

## Magnesium Hydrides for Hydrogen Storage: A Mini Review

Attuluri.R.Vijay Babu<sup>1\*</sup>, Nagaraju Devunuri<sup>2</sup>, Manisha.D.R<sup>3</sup>, Y.Prashanthi<sup>4</sup>,  
Ramchander Merugu<sup>4</sup>, Attuluri.J.R.Ravi Teja<sup>5</sup>

<sup>1</sup>School of Electrical Engineering, Vignan's University, Guntur, India.

<sup>2</sup>Department of Science and Humanities, Vignan's University, Guntur, India.

<sup>3</sup>Department of Biochemistry, Osmania University, Hyderabad, India.

<sup>4</sup>University College of Science and Informatics, Mahatma Gandhi University, Nalgonda

<sup>5</sup>Department 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 on earth. The hydrogenation of magnesium can be divided into three steps: hydrogen dissociation, hydrogen diffusion and  $\text{MgH}_2$  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  $\text{MgH}_2$  and the hydrogen diffusion and the morphology and structure of  $\text{MgH}_2$  around the magnesium surface are the third step of  $\text{MgH}_2$  formation which is also complex. According to the theory,  $\Delta H_{\text{des}}$  in the range of 38–55 kJ/mol is required for desorption temperature of  $\text{MgH}_2$  at 150°C. The desorption temperature of  $\text{MgH}_2$  can be reduced by modification of thermodynamic property,  $\Delta H_{\text{des}}$  which can be done by Mg alloying with Ni to form  $\text{Mg}_2\text{Ni}$ . 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,  $\text{Nb}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  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  $\text{MgH}_2/\text{Fe}$  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  $\text{Mg}_2\text{Cu}$ ,  $\text{Mg}_{17}\text{La}_2$  and MgAl, react readily with hydrogen and decompose into  $\text{MgH}_2$  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  $\text{Mg}_2\text{Ni}$  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 <sub>ads</sub>	T <sub>des</sub>		
MgH <sub>2</sub> + 10 wt% BCC (Ti <sub>0.4</sub> Cr <sub>0.1</sub> Mn <sub>0.22</sub> V <sub>0.28</sub> ) + 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 <sub>2</sub> + 10 wt% TiF <sub>3</sub>	300	280	6.27(abs) 5.98(des)	[4.]
MgH <sub>2</sub> + 10 wt% FeF <sub>3</sub>	300	280	6.33(abs) 4.82(des)	[4.]
MgH <sub>2</sub> - 20 wt% AB <sub>2</sub> alloy	300	300	5.7	[5.]
MgH <sub>2</sub> - 40 wt% AB <sub>2</sub> 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 <sub>2</sub> O <sub>3</sub> -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 <sub>2</sub> O <sub>3</sub>	300	300	5.38 (ads), 5.28(des)	[11]
Mg <sub>x</sub> Cu <sub>5</sub> Ni <sub>5</sub> Y <sub>1-x</sub>	300	200	4.2-4.5 (abs) 2.6 (des)	[12.]
Cat-MgH <sub>2</sub> (MgH <sub>2</sub> - 5 wt% Nb <sub>2</sub> O <sub>5</sub> - 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 <sub>2</sub> O <sub>3</sub>	300	300	3.28(ads) 3.37(des)	[14.]
Mg-10 wt % Fe <sub>2</sub> O <sub>3</sub>	300	320	4.37 (ads) 0.88 (des)	[15.]
Mg-14Ni-2Fe <sub>2</sub> O <sub>3</sub> -2Ti-2Fe	300	300	4.41(abs) 3.5(des)	[15.]
Mg-14Ni-3Fe <sub>2</sub> O <sub>3</sub> -3Ti	300	300	4.00(abs) 3.98 (des)	[15.]
Mg-23.5 wt% Ni -5 wt % Fe <sub>2</sub> O <sub>3</sub>	320	320	2.69 (ads) 2.27 (des)	[15.]

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

## References

1. Ranjbar, M. Ismail, Z.P. Guo, X.B. Yu, H.K. Liu ,Effects of CNTs on the hydrogen storage properties of MgH<sub>2</sub> and MgH<sub>2</sub>-BCC composite International Journal of Hydrogen Energy, Volume 35, Issue 15, August 2010, Pages 7821-7826.
2. Myoung Youp Song, Sung Nam Kwon, Jean-Louis Bobet, Hye Ryoung Park , Enhancement of hydrogen-storage properties of Mg by reactive mechanical grinding with oxide, metallic element(s), and hydride-forming element, Ceramics International, Volume 37, Issue 3, April 2011, Pages 897-902.
3. Myoung Youp Song, Sung Nam Kwon, Hye Ryoung Park, Jean-Louis Bobet, Improvement of hydriding and dehydriding rates of Mg via addition of transition elements Ni, Fe, and Ti, International Journal of Hydrogen Energy, Volume 36, Issue 20, October 2011, Pages 12932-12938.
4. PENG Shu-keXIAO Xue-zhang,, XU Rui-juan, LI Luo,W Fan, LI Shou-quan, WANG Qi-dong, CHEN Li-xin, Hydrogen storage behaviors and microstructure ofMF3 (M=Ti, Fe)-doped magnesium hydride, Trans.Nonferrous Met.Soc.China, 2010, 20: 1879-1884.
5. Jin-Ho Kim, Ji-Ho Kim, Kwang-Taek Hwang, Yong-Mook Kang,Hydrogen storage in magnesium based-composite hydride through hydriding combustion synthesis International Journal of Hydrogen Energy, 35(18), 2010: 9641-9645.
6. Myoung Youp Song, Sung Nam Kwon, Hye Ryoung Park, Seong-Hyeon Hong .Improvement in the hydrogen storage properties of Mg by mechanical grinding with Ni, Fe and V under H<sub>2</sub> atmosphere InternationalJournal of Hydrogen Energy, Volume 36, Issue21, October2011, Pages 13587-1359.

7. Seong-Hyeon Hong, Jong-Soo Bae, Sung Nam Kwon, Myoung Youp Song , Hydrogen storage properties of Mg-23.5Ni-xCu prepared by rapid solidification process and crystallization heat treatment International Journal of Hydrogen Energy, Volume 36, Issue3, February2011, Pages 2170-2176.
8. Yunfeng Zhu, Zhibing Liu, Yang Yang, Hao Gu, Liquan Li, Mei Cai, Hydrogen storage properties of Mg-Ni-C system hydrogen storage materials prepared by hydriding combustion synthesis and mechanical milling International Journal of Hydrogen Energy, Volume 35, Issue 12, June 2010, Pages 6350-6355.
9. Myoung Youp Song, Sung Nam Kwon, Hye Ryoung Park, Seong-Hyeon Hong. Improvement in the hydrogen storage properties of Mg by mechanical grinding with Ni, Fe and V under H<sub>2</sub> atmosphere International Journal of Hydrogen Energy, 36(21) 2011:13587-13594.
10. V.M. Skripnyuk, E. Rabkin, L.A. Bendersky, A. Magrez, E. Carreño-Morelli, Y. Estrin ,Hydrogen storage properties of as-synthesized and severely deformed magnesium – multiwall carbon nanotubes composite ,International Journal of Hydrogen Energy, 2010 35(11): 5471-5478.
11. Sung-Nam Kwon, Seong-Hyeon Hong, Hye-Ryoung Park, Myoung-Youp Song, Hydrogen-storage property characterization of Mg-15 wt%Ni5 wt%Fe<sub>2</sub>O<sub>3</sub> prepared by reactive mechanical grinding International Journal of Hydrogen Energy, Volume 35, Issue 23, December2010, Pages 13055-13061
12. Siarhei Kalinichenka, Lars Röntzsch, Thomas Riedl, Thomas Gemming, Thomas Weißgärber, Bernd Kieback ,Microstructure and hydrogen storage properties of melt-spun Mg-Cu-Ni-Yalloys International Journal of Hydrogen Energy, 2011. 36(2): 1592-1600.
13. Ashish Khandelwal, Filippo Agresti, Giovanni Capurso, Sergio Lo Russo, Amedeo Maddalena, Stefano Gialanella, Giovanni Principi. Pellets of MgH<sub>2</sub>-based composites as practical material for solid state hydrogen storage International Journal of Hydrogen Energy, Volume 35, Issue 8, April 2010, Pages 3565-3571.
14. Q.A. Zhang, C.J. Jiang, D.D. Liu,Comparative investigations on the hydrogenation characteristics and hydrogen storage kinetics of melt-spun Mg<sub>10</sub>NiR (R = La, Nd and Sm) alloys. Comparative investigations on the hydrogenation characteristics and hydrogen storage kinetics of melt-spun Mg<sub>10</sub>NiR (R = La, Nd and Sm) alloys, international Journal of Hydrogen Energy, Volume 37, Issue 14, July 2012, Pages 10709-10714.
15. Myoung Youp Song, Young Jun Kwak, Byung-Soo Lee, Hye Ryoung Park, Byoung-Goan Kim ,Effects of Ni, Fe<sub>2</sub>O<sub>3</sub>, and CNT addition by reactive mechanical grinding on the reaction rates with H<sub>2</sub> of Mg-based alloys, International Journal of Hydrogen Energy 2012, 37(2):1531-1537.
16. Myoung Youp Song, Sung Nam Kwon, Hye Ryoung Park ,Hydriding–dehydriding cycling behavior of magnesium–nickel–iron oxide alloy, Materials Research Bulletin, Volume 47, Issue 5, May 2012 , Pages 1191-1196.
17. Young Jun Kwak, Byung-Soo Lee, Hye Ryoung Park, Myoung Youp Song ,Hydrogen-storage characteristics of Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>-2CNT prepared by reactive mechanical grinding Materials Research Bulletin, Volume 47, Issue 12, December 2012, Pages 4059-4064.
18. S.A. Pighin, G. Capurso, S. Lo Russo, H.A. Peretti , Hydrogen sorption kinetics of magnesium hydride enhanced by the addition of Zr<sub>8</sub>Ni<sub>21</sub> alloy Journal of Alloys and Compounds. 2012,530( 25):111-115.
19. Eric A. Lass ,Hydrogen storage in rapidly solidified and crystallized Mg-Ni-(Y,La)-Pd alloys, International Journal of Hydrogen Energy, Volume 37, Issue 12, June 2012, Pages 9716-9721.

\*\*\*\*\*