

Magnesium Hydrides for Hydrogen Storage: A Mini Review

Attuluri.R.Vijay Babu^{1*}, Nagaraju Devunuri², Manisha.D.R³, Y.Prashanthi⁴,
Ramchander Merugu⁴, Attuluri.J.R.Ravi Teja⁵

¹School of Electrical Engineering, Vignan's University, Guntur, India.

²Department of Science and Humanities, Vignan's University, Guntur, India.

³Department of Biochemistry, Osmania University, Hyderabad, India.

⁴University College of Science and Informatics, Mahatma Gandhi University, Nalgonda

⁵Department of Chemical Engineering, RVR & JC College of Engineering,
Guntur, India.

*Corres.author: 202vijay@gmail.com

Abstract: Hydrogen storage in solids of hydrides is advantageous in comparison to gaseous or liquid storage. Magnesium based materials are being studied for solid-state hydrogen storage. Compared to other materials, magnesium can hold about 6% wt and is more abundant one earth. Although metal hydride storage is safe, problems like the temperature of about 300°C required for desorption, limits its use. This paper aims at reviewing recent literatures on the progress made in the usage of magnesium and its limitations.
Key words: Hydrogen storage, magnesium hydrides, catalysts

Introduction

Hydrogen production is done by chemical or biological methods. Among the existing methods steam reforming is widely used direct method for production. Electrolysis and thermolysis are the other methods for hydrogen production. Biological methods are considered to be more environmental friendly. Along with the production of hydrogen other useful products can also be obtained in biological production of hydrogen. In chemical methods or biological methods of production of hydrogen one of the major limitations of using hydrogen include is its storage. Hydrogen can be stored as solid fuel as chemical or physical combination with metals, pressurized gas and as cryogenic liquid. Hydrogen storage in liquid or gaseous form poses safety problems for on-board transport applications. Hence, metal hydrides, alanates, amides, nano structural carbon, metal organic frameworks (MOFs) and ammonia and ammonia borane are used for storage as solid fuel. Although the advantages are fast adsorption and desorption but disadvantage is the low hydrogen capacity due to physisorption by weak vander waals forces. Metal hydride storage of hydrogen above room temperatures is an advantage but it requires high temperatures for desorption to take place. Hydrogen adsorption on adsorbent requires cryo adsorption which is not economically feasible. An ideal hydrogen storage material should have: (i) high hydrogen storage gravimetric/volumetric capacity; (ii) ambient reaction temperature for charging/discharging hydrogen and fast kinetics (iii) excellent reversibility (iv) low cost and (v) low toxicity. The hydrogen adsorption and desorption properties of magnesium hydrides and the ongoing research work in this area are shown in Table 1 along with the references.

Hydrogen forms metal hydrides with some metals and also alloys leading to solid-state storage under moderate temperature and pressure. The process of hydrogen absorption includes two phases where in first

phase only some hydrogen is absorbed and in the second phase hydride is fully formed. Magnesium based hydrides possess properties such as heat-resistance, vibration absorbing, reversibility and recyclability and are very economical. Moreover, Mg-based materials for hydrogen storage can store hydrogen about 7.7 mass%. For portable and stationary energy storage with magnesium hydride system, Solid oxide fuel cell (SOFC) can be used. Magnesium hydrides are generally stable and require a high temperature to decompose. Even though complex hydrides like $\text{Mg}(\text{BH}_4)_2$ can be easily destabilized but slow kinetics and irreversibility limits their use. The metal surface is an important factor responsible for dissociation of hydrogen molecules and diffusion of hydrogen. Ball milling method, hydrogen metal combustion, metal plasma, gravity casting and Equal Channel Angular Pressing (ECAP), mechanical alloy are the other methods of synthesis of magnesium hydride. Ball-milling method is an economic process which is applied to metal hydrides to achieve good surface properties.

Process of Hydrogenation

Compared to other materials, magnesium can hold more amounts of hydrogen and is more abundant one earth. The hydrogenation of magnesium can be divided into three steps: hydrogen dissociation, hydrogen diffusion and MgH_2 formation. The first step of hydrogen dissociation involves the interaction of hydrogen gas and metallic atoms on the magnesium surface. The second step is complex and involves temperature, structure, materials, hydrogen dissociation rate, hydrogen pressure, grain boundary modifications and catalytic elemental atoms. The interactions between the formation of MgH_2 and the hydrogen diffusion and the morphology and structure of MgH_2 around the magnesium surface are the third step of MgH_2 formation which is also complex. According to the theory, ΔH_{des} in the range of 38—55 kJ/mol is required for desorption temperature of MgH_2 at 150°C. The desorption temperature of MgH_2 can be reduced by modification of thermodynamic property, ΔH_{des} which can be done by Mg alloying with Ni to form Mg_2Ni . The kinetics of hydrogenation is controlled by three factors, (i) the rate at which hydrogen molecules dissociate, (ii) diffusion through the hydride layer formed and into the bulk metal and (iii) difficulty for hydrogen penetration from the surface into the metal. Dehydrogenation involves the steps (i) stages proceeding in the bulk, including chemical and structural changes, (ii) bulk to surface transfer and (iii) recombination on the surface.

To improve the process catalysts can be used to enhance kinetics by decreasing activation energy barriers. Nickel and palladium are well known catalysts for molecular hydrogen dissociation, for hydrogen storage on metal hydrides. Nickel alloys with palladium usually show a fast kinetics which can be attributed to the catalytic effect of nickel. Enhanced kinetics and significant lowering of hydrogenation and dehydrogenation temperature from 275 to 175°C and from 350 to 275°C, respectively was obtained by adding 1% nickel to magnesium. Apart from nickel, other transition metals like Ti, Cr, Nb_2O_3 and Cr_2O_3 and their oxides are under active research as catalysts for improving kinetics of hydrogen storage on metal hydrides. Lanthanide oxides, addition of carbon nanotubes (5 wt%) to magnesium and to MgH_2/Fe Tin nano-composites resulted in significant improvement of hydrogen uptake kinetics and lowering of sorption temperature. The high oxidation sensitivity of the magnesium surface and slow kinetics arises both from diffusion limitations and stability. Various additives like Ni, LaNi or La-Mg-Ni alloys, reducing the particle and grain size by mechanical milling, have been tried to improve the hydrogen storage properties. Alloys of Mg_2Cu , $\text{Mg}_{17}\text{La}_2$ and MgAl , react readily with hydrogen and decompose into MgH_2 and another compound or hydride which are reversible only at high temperature. Hydrogen storage properties of magnesium can be enhanced by decreasing the particle size of the crystallites to approximately 1.3 nm resulting in a substantial decrease of the hydrogen desorption enthalpy. Magnesium and magnesium based alloys are the most attractive materials that satisfy the main requirements which are excellent reversibility, low cost and non-toxicity amongst all possible candidates. The limitations of magnesium as hydrogen storage material are: (i) the temperatures for hydrogenation and dehydrogenation are too high. (ii) Both hydrogenation and dehydrogenation reactions are too slow. Recently addition of CNTs has also been found to be more effective than other forms of carbons. Alloying another element with magnesium also enables the hydriding/ dehydriding at less mild conditions. Amorphous Mg-10Ni-5Y with newly developed nanocarbon supported metallic catalyst, at an average grain size of 4.7 nm and dispersed with Mg_2Ni nanoparticles at a size of 2.7 nm was also used for hydrogen storage. Maximum hydrogen capacity of 6 wt% was seen as there was an increase in hydrogen absorption kinetics.

Conclusion and Future Directions

Although magnesium is promising for hydrogen storage materials it has limitations such as high operational temperature and slow kinetics. The obstacles are removed by the use of catalyst, nanostructuring and/or alloying. Remarkable improvement has been obtained in increasing hydrogenation kinetics, at a low

temperature demonstrating that the limitation of slow kinetics of hydrogenation can be removed but further investigation is required. The hydrogenation process of magnesium is very complicated and the hydrogenation mechanism has not been fully understood and hydrogen desorption becomes the “bottleneck” of application of magnesium to practical hydrogen storage.

Table 1: Magnesium hydrides for hydrogen storage

Material	Temperature (°C)		Max hydrogen Wt%	Reference
	T _{ads}	T _{des}		
MgH ₂ + 10 wt% BCC (Ti _{0.4} Cr _{0.1} Mn _{0.22} V _{0.28}) + 5 wt% MWCNTs	300	300	6	[1.]
71.5 wt% Mg-23.5 wt% Ni-5 wt% Fe	320	350	3.32(abs),2.42 (des)	[2.]
Mg-14 wt%Ni-2 wt%Fe-2 wt% Ti-2 wt% Mo	300	300	4.6	[2.]
Mg-10 wt%Ni-5 wt%Fe-5 wt% Ti	300	300	5.51(ads) 5.15(des)	[3.]
MgH ₂ + 10 wt% TiF ₃	300	280	6.27(abs) 5.98(des)	[4.]
MgH ₂ + 10 wt% FeF ₃	300	280	6.33(abs) 4.82(des)	[4.]
MgH ₂ - 20 wt% AB ₂ alloy	300	300	5.7	[5.]
MgH ₂ - 40 wt% AB ₂ alloy	300	300	4.1	[5.]
Mg-5wt%Ni-2.5wt%Fe-2.5wt% V	300	300	5.67 (ads) 4.91(des)	[6.]
Mg-23.5wt%Ni-2.5wt%Cu	300	300	4	[7.]
90Mg-6Ni-4C	100	250	5.23(abs) 3.74(des)	[8.]
Mg-14Ni-2Fe ₂ O ₃ -2Ti-2Fe	300	300	4.56 (ads) 3.32 (des)	[9]
Mg- 2 wt% MWCNTs	300	300	5(ads) 4(des)	[10]
Mg-15 wt% Ni -5 wt%Fe ₂ O ₃	300	300	5.38 (ads), 5.28(des)	[11]
Mg _x Cu ₅ Ni ₅ Y _{1-x}	300	200	4.2-4.5 (abs) 2.6 (des)	[12.]
Cat-MgH ₂ (MgH ₂ - 5 wt% Nb ₂ O ₅ - 1 wt% Graphite) + 5 wt% Al	320	320	5.3	[13.]
Mg-10Ni-R (R=La,Nd,Sm)	150	250	3.5-4	[13.]
Mg-14Ni-6Fe ₂ O ₃	300	300	3.28(ads) 3.37(des)	[14.]
Mg-10 wt % Fe ₂ O ₃	300	320	4.37 (ads) 0.88 (des)	[15.]
Mg-14Ni-2Fe ₂ O ₃ -2Ti-2Fe	300	300	4.41(abs) 3.5(des)	[15.]
Mg-14Ni-3Fe ₂ O ₃ -3Ti	300	300	4.00(abs) 3.98 (des)	[15.]
Mg-23.5 wt% Ni -5 wt % Fe ₂ O ₃	320	320	2.69 (ads) 2.27 (des)	[15.]

Material	Temperature (°C)		Max hydrogen Wt%	Reference
	T _{ads}	T _{des}		
Mg-15 wt% Ni- 5 wt % Fe ₂ O ₃	300	350	3.73(ads) 3.32(des)	[16.]
Mg-14Ni-6Fe ₂ O ₃ -2MWCNTs	300	300	2.92 (ads) 1.75 (des)	[17.]
MgH ₂ + 5 wt% Zr ₈ Ni ₂₁	250	300	6.50	[17.]
Mg ₈₀ Ni ₁₅ Y ₁ Pd ₄	200	200	4.4	[18.]
Mg ₈₀ Ni ₁₅ Y ₁ Pd ₄	300	300	4.4	[19.]
Mg ₈₀ Ni ₁₅ La ₁ Pd ₄	200	200	4.2	[19.]
Mg ₈₀ Ni ₁₅ La ₁ Pd ₄	300	300	3.9	[19.]
Mg ₈₀ Ni ₁₅ Y _{2.5} Pd _{2.5}	200	200	4.6	[19.]
Mg ₈₀ Ni ₁₅ La _{2.5} Pd _{2.5}	300	300	4.3	[19.]
Mg ₈₀ Ni ₁₅ Y _{2.5} Pd _{2.5}	200	200	4.5	[19.]
Mg ₈₀ Ni ₁₅ La _{2.5} Pd _{2.5}	300	300	4.2	[19.]
Mg-23.5Ni-2.5Cu	300	300	4.01(ads) 3.96(des)	[19.]
88(87.5Mg-10Ni-2.5Cu)+5 wt% Nb ₂ O ₅ +7 wt% NbF ₅	300	300	3.14(ads) 1.51(des)	[15.]
MgH ₂ -10Ni-2LiBH ₄ -2Ti	300	300	4.44(ads) 1.97(des)	[16.]
Mg ₃ Cd	300	300	2.8	[15.]
MgH ₂ -10 wt% Nb ₂ O ₅ +5 wt% (ENG)	310	310	4.5(ads) 4.9(des)	[15.]
MgH ₂ -10 wt% NiB	300	300	6	[15.]
Ultrafine Mg-Ti particles	400	400	4.3	[15.]
Mg (MgH ₂)-based composites, using carbon nanotubes (CNTs) and with TCat	200	310	6	[16.]

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