount of available energy, low dissociation temperature, moderate dissociation pressure, low heat of formation in order to minimize the energy necessary for hydrogen release, low heat dissipation during the exothermic hydride formation, reversibility, limited energy loss during charging and discharging, fast kinetics, high stability against oxygen and moisture for long cycle life, low cost of infrastructures and safety. In this study, the hydrogen storage properties of metal hydrides and carbon materials are compared. The work will serve to evaluate solid fuel hydrogen store for industrial on-board hydrogen storage tank design.

2. Metal Hydrides

Metal hydrides compose of metal atoms that constitute a host lattice and hydrogen atoms that are trapped in interstitial sites, such as lattice defects. They store hydrogen in a solid state under moderate temperature and pressure that gives them the important safety advantage by high volume-efficient storage over the gas and liquid storage methods [2-8].
The light metals such as Li, Be, Na, Mg, B and Al, form a large variety of metal–hydrogen compounds. They are especially interesting due to their light weight and ability to accommodate a number of hydrogen atoms per metal atom, which is in many cases equals to 2. Heavier ones may enter the multiple component system only as a low-content additive for alteration of properties or as a catalyst.

2.1. Mg-Based Metal Hydrides

Magnesium hydride, MgH\(_2\), has the highest energy density of 9 MJ.kg\(^{-1}\).Mg\(^{-1}\) among the reversible hydrides applicable for hydrogen storage. For onboard hydrogen storage, there is considerable research on magnesium and its alloys. They pose high hydrogen storage capacity of 7.7 wt %, good-quality functional properties, such as heat-resisting, vibration absorbing, good reversibility properties and low cost associated with good recycling [6,9,10]. However, high thermodynamic stability of MgH\(_2\) results in a relatively high desorption enthalpy, which corresponds to an unfavorable desorption temperature of 300 °C at 1 bar H\(_2\) [6,11].

Efforts has been made on Mg-based hydrides in recent years to reduce the desorption temperature and to increase the re/dehydrogenation reaction rates. Hydrogenation properties of recently studied Mg-based hydrides are briefly summarized in Table 1. Hydrogen storage capacities varies between 3.5 and 7.3 wt % and desorption temperatures varies between 180 and 450 °C according to synthesis method. There are only few publications regarding high number of cyclic tests. Reiser et al. [12] indicated that Ni-doped Mg and Mg\(_2\)CoH\(_5\) are almost stable after even 800 cycles with small fluctuations in the hydrogen capacity. MgH\(_2\)–5 wt % V shows no change in isotherms and no disintegration of the materials after 2000 cycles [13].

Table 1. Hydrogen absorption / desorption properties of Mg-based hydrides

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Kinetics (min)</th>
<th>Max wt % of H(_2)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanosized MgH(_2) (Al-doped)</td>
<td>180 - 347</td>
<td>1.00</td>
<td>420</td>
<td>7.3</td>
<td>[11]</td>
</tr>
<tr>
<td>Mg - 0.5 wt % Nb(_2)O(_5)</td>
<td>300</td>
<td>8.40</td>
<td>1.0 - 1.5</td>
<td>7.0</td>
<td>[14]</td>
</tr>
<tr>
<td>MgH(_2)</td>
<td>300 - 350</td>
<td>3.00 – 10.00</td>
<td>12.5 – 50</td>
<td>7.0</td>
<td>[15]</td>
</tr>
<tr>
<td>Mg/MgH(_2) (Ni doped)</td>
<td>230 - 370</td>
<td>4.00 – 1.40</td>
<td>90</td>
<td>6.0</td>
<td>[12]</td>
</tr>
<tr>
<td>MgH(_2) - 5 wt % V</td>
<td>200 - 300</td>
<td>0.15 – 10.00</td>
<td>4 – 33</td>
<td>5.8</td>
<td>[16]</td>
</tr>
<tr>
<td>MgH(_2) - 5 at %Ti</td>
<td>200 - 300</td>
<td>0.15 – 10.00</td>
<td>3.3 - 0.8</td>
<td>5.0</td>
<td>[17]</td>
</tr>
<tr>
<td>MgH(_2) - 5 at %Ni</td>
<td>200 - 300</td>
<td>0.15 – 10.00</td>
<td>5 - 16</td>
<td>5.0</td>
<td>[17]</td>
</tr>
<tr>
<td>Mg - 50 wt % LaNi(_5)</td>
<td>250 - 300</td>
<td>10.00 – 15.00</td>
<td>3</td>
<td>4.1</td>
<td>[18]</td>
</tr>
<tr>
<td>Mg - 20 wt % Mm</td>
<td>300 - 450</td>
<td>10.00</td>
<td>10 – 5</td>
<td>3.5</td>
<td>[19]</td>
</tr>
</tbody>
</table>

Figure 1. Hydrogen desorption curves of unmilled MgH\(_2\) (filled symbols) and ball-milled MgH\(_2\) (hollow symbols) under a hydrogen pressure of 0.15 bar [15].
The reported properties can be achieved to some extent by changing the microstructure of the hydride by ball-milling (mechanical alloying) with elements which reduce the stability of the hydrides. Further improvement in properties is achieved by using proper catalysts to improve the absorption / desorption kinetics [20].

It is possible to control properties of the store material, according to specific applications, by changing the alloy composition, surface properties, microstructures and grain size by ball-milling without the additional cost of catalyst and with minimal loss of storage capacity [15]. A reduction in desorption temperature of 64 °C was achieved by milling as seen in Figure 1. It is due to faster hydrogen desorption kinetics, reduction in activation energy and also enhanced kinetics.

2.2. Complex Hydrides

Sodium, lithium and beryllium are the only elements lighter than magnesium that can also form solid-state compounds with hydrogen. Use of complex hydrides for hydrogen storage is challenging because of both kinetic and thermodynamic limitations. Intense interest has developed in low weight complex hydrides such as alanates \([\text{AlH}_4^-]\), amides \([\text{NH}_2^-]\), imides and borohydrides \([\text{BH}_4^-]\).

Sodium aluminum hydride, \(\text{NaAlH}_4\), would seem to be a possible candidate for application as a practical onboard hydrogen-storage material due to the theoretical hydrogen capacity of 5.6 wt %, low cost and its availability in bulk. Recently, numerous studies have been carried out to enhance the hydriding properties of \(\text{NaAlH}_4\) as given in Table 2. Although they have good hydrogen storage capacity, between 2.5 wt % and 5.0 wt %, complex aluminum hydrides are not considered as rechargeable hydrogen carriers due to irreversibility and poor kinetics. However, using appropriate transition or rare earth metals as catalysts, the reversibility of complex hydrides can be improved. Bogdanovic and Schwickardi [21,22] have demonstrated upon doping with proper titanium compounds, the dehydridding of aluminum hydrides could be kinetically enhanced and maintain reversibility under moderate conditions in the solid state. Newest results showed that using titanium nanoclusters consisting of only 13 atoms can drastically improve the reaction kinetics with hydrogen and lower the release temperature even further [23,24]

### Table 2. Hydrogen absorption / desorption properties of sodium alanates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Kinetics (min)</th>
<th>Max wt % of H₂</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NaAlH}_4)</td>
<td>80 - 180</td>
<td>76 - 91</td>
<td>120 - 300</td>
<td>5.00</td>
<td>[25]</td>
</tr>
<tr>
<td>(\text{NaAlH}_4) - 2 mol % (\text{TiCl}_3)</td>
<td>100 - 125</td>
<td>83 - 91</td>
<td>20</td>
<td>4.00</td>
<td>[26]</td>
</tr>
<tr>
<td>(\text{NaAlH}_4) (Ti-doped)</td>
<td>25 - 120</td>
<td>20 - 120</td>
<td>40 - 720</td>
<td>3.80</td>
<td>[27]</td>
</tr>
<tr>
<td>(\text{NaAlH}_4) (Ti-Zr doped)</td>
<td>125 - 165</td>
<td>101 - 202</td>
<td>60 - 180</td>
<td>3.00</td>
<td>[26]</td>
</tr>
<tr>
<td>(\text{Na}_2\text{LiAlH}_6)</td>
<td>210</td>
<td>45</td>
<td>100</td>
<td>2.50</td>
<td>[28]</td>
</tr>
</tbody>
</table>

A survey of lithium based hydrogen storage compounds are summarized in Table 3. High capacities of stored hydrogen per weight percent material are clearly seen.

Lithium nitride is usually used as an electrode, or as a starting material for the synthesis of binary or ternary nitrides. Consequently, \(\text{Li}_3\text{N}\) can theoretically store 10.4 wt % hydrogen. It has two plateaus in the pressure-concentration isotherm and desorption isotherms cannot return to the origin. About 55% hydrogen can be desorbed at temperatures above 230 °C.

The absorbed hydrogen content reaches up to 18 wt % for \(\text{LiBH}_4\). Despite its great absorbing capacity, all attempts to synthesize \(\text{LiBH}_4\) from the elements at elevated temperatures up to 650 °C and pressure of 150 bar \(\text{H}_2\) failed to date [29,30]. Moreover, \(\text{LiBH}_4\) is an expensive compound [6]. The theoretical hydrogen contents are 10.5 wt % and 11.2 wt % for \(\text{LiAlH}_4\) and \(\text{Li}_3\text{AlH}_6\) respectively. However, \(\text{LiAlH}_4\) is an example of unstable hydride, which decomposes easily, but cannot be re-hydrogenated [31]. Lack of reversibility is the major hindrance for these materials.
Table 3. Hydrogen absorption / desorption properties of Lithium based hydrides.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Kinetics (min)</th>
<th>Max wt % of H₂</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄ + 1/2 MgH₂ (Ti-doped)</td>
<td>315 – 450</td>
<td>2 - 19</td>
<td>240</td>
<td>10.00</td>
<td>[32]</td>
</tr>
<tr>
<td>LiNH₂/LiH</td>
<td>210</td>
<td>10</td>
<td>120</td>
<td>6.50</td>
<td>[33]</td>
</tr>
<tr>
<td>Li₃N</td>
<td>50 - 270</td>
<td>0.5</td>
<td>20</td>
<td>6.00</td>
<td>[34]</td>
</tr>
<tr>
<td>Li₂MgN₂H₂</td>
<td>180</td>
<td>1 - 90</td>
<td>60</td>
<td>5.50</td>
<td>[35]</td>
</tr>
<tr>
<td>Li₂NH</td>
<td>230 - 200</td>
<td>7</td>
<td>10 - 300</td>
<td>3.10</td>
<td>[36]</td>
</tr>
</tbody>
</table>

2.3. Intermetallic Compounds

Research on intermetallic compounds for hydrogen storage was initiated more than 20 years ago. The different families of intermetallic compounds classified on the basis of their crystal structures, such as AB₂ type (Laves) phases, AB₅ type phases and Ti-based Body Centered Cubic (BCC) alloys are well known as hydrogen store materials.

The discovery of hydrogen absorption by LaNi₅ [37] and FeTi [38], opened new possibilities for industrial developments. However for on-board storage, they remained at the stage of prototypes due to their weight penalty and low hydrogen storage capacity [39]. The hydrogen capacity of the most popular LaNi₅-based alloys operating at moderate temperature does not exceed 1.4 wt %. The pressure-concentration diagram shows a flat plateau, low hysteresis, but unfortunately the hydrogen capacity is degraded after a few cycles. Also, FeTi is a well-known hydrogen storage compound having a total hydrogen capacity of about 1.9 wt % with inexpensive elements [40]. For practical applications at ambient temperature and pressure, their low energy density per unit weight is known as a critical disadvantage.

3. Carbon based Materials

For many years research field of hydrogen storage in carbon materials was dominated by announcements of high storage capacities in carbon nanostructures. However, the experimental results on hydrogen storage in carbon nanomaterials scatter over several orders of magnitude.

Extremely large hydrogen contents in graphite nanofibers (GNFs) were announced in 1998 by Chambers et al. [41]. However, these values have never been confirmed by others, e.g. [42-48]. In alkali metal doped GNFs, a high hydrogen uptake was measured by thermal gravimetric analysis [49]. However, these results have been seen doubtful by several groups [50-52] and ascribed to the uptake of water. Several different results have been obtained on single walled carbon nanotubes (SWCNTs) which lie in the range between 4 and 8 wt%. The most promising one claims a rapid hydrogen uptake at room temperature and ambient pressure with a storage capacity of 7.5 wt% after a special ultra-sonic treatment [53,54]. However, these results could not be reproduced by any other group. The overall hydrogen storage was found to be 1.5 wt% by Hirscher at al. [55], however, the observed hydrogen storage is attributed to Ti-alloy particles incorporated during the high-power ultra-sonic treatment.

On the other hand, microporous carbon based materials show good potential for hydrogen storage, 4.5 wt % by adsorption at low temperature, -196 °C [56]. Carbon nanomaterials possess high specific surface area, microporosity, and low mass. Apart from these characteristics, materials like activated carbons are cheap and easy to produce. It can be shown for different carbon nanomaterials that the storage capacity depends linearly on the Brunauer-Emmet-Teller (BET) [57] specific surface area (SSA) both at room temperature and at low temperature and is independent of the individual nanostructure [56].

In summary, the experiments to date claiming very high values could not independently be reproduced in a different laboratory. In view of today’s knowledge although they have good reversibility properties, carbon nanostructures cannot store the amount of hydrogen required for automotive applications [58]. As an example, Figure 2 shows the storage capacity of SWNTs and activated carbon at room temperature in comparison to LaNi₅ [59]. In contrast to LaNi₅, no plateau is observed for all measured carbon materials and their hydrogen storage capacity is much smaller even at high pressures.
There is an intensive research on solid hydrogen store materials. A brief review of state-of-the-art is reported on two different kinds of storage materials, namely metal hydrides and carbon based materials. The work is carried out in an attempt to facilitate prospectus material choice for further tank design aiming at on board applications.

Metal hydrides are promising candidates due to their safety advantage with highly volume-efficient storage capacity for onboard vehicles. By this way an effective storage option may be achieved comparable to the traditional methods. Recent research work has been conducted on metal hydrides to improve adsorption / desorption properties.

Although the storage capacities of complex hydrides are theoretically good, there is a large difference between the theoretical and the practically attainable values. Moreover, the slow kinetics and reversibility drawbacks are significant obstacles for practical applications. The intermetallic compounds do not satisfy the requirements for mobile storage due to their low storage capacities of only 2 wt % maximum and high costs. Group of Mg based hydrides is seen as a good candidate for competitive hydrogen store with reversible hydrogen capacity up to 7.6 wt %. However, slow kinetics and high hydrogen desorption temperatures of up to about 300 °C reduce the storage efficiency. Many efforts have been devoted to those materials in order to decrease their decomposition temperature, enhance the kinetics and cycle life.

For hydrogen storage in carbon nanostructures, the high values up to 8 wt % claimed at room temperature could never be reproduced, however, can be traced back to erroneous measurements. Nevertheless, carbon nanomaterials possessing high specific surface areas show high storage capacities, 4.5 wt % by adsorption of hydrogen molecules at lower temperatures. Owing to the small interaction energy involved these materials show fast kinetics and high reversibility, which makes them to promising hydrogen storage materials.

There is not a perfect choice of hydrogen store material to meet the set US Department of Energy, DOE goals for transport applications. Although some results are encouraging, such as improved kinetics and lower decomposition temperatures for metal hydrides, or high surface areas for carbons, further research is needed to develop materials satisfying the needs for technical applications. In the light of the achievements, there is high potential in developing, on the one hand, novel carbon materials with high specific surface area and well defined pore size in order to optimize the physisorption properties, and on the other hand, in developing better hydride materials with high reversible hydrogen capacity at ambient temperature. In addition, technological improvements in vehicle design and system integration along with cost efficiency will determine the on-board applicability of the selected material.

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References


