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The composites of metal amide and magnesium hydride: Promising hydrogen storage materials

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Abstract- One of the possible contender for hydrogen storage materials is the amide-hydride system, as decomposition of amides can deliever hydrogen at low temperatures. Although the decomposition of Amides is observed under favourable conditions but the pristine amides are not so efficient as these desorb ammonia during the decomposition which affects the reversibility, thus composites of amide with different materials are studied. As magnesium hydride is a good candidate of hydrogen storage system, composites of amide and magnesium hydride are interesting composite to be studied. Various composites of amide - hydride are reviewed in this paper.

Keywords - *Energy Storage, Hydrogen Storage, Amides, MgH_2.*

I. INTRODUCTION

Currently, there is growing global concern about issues such as energy security, the availability of energy, greenhouse gas emissions and overarching challenge of change in atmosphere. The world is increasingly seeking clean and sustainable energy sources to replace fossil fuels in order to reduce the greenhouse effect and mitigate climate change, which pose significant threats to our survival. The most promising alternatives are solar energy, wind energy, and hydrogen energy, each of which holds considerable potential to mitigate the deleterious impacts of fossil fuel consumption on both the environment and the climate.

Hydrogen can be an ideal candidate as future fuel because of the reasons that it has high gravimetric energy content (about 143 MJ Kg^{-1}) which can provide solutions for decarbonizing various sectors, such as long-haul and heavy-duty transport, chemicals, and iron and steel, where reducing emissions has been particularly challenging [1][2] . Additionally, it can enhance air quality and boost energy security. Climate change is a key driver for hydrogen in the energy transition. To limit global warming to below 1.5°C, CO_2 emissions must be reduced by approximately 25% by 2030 compared to 2010 levels, and reach net zero by around 2070 (IPCC, 2018) [3].

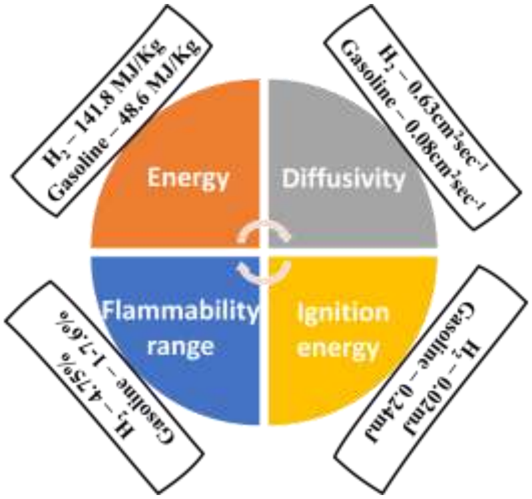

FIG 1. Comparison between properties of Hydrogen and Gasoline.

Hydrogen storage is a critical technology for advancing hydrogen and fuel cell technologies in automotive powertrains. Although hydrogen has the highest energy content per unit of mass compared to other fuels [4], [5], its low density at ambient temperature results in a relatively low energy density per unit of volume.

Hydrogen storage technologies can majorly divided into physical containment systems [6] , which store hydrogen in different states for transport and use [7]. These methods include:

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Compressed Gas Storage: Hydrogen is stored as a gas under high pressure, typically between 350 and 700 bar. This requires the use of durable, high-pressure tanks to maintain the gas in a stable and compact form [8].

Liquid Hydrogen Storage: Hydrogen is stored as a cryogenic liquid at extremely low temperatures of about −253°C, in specialized vessels called tanks. These systems usually operate at pressures below 5 bar to prevent the liquid from vaporizing.

Cryo-Compressed Gas Storage: This hybrid method combines cryogenic and high-pressure gas storage. Hydrogen is stored as a cold, compressed gas at around 20K (−253°C), and the system is designed to manage boil-off pressures of about 350 bar. Although still under development for automotive applications, this approach offers an efficient solution for in-vehicle storage [9][10].

In addition to physical storage, hydrogen can also be stored within or on the surface of solid materials through processes like absorption or adsorption[11][12]. Some of the most promising materials for these applications, particularly for vehicle integration, include:

Absorbents: Materials such as Metal-Organic Frameworks (MOFs), like MOF-5, are used to absorb hydrogen gas at relatively low pressures and temperatures, thanks to their high surface areas.

Chemical Hydrogen Storage: Hydrogen can be stored in chemical compounds, either in solid or liquid form, through covalent bonding. This method offers the potential for efficient and stable storage.

Interstitial Storage in Metal Hydrides: Metal hydrides (MH_x), which are alloys capable of absorbing and releasing hydrogen, represent a well-researched method for storing hydrogen in a solid, stable form. These materials store hydrogen within the interstitial spaces of the metal lattice, providing a compact and reversible storage solution.

Each storage method has its own set of advantages and challenges. Continued advancements in these technologies are essential for enabling the widespread adoption of hydrogen as a clean and efficient energy carrier.

II. METAL AMIDE SYSTEMS AS HYDROGEN STORAGE MATERIAL

Metal-N-H systems have gained significant attention as a new class of hydrogen storage materials, especially since Chen's report in 2002 [13]. These systems, which involve metal, nitrogen, and hydrogen interactions, have shown promises for efficient hydrogen storage due to their potential for high hydrogen density and reversible absorption and release of hydrogen [14].

To supress the ammonia, composites of amide with hydride are successfully demonstrated. so different composites of amide and hydride are made for higher hydrogen storage and high reversibility. Jain et al. demonstrated the ammonia suppression during decomposition of sodium amide by mixing sodium hydride [15] with it. It has been concluded that decomposition follows ammonia mediated reaction and other hydride namely LiH, KH, MgH_2 and CaH_2 have also been suitable to suppress ammonia during decomposition process.

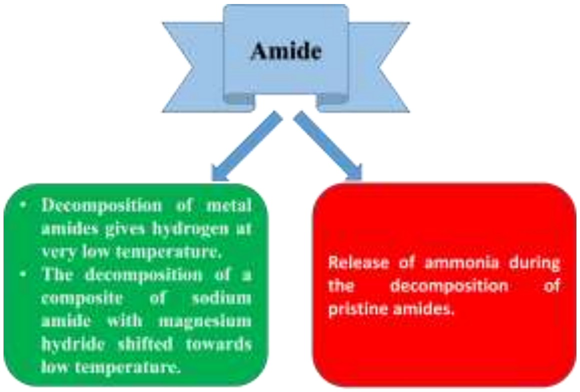

Fig 2. Advantages and disadvantage of amides to store hydrogen

A. Li-Mg-N-H systems

S.N.	Composites	Observations and Results
1.	$LiNH_2$ + MgH_2	On heating the composite 3.4 wt% hydrogen is desorbed peaks of ammonia is detected. formation of $Li_2Mg_2(NH_3)$ occurs
2.	$LiNH_2$ + LiH	6.5 wt% hydrogen is released during the desorption below 300°C

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3 .	$2LiNH_2$ + 2LiH	The desorption temperature of this composite us is found lower than $LiNH_2$ + LiH. .It is analysed that more ball milling gives less ammonia during decomposition. Stability on cycling with products.
4.	$Mg(NH_2)_2$ + LiH	Desorption started at 200° C release of ammonia at 150° C. $Li_2Mg_2N_2H_3$ if formed and on rehydriding only 0.5 wt% hydrogen uptake up to 210° C
5.	$Mg(NH_2)_2$ + 4LiH	On heating 4.5wt% hydrogen release upto 250° C and 6.5wt% H_2 release up to 600° C. Mg_3N_2 and Li_3N as products .
6.	$3Mg(NH_2)_2$ + 8LiH	Desorption temperature is higher as compare with others and 7wt% hydrogen is desorbed, hydrogenated under 30 bar H_2 and 200° C.

From above results , it can be seen that Li-Mg-N-H system is seen more efficient in kinetics and thermodynamics than $LiNH_2$- LiH system [16][17], [18], [19], [20]. since sodium is cheaper than lithium due to large abundance of sodium and sodium amide is less stable than lithium amide which can be seen from enthalpy of formation. This low stability should assist in release of hydrogen from amide hydride system containing sodium amide. so sodium is preferable over litium [21][22], [23].

B. Na-Mg-N-H systems

When $NaNH_2$ and MgH_2 were heated together in molar ratio 1:1. it can be seen from temperature programmed desorption mass spectroscopy, hydrogen was major gas desorbed with a very small amount of NH_3.The peak of desorption was observed at 155°C and the second desorption of major hydrogen release was peaked at 245°C. A total of 5.3 wt% hydrogen mass was released after heating to 350°C which is matched with theoretical mass loss of 5.4%. The rehydriding conditions was also observed on heating upto 300°C for 12 hours. Liu. et. al. investigated and found that the hydrogen desorption kinetics of Na containing reactions were improved upon Li-Mg-N-H system. Ammonia desorption was also supressed. As activation energy is low, sodium containing reactions desorbed hydrogen faster and at lower temperature [24][25].

When Sodium amide and Hydride are heated together in molar ratio 2:1, The decomposition of this composite gave hydrogen with very small amount of ammonia desorbed at peak of hydrogen desorption. Three major peaks of hydrogen release were observed at 155°C, 234°C and 316°C. When this composite was heated on a TGA-MS apparatus at rate of 2°C min^{-1} up to 350°C, no ammonia was observed. The mass loss from this composite while heating was 3.7 wt% which is close to theoretical of hydrogen capacity of 3.9 wt%. After hydrogenation the products are more hydrogen rich as compare to before when it is observed further heating at 300°C for 12 hours at 75 bar. Pireddu et al. [26] also investigated the $2NaNH_2 + MgH_2$ system and show that for thermally activated material at higher temperature new imide - amide phase is detected which is stable up to 300°C while for mechanochemical processing even at long milling there is no formation of new phases. The hydrogen release in mechanically activated sample starts already at 100° C [27].

The $NaNH_2$ and MgH_2 were heated in a 3:2 ratio, and a TPD-MS reaction was conducted to determine hydrogen desorbed like other $NaNH_2$-MgH_2 systems. The reaction showed hydrogen desorption, with a small amount of ammonia. The rate of desorption increased, peaking at 154°C and dropping at 243°C. At the same temperature as the initial hydrogen desorption, there was a very slight variation in the temperature trace. The temperature variations for the other $xNaNH_2 + yMgH_2$ reactions were identical to this. The variation was reflected in the furnace power suggesting the previously mentioned exothermic reaction. This suggested an exothermic occurrence. On TPD-MS, the first, sharp peak appeared at 181 °C, 30 °C after the first peak. Although the sample size was less than in the TPD-MS, a smaller amount of ammonia was released, which might not be detectable beyond the mass spectrometer's detection limit, but no ammonia was found in the TGA. At 350 °C, the heating was stopped. The products after TGA were Na and phase C along with remaining $NaNH_2$.There was no $MgNa_{2y}(NH)_{1+y}$ present here. This was

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the first time the presence of phase C was observed in the absence of $MgNa_{2y}(NH)_{1+y}$ [28].

When the composite $2NaNH_2$-$3MgH_2$ is heated, hydrogen trace showed desorption starts at 120℃ with a number of distinct peaks. The first peak is observed at 150℃ with less amount of hydrogen. Second peak is observed at 255℃. Rehydriding studies suggests that after rehydriding if was found to have absorbed 1.82wt% of hydrogen which was in comparison to a theoritical uptake of 2.6wt%. Singh et al. Studied mechanochmical transformations of $NaNH_2$ - MgH_2 mixtures in different molar ratios (2:3 and 2:1), they concluded that for a system with 2:3 molar ratio, 5% of Hydrogen is released and for molar ratio 2:1 no gaseous Hydrogen is released during milling. Dolotko et al. [30] investigated the $2MNNH_2$ -$3MgH_2$ (M=Li, Na) system. They concluded that dehydrogenation process could be described by following reaction:

$2MNH_2 + 3MgH_2 \rightarrow Mg_3N_2 + 2MH + 4H_2$

In both cases (either Li or Na) different intermediates arises. For M=Li, ($Li_2Mg(NH)_2$) and M = Na, $Na(Mg(NH_2)_2$ and $NaMgH_3$ are observed. The samples with Li atoms do not show good dehydrogenation properties [31], [32].

III. CONCLUSIONS

The metal–N-H systems can be a good candidate for hydrogen storage materials but the decomposition of pristine amide gives large amount of ammonia provides low hydrogen content and affects the reversibility. Thus, to reduce the ammonia evolution, composites of amide with hydrides are made and effective ammonia suppression can be seen. Different composites of lithium amide with hydrides are studied. As sodium is cheaper and more abundant than lithium, sodium amide is more preferred than lithium amide. In different molar ratios of sodium amide and magnesium hydride, the decomposition of composites is observed. Combined structure property investigations revealed that the transformations in the lithium containing system proceed in two steps. In the first step, lithium amide reacts with MgH_2 to form $Li_2Mg(NH)_2$ and hydrogen in the second step, reaction between $Li_2Mg(NH)$ and MgH_2 leads to the formation of the Mg_3N_2 nitride, lithium hydride and additional gaseous hydrogen. The transformation mechanism in the sodium containing system proceeds through a series of competing solid state processes in which $Mg(NH_2)_2$ and $NaMgH_3$ form as intermediates. By observing all the composites containing lithium and sodium amide with hydride in different ratios, Amide-Hydride system can be ideal candidate for hydrogen storage systems but many work is to be done on thermochemical properties, reversibility, suitable conditions and effective hydrogen storage.

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