REPORT ON HYDROGEN STORAGE
AND APPLICATIONS OTHER THAN TRANSPORTATION

Prepared by

FOREWORD

Storage forms an important link in the hydrogen utilization chain. There are many challenges to storing hydrogen in efficient, safe and cost-effective manner for a variety of applications like stationary power generation or on-board/mobile applications, mainly because hydrogen is a light gas and combustible. Hydrogen may be stored in gaseous form at high pressures at normal temperatures, in liquid form at cryogenic temperatures at normal pressures, and in chemically bound solid state at normal temperatures and pressures. These different storage modes are application dependent.

India is committed to contributing significantly to the climate change and has been giving utmost importance to the utilization of clean and renewable energy sources. In the light of this, hydrogen energy has also been a focus of attention. With this in mind, the Ministry of New and Renewable Energy, Government of India constituted a high power Steering Committee to prepare a status report and suggest the way forward for hydrogen energy and fuel cell technologies in India. One of the five sub-committees was entrusted under my Chairmanship with the responsibility of preparing this document concerning “Hydrogen Storage and Applications other than Transportation”.

I express my sincere thanks to all the members of the Sub-Committee who shared their immense expertise, Dr. M. R. Nouni, Scientist ‘G’, Ministry of New and Renewable Energy, and also other the officials of the Project Management Unit – Hydrogen Energy and Fuel Cells at the Ministry, especially Dr. Jugal Kishor and Dr. S. K. Sharma, for their active role in organizing meetings and preparing this document. It was my pleasure and honour working under the guidance of the Chairman of the Steering Committee, Dr. K. Kasturirangan.

30th June, 2016

(Prof. S. Srinivasa Murthy),
Chairman,
Sub-Committee on Hydrogen Storage and Applications other than Transportation
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I. Composition of Sub-Committee on Hydrogen Storage and Applications other than Transportation

1. Prof. S. Srinivasa Murthy, Indian Institute of Science, Bengaluru (Formerly Indian Institute of Technology Madras, Chennai) - **Chairman**


3. Dr. O. N. Srivastava, Emeritus Professor, Banaras Hindu University, Varanasi

4. Prof. L. M. Das (Retired on 30.06.2014 and engaged as Emeritus Professor), Indian Institute of Technology Delhi, New Delhi

5. Dr. B. Viswanathan, Emeritus Professor, Indian Institute of Technology Madras, Chennai

6. Dr. S. Aravamuthan, Sci. Engr. ‘H’ & Deputy Director, Vikram Sarabhai Space Centre, Indian Space Research Organization, Thiruvananthapuram

7. Shri R.S. Hastak, Outstanding Scientist and Director, Naval Materials Research Laboratory (Defence Research Development Organization), Ambernath

8. Dr. P. K. Tiwari, Bhabha Atomic Research Centre (BARC), Mumbai (Retired on 31.01.2015) and currently as Raja Ramanna Fellow at Professor Homi Bhabha National Institute, BARC, Mumbai

9. Dr. R. R. Sonde, Executive Vice President, Thermax India Limited, Pune - Representative of Confederation of Indian Industry

10. Dr. K. Balasubramanian, Director, Non-Ferrous Technology Development Centre, Hyderabad

11. Dr. Rajesh Biniwale, National Environment & Energy Research Institute, Nagpur

12. Dr. V. Shrinet, Electrical Research Development Association, Vadodara (Left)
13. Dr. R. Ramamurthi, Visiting Professor, Indian Institute of Technology Madras, Chennai & former Deputy Director, Liquid Propulsion System Centre, Indian Space Research Organization

14. Shri S. B. Menon, SO/G, Chemical Technology Division, Bhabha Atomic Research Centre, Mumbai

15. Dr. Hari Om Yadav, Scientist, Planning and Performance Division, DSIR, New Delhi - Representative of DSIR
I. Terms of Reference

1. To identify other applications of hydrogen and fuel cell technologies suitable for Indian conditions and suggest technologies relevant for such applications with their specifications.

2. To identify gaps in technology at national level compared to international status of the technologies and to suggest strategy for bridging the gaps quickly by developing in-house technologies with involvement of industries or acquiring technologies from abroad.

3. To review national and international status of hydrogen storage methods and suggest suitable strategies for on-board as well as stationary hydrogen storage for Indian conditions.

4. To identify technological constraints in developing suitable hydrogen storage materials to store adequate amount of on-board hydrogen for a given range of travel and accordingly suggest RD&D projects to be supported.

5. To identify institutes to be supported for augmenting infrastructure for development and testing of hydrogen storage materials / systems / other applications of hydrogen including setting-up of Centre(s) of Excellence and suggest specific support to be provided.

6. To provide recommendations for promoting use of surplus hydrogen for supplying back-up power to telecom towers and for captive power generation.

7. To examine use of light weight composite for on-board hydrogen / CNG storage and suggest the strategy to be adopted for indigenous production of such cylinders.

8. To re-visit National Hydrogen Energy Road Map with reference to other applications of hydrogen including storage.
Additional Terms of Reference suggested by the Steering Committee

- To identify technological constraints in developing suitable hydrogen storage materials to store adequate amount of on-board hydrogen for a given range of travel and accordingly suggest RD&D projects to be supported

- To provide recommendations for promoting use of surplus hydrogen for supplying back-up power to telecom towers and for captive power generation
III. Details of Meetings of Sub-Committee on Hydrogen Storage and Applications other than Transportation

The Sub-Committee on Hydrogen Storage and Applications other than Transportation met twice i.e. on 28.10.2013 and 03.07.2015 in the Ministry of New and Renewable Energy (MNRE). In the first meeting the expert members made presentations in the areas of their expertise and had detailed discussions. In the second meeting, the expert members presented and discussed write-ups, based on which draft report on Hydrogen Storage and Applications other than Transportation was prepared. The report, so prepared was presented in the 3rd meeting of the Steering Committee on Hydrogen Energy and Fuel Cells on 26.03.2015 in MNRE. As decided in this meeting, the next meeting was held with the selected members of the Sub-Committee on Hydrogen Storage and Applications other than Transportation and other Sub-Committees under the Chairmanship of Dr. K. Kasturirangan, Chairman, Steering Committee on Hydrogen Energy and Fuel Cells at the Raman Research Institute (RRI), Bengaluru on 22.07.2015 to discuss about on hydrogen storage aspects for specific applications. The draft report was modified as per suggestions given various meetings including the meeting (held on 11.09.2015, 16.12.2015 and 18.01.2016) of the Chairpersons of all five Sub-Committees on various aspects of hydrogen energy and fuel cells (viz. Hydrogen Production; Fuel Cell Development; Transportation through Hydrogen / Hydrogen Blend fueled Vehicles; Hydrogen Storage & other Applications; and IPR, Safety, Standards, PPP, Awareness & HRD).
EXECUTIVE SUMMARY
1.0 EXECUTIVE SUMMARY

PREAMBLE
1.1 The current global energy consumption is rapidly increasing together with the demand for primary energy sources/fossil fuels, thereby causing rapid depletion of these limited sources. The environmental pollution is also increasing with the consumption of fossil fuels, which is affecting the health of living beings on the earth. The influence of greenhouse gas emission on global warming is also well documented. Thus, energy security and environmental degradation are of global concern. The conventional / commercial energy sources are not likely to meet the energy demand which necessitates alternate energy sources. This has compelled to take initiatives to shift from carbon based to carbon neutral technologies like solar, hydro, wind, biomass & biofuel based technologies, etc.

1.2 Hydrogen has been widely recognized as an alternate energy carrier to address the three main concerns viz. energy security, environmental issues and peak energy demand. Currently, global hydrogen production is 48% from natural gas, 30% from oil, 18% from coal and 4% from water electrolysis. Several industries, especially the chlor-alkali, produce substantial amounts of hydrogen as byproduct. Hydrogen may also be produced from different kinds of urban and industrial wastes etc.

1.3 Safe and efficient storage and delivery of hydrogen is essential for the success of hydrogen economy. Hydrogen can be stored by the following ways:-
(i) High-pressure gas cylinders (up to 800 bar)
(ii) Liquid hydrogen in cryogenic tanks (at 21°K)
(iii) Physisorbed hydrogen on materials with a large specific surface area
(iv) Chemisorbed on interstitial sites in host metals and Inter-metallics
(v) Chemically bonded in covalent and ionic compounds
(vi) Oxidation of reactive metals such as. Li, Na, Mg, Al, Zn with water.
A comprehensive list of hydrogen storage technologies is given in Table 1.1.
Table 1.1: Various Hydrogen Storage Technologies and Their Main Characteristics (Handbook of Hydrogen Energy, CRC Press, 2015)
STORAGE TECHNOLOGIES

Gas Storage
1.4 Hydrogen is generally stored as gas in compressed form because it is very light with low density of 0.084 kg/m$^3$. The energy content of hydrogen gas at ambient pressure and temperature is 10 MJ/m$^3$, which demands extremely large volume for hydrogen storage. The conventional hydrogen storage tank is significantly heavier than hydrocarbon storage tank for storing the equal amount of energy. Hydrogen storage needs special attention due to embrittlement (caused by hydrogen diffusion being smallest molecule in size) of materials of construction of pressure vessels. Therefore, it becomes necessary to use special alloys or composite fiber reinforced containers. Compressed gas storage also poses issues of high potential energy and safety hazards due to possibility of explosion of pressure vessels. However, it is possible to have necessary safety practices with suitable blast walls and monitors/sensors and ensure compatible and safe high pressure storage bottles. Hydrogen is being stored in gaseous form on-board for transportation applications, with focus primarily on the driving range of 500 km. Some automakers have demonstrated their prototype vehicles qualifying this range.

1.5 Hydrogen in compressed mode has been widely used in on-board mobile applications like in the vehicles for road transportation, stationary application for dispensing hydrogen at re-fueling stations and at sites for stationary power generation. Hydrogen, while storing at high pressures reacts with the materials of construction of containers and makes them brittle; therefore, the containers are made of special alloys and also with reinforced composite carbon fiber. Currently, hydrogen is being stored in compressed form at 350 bar (5,000 psi) in on-board in demonstration vehicles and 700 bar (10,000 psi) in Type IV carbon composite cylinders. Carbon composite cylinders to store hydrogen at 700 bar (10,000 psi) are not being manufactured in the country.
**Liquid Storage**

1.6 Storage and transportation of hydrogen as a liquid is another possibility. The cryogenic hydrogen is to be stored in specially insulated vessels at \(-252.88^0C\). The energy required to liquefy hydrogen (gas at 300ºK and 1 bar pressure) is about 47 MJ / kg of hydrogen. The energy also is dependent on the size of the plant. With improved technologies and small plants involving magnetic regenerative liquefaction about half of this energy may be adequate. Thus, energy required for bulk storage and transport cryogenic liquid hydrogen gas can be about 10 to 20% lower. Like hydrogen in gaseous form, the liquid hydrogen also has tendency to diffuse into the material of construction at high pressures and make them brittle. To check this problem of embrittlement, the storage vessels may be made of FCC (as material of construction) with special insulation, comprising double walled with vacuum in between, opacifiers and multi-layer insulations.

1.7 Hydrogen can be stored in liquid form in cryogenic conditions. So far, LH2 application has been mainly in space application. These forms of storage are not suitable for widespread commercial application. Liquid organic hydrides are also potential candidates for hydrogen storage and delivery. The concept has been demonstrated successfully at laboratory level. Pilot level studies demonstrate the efficacy of the system and possibilities of up-scaling. Considerable work has also been carried out at National level leading to generation of IPR for country. Further work is being conducted and expected to be supported by government/industry may lead to development of a technology for safe hydrogen storage and delivery at near ambient conditions for long distance transportation. In order for the hydrogen program to be successful in India, development of required testing facilities, standards codes and regulations for cylinders, components, vehicles and fuel need to be developed in line with international regulations.
Solid State Storage

1.8 Solid state storage of hydrogen is a much safer and efficient method than pressurized or cryogenic storage of hydrogen. The basic parameters of hydrogen storage materials as targeted by Department of Energy (DoE), USA are given in Table 1.2.

Table 1.2: Hydrogen Storage Targets Specified by US DoE

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Target Year</th>
<th>2010</th>
<th>2015(old)</th>
<th>2015(new)</th>
<th>2020*</th>
<th>Ultimate Full Fleet</th>
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<tr>
<td>Gravimetric Capacity (Specific energy)</td>
<td>2010</td>
<td>2.0 kWh/kg</td>
<td>0.060 kg H₂/kg</td>
<td>3.0 kWh/kg</td>
<td>0.090 kg H₂/kg</td>
<td>1.8 kWh/kg</td>
</tr>
<tr>
<td>Volumetric Capacity (Energy Density)</td>
<td>1.5 kWh/L</td>
<td>0.045 kg H₂/L</td>
<td>2.7 kWh/L</td>
<td>0.081 kg H₂/L</td>
<td>1.3 kWh/L</td>
<td>0.040 kg H₂/L</td>
</tr>
<tr>
<td>Storage system cost</td>
<td>$4 /kWh</td>
<td>$2 /kWh</td>
<td>-</td>
<td>$10 /kWh</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>System Cost:</td>
<td>$ 666</td>
<td>$ 333</td>
<td>-</td>
<td>$ 333</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Refueling rate</td>
<td>1.5 kg H₂/min</td>
<td>2.0 kg H₂/min</td>
<td>1.5 kg H₂/min</td>
<td>1.5 kg H₂/min</td>
<td>2.0 kg H₂/min</td>
<td></td>
</tr>
<tr>
<td>Refueling Time:</td>
<td>3.3 min</td>
<td>2.5 min</td>
<td>3.3 min</td>
<td>3.3 min</td>
<td>2.5 min</td>
<td></td>
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The new “Ultimate Full Fleet” targets are similar in philosophy to the previous 2015 targets in that they represent the hydrogen storage system performance that is required for full vehicle penetration into the light-duty market across a broad range of makes and models. The “Ultimate Full Fleet” targets also approximate current gasoline ICE vehicle systems for packaging volume across the most demanding vehicle platforms. While the “Ultimate Full Fleet” targets allow increases in weight and volume compared to current vehicle fuel tank systems, these increases are manageable across the range of light-duty vehicle platforms. Storage systems that can meet the “Ultimate Full Fleet” targets would therefore have driving ranges that are competitive with most of the current ICE vehicle fleet.

1.9 While literally hundreds of intermetallic alloys have been prepared and their hydrogenation potentials assessed, relatively few have the right combination
of properties that permit their use for hydrogen storage or other applications. The most viable candidates include alloys with the following compositions: A2B (e.g., Mg2Ni), AB (e.g., TiFe), AB2 (e.g., ZrMn2) and AB5 (e.g., LaNi5). A key advantage of many intermetallic alloys is the ability to alter their hydrogen sorption behavior by substitution for either or both the A and B metals that often improve their performance in various applications.

A variety of solid-state hydrogen storage materials viz. MgH2, Mg2NiH4, NaAlH4, other alanates, borohydrates (gravimetric capacity of >7wt%), commercial hydrides such as FeTiH2 and LaNi5H6, adsorbents like carbon, nanostructured carbons (including CNTs) MoFs and hydrogen clathrate hydrate have been investigated for hydrogenation and dehydrogenation reaction conditions and their kinetics, retention of cycling capacity, susceptibility to impurities and reversible capacities. The need for material with practical operative conditions of pressure (1-10 bar) and temperature (300°C-100°C) has simulated the interest of many researchers. Other major areas of research are improvement of kinetics of hydrogen uptake/release and enhancement of cycling capacity.

1.10 Pure hydrogen physisorption has been demonstrated at cryogenic temperatures (up to ca. 6 wt% H2) for which extremely high surface area carbon is required. Pure atomic H-chemisorption has also been demonstrated to ca. 8 wt% H2, but the covalent-bound H is liberated only at impractically high temperatures (above ca. 400°C). The activated carbon materials made from carbon nanotubes, graphite nanofibers, known as next generation of energy systems are capable of storing hydrogen. For example, porous carbons with a specific surface area of 3220 m²/g are capable of storing hydrogen of 1.3 wt% at room temperature.

1.11 Nanostructured systems including carbon nanotubes, nano-magnesium based hydrides, complex hydride / carbon nanocomposites, boron nitride nanotubes, sulphide nano-tubes of titanium and molybdenum, alanates, polymer
nanocomposites, and metal organic frameworks are considered to be potential candidates for storing large quantities of hydrogen. The synergistic effects of nanocrystallinity and nanocatalyst doping on the metal or complex hydrides improve thermodynamics and hydrogen reaction kinetics. In addition, various carbonaceous nanomaterials and novel sorbent systems (e.g. carbon nanotubes, fullerenes, nanofibers, polyaniline nano-spheres and metal organic frameworks etc.) and their hydrogen storage characteristics are considered. In spite of these consistent and persistent efforts, these materials are yet to satisfy the required characteristics like storage capacity of around 6 weight percent, favourable and tuning thermodynamics around 30-55 KJ/mol of hydrogen and temperature of operation around 373 K with about 1000s of cycles of operation.

**Emerging Storage Technologies**

1.12 Liquid organic hydrides consisting of various cycloalkanes can conveniently be transported from one place to another. These hydrides may be prepared by the reaction of hydrogen with toluene under specific conditions. Hydrogen and toluene may be recovered by the dehydrogenation of the cyclohexane at or near fueling stations for dispensing hydrogen into vehicles / other applications. Toluene is transported back for reuse. The advantage associated with these organic hydrides is higher storage capacity of hydrogen, which is more than 6 wt% and 60 kg/m$^3$.

1.13 Compressing hydrogen inside hollow glass microspheres or microcapsules has been suggested to give high volumetric storage densities. Loading and unloading of hydrogen gas in and out is based on the fact that gas permeation through the solid shell increases exponentially with temperature. Hollow microspheres are also called microcapsules, microcavities, microbubbles, or microballoons. Hydrogen storage in hollow glass microspheres presents several advantages. First, hollow microspheres have high gravimetric energy density. Hydrogen can be stored under internal pressure higher than that inside
conventional cylinders. Hydrogen-filled hollow glass microspheres are also easy and safe to handle at atmospheric pressure and ambient temperature and can be poured or pumped in tanks of any arbitrary geometries made of lightweight materials. The technology is inexpensive and requires low energy consumption for producing large quantities of micro containers.

**DESIGN CONSIDERATIONS**

In order to achieve the optimum performance from a hydrogen storage material in a given application, comprehensive system engineering must be carried out with respect to the vessel design as well as the physical, chemical and thermos-physical properties of the storage media and the components that are used to enhance heat and mass transfer during both the charging and discharging operations.

1.14 In addition to meeting high degrees of safety, efficiency and cost effectiveness, the main challenge in all hydrogen storage systems design is to meet the following basic requirements:

a) The **weight and volume** of hydrogen storage systems are presently too high compared to conventional petroleum-fueled vehicles. Use of lightweight materials and components are needed to enable more than 300-mile range for the light-duty vehicles.

b) Optimized **Thermal and Mechanical Design** of the reactor ensures that the storage capacity and kinetics are well balanced for a given application. High efficiencies coupled with low total weights should be achieved by proper design practices.

c) **Energy efficiency** is a challenge for all hydrogen storage approaches. The energy required to get hydrogen in and out is an issue for reversible solid-state materials. The energy associated with compression and liquefaction must be considered for compressed and liquid hydrogen technologies.
d) **Durability** of hydrogen storage systems is required with a lifetime of 1500 cycles.

e) **Refueling time** may be targeted to less than three minutes.

f) **Cost** of on-board hydrogen storage systems is too high, particularly in comparison with conventional storage systems for petroleum fuels. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.

g) Applicable **codes and standards** for hydrogen storage systems and interface technologies, which will facilitate implementation / commercialization and assure safety and public acceptance, are to be established.

**APPLICATIONS OTHER THAN TRANSPORTATION**

1.15 Energy storage in the form of hydrogen obtained by electrolysis from wind power has been demonstrated at the Electric Research Development Association, Vadodara under a project supported by MNRE. This demonstration encouraged to scale up wind hydrogen system particularly for remote locations such as villages, islands. India also can explore possibility of acquiring this technology (especially high pressure alkaline electrolyser). In addition, feasibility of such projects in India may be studied in collaboration with stake holders like Oil and Natural Gas Commission (ONGC), Gas Authority of India Limited (GAIL), and PGCIL, Utilities, Central Electricity Authority (CEA). Projects for demonstration of MW scale wind hydrogen system may be taken-up.

1.16 Hydrogen has the potential to replace LPG and CNG for cooking because it has superior characteristics to LPG and PNG fuel in terms of ignitability, low ignition delay and higher flame stability. A special design of fuel distribution would be required for reasonable mixing of hydrogen with ambient air entering at the bottom of the catalyst body. Therefore, a catalytic burning of the hydrogen in the home cooker is the best way to use the hydrogen for cooking. Several catalysts such as metals like Cu, Zn, Fe, Ni, Co; alloys like Co-
Mn-Ag; storage alloys like MmNi₅, ZrFe₂ can dissociate H₂. There are two catalytic techniques, which are relevant to hydrogen fueled catalytic cookers. One is use of porous ceramic plate embedded with platinum in pores. This produces flameless situation. Under the project supported by MNRE, BHU Group has targeted development of catalysts including new catalysts for hydrogen catalytic combustion cooker, synthesis and development of hydride of choice, development and optimization of hydrogen catalytical combustion cooker, optimization of safety aspects of hydrogen catalytic combustion cooker, etc. However, safety related issues for handling H2 in Domestic Sectors must be addressed.

1.17 Utilizing the exothermic and endothermic processes during sorption and desorption of hydrogen respectively in metal hydrides, highly efficient, compact and cost-effective chemi-sorption thermal energy storage devices can be developed. This could significantly contribute to the widespread utilization of solar thermal energy. Such demonstration systems suitable for small capacity ORC power packs are being studied at IISc-Bangalore.

1.18 The hydrogen chemisorption – desorption heat exchanges during the hydrogen sorption process in metal hydrides can also be utilized to develop a variety of thermal devices, especially refrigeration and heat pump systems. The temperatures can range from cryogenic to very high values. For example, exhaust heat operated automobile airconditioners have been built by several agencies. One such prototype was developed by IIT Madras in collaboration with Thermax.

**SUGGESTED ACTION PLANS**

Action plans stretch up to 2022 in phases.
1.19 High Pressure Hydrogen Gaseous Storage: CNG cylinders may be deployed in demonstration fleets of vehicles up to a pressure of 200 bar. For pressure more than 200 and up to 400 bar, hydrogen cylinders may be imported for the vehicle like buses and trucks. Such 50 vehicles may be taken up for public demonstration. Simultaneously, 500 to 1000 hydrogen fueled vehicles be prepared in about 5 to 8 years for large scale demonstration. Consortium collaboration approach may be followed among HINDALCO, Indore; NPL, New Delhi; IOCL Nasik and BHEL (Hyderabad) to produce Al cylinders reinforced with carbon fibre tapes and other high strength wrappings. This consortium may prepare 50 such high pressure cylinders up to 400 bar and test them.

1.20 Solid State Storage (Metal, Intermetallic and Complex Hydrides): Production of optimized, well known and already deployed Mischmetal based hydride (India has one of the largest Mischmetal deposits in the world) e.g. Mm-Ni-Fe may be taken up on pilot plant level (100 kg to 1 Ton Level) and simultaneously, its demonstration in the vehicles for on-board applications in around 50 three wheelers (hydride requirement around 2000 kg); 10 small cars (hydride requirement around 500 Kg).

1.21 Solid State Storage (Metal, Intermetallic and Complex Hydrides): The off-board (Stationary) application for power generation in around 1000 Gen-Sets of 5-15 kW capacity (required hydride quantity 10 Tons) may be deployed. R&D efforts may be intensified for obtaining gravimetric and volumetric efficiencies of 5 to 6 wt% and 60 kg/m$^3$ for metal hydrides particularly catalyzed MgH$_2$ and gravimetric efficiency of 3 to 6 wt% for other intermetallic hydrides e.g. Zr Fe$_2$, Mg$_2$Ni type. R&D efforts may be upgraded for evaluation of reproducible high efficiencies 5 to 6 wt% in complex hydrides with particular emphasis on catalyzed MgH$_2$, NaAlH$_4$, LiAlH$_4$, NaAlH$_4$-MgH$_2$, Li-Mg-N-H system. Enhancement of R&D efforts are required to increase hydrogen storage capacity from 1 to 3 wt% at ambient conditions and 5 to 8 wt% at Liquid N$_2$ temperature in nano/porous carbons.
1.22 Intensive developmental efforts may be taken up on Liquid Hydrides. Petroleum industry may also be networked to support the pilot runs. There is need to support R&D projects for further development of selective and stable catalysts. A demonstration may be done by setting up pilot facilities near a refinery and providing hydrogen to telecom towers in the range of 50 to 100 Km.

1.23 An Interdisciplinary, Inter-Institutional Center may be set up to evaluate the thermodynamic, thermophysical and kinetic properties, cyclic stability, performance augmentation based on mechanical and thermal design of solid state storage devices. Testing and certification of such devices should also be done by this facility.

1.24 Development of miscellaneous energy related applications of hydrogen such as High Intensity Thermal Energy Storage and Heat Pump/Heat Transformer may be encouraged at the Institutions which have shown the feasibility, through demonstration projects.

1.25 Action plan may include efforts for the development, distribution and monitoring of 1000 to 10,000 hydrogen fueled home cookers. It will sensitize the public and this may be followed by 25% to 50% replacement of LPG by hydrogen through manufacturing and use of home cookers through public-private partnership.

1.26 Further developments on High Pressure Hydrogen Gaseous Storage may be taken up based on the feedback received about the cylinders, 1,000 nos. may be procured from the companies abroad and 9,000 nos. may be manufactured by Bharat Pumps and Compressors and other similar companies in India. Efforts are to be made to have 100% indigenous production during 2020-2035. These cylinders may be used in hydrogen fueled 3 wheelers, buses, vans, cars and in stationary systems like power generating system (>10kW) around 1000 IC
engine Gen Sets and 500 in fuel cells power generating systems. Area-wise replacement of 50% diesel Gen Sets (10kW and higher) may be taken-up in crowded areas in the country. Efforts may be made to use such vehicles and Gen Sets to reach at least 30% of the total such devices in specific cities.

1.27 Solid State Storage (Metal, Intermetallic and Complex Hydrides): Manufacturing of mischmetal based hydrides on pilot plant scale (1 Ton) may be taken up. These may be manufactured on large scale for (i) on-board applications in 500 three wheelers and 150 cars (ii) stationary application in 1000 Gen-Sets of 5 to 15 kW capacity and 500 fuel cells vehicles with 5 kW to 15kW fuel cells systems. The non- mischmetal based viable intermetallic hydride developed out of R&D efforts in Phase-I may be picked-up for initiation of manufacturing at pilot plant level (1 to 10 Tons). R&D efforts may be intensified on Mg/MgH$_2$ hydrides to produce large quantities (100kg to 1 ton), to decrease desorption, absorption temperature to about 200$^\circ$C through the use of effective catalysts, to enhance the desorption / absorption kinetics, to improve recyclability from 100 to 1000 cycles through Mg agglomeration checking systems, to develop MgH$_2$ based vehicular transport, to optimize gravimetric and volumetric efficiencies of complex hydrides (catalyzed NaAlH$_4$, Mg (AlH$_4$)$_2$, LiAlH$_4$ types) coming out of R&D in phase-I, to evaluate reversibility and cyclability, to adopt PEM fuel cell instead of IC Engines for 25% of the above said vehicles, to enhance hydrogen storage in nano/porous carbon and to use it in small vehicles.

**CONCLUDING REMARKS**

1.28 Storage, Transportation and Distribution of hydrogen are important for the success of ‘Hydrogen Economy’. Traditional methods of storage may not be directly applicable for use of hydrogen as a ‘fuel’. The technologies and devices should satisfy various stringent requirements such as; safety, economy, efficiency, flexibility, durability and environmental / ecological standards. The
abovementioned actions can go a long way in facilitating the widespread use of hydrogen in our country.
### ACTIVITIES ON HYDROGEN STORAGE & OTHER APPLICATIONS

**MMP:** Mission Mode Projects; **RD&DP:** Research & Development Projects;  
**B/FRP:** Basic / Fundamental Research Projects

<table>
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<th>Category of Projects</th>
<th>Time Frame (Year)</th>
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<td>Phase III (Large Capacity up to 250 kW)</td>
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<td><strong>SUBTOTAL</strong></td>
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<td><strong>Grand Total</strong></td>
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INTRODUCTION
2.0 INTRODUCTION

2.1 Our current global energy consumption is rapidly increasing and while our primarily energy sources (fossil fuels) are rapidly depleting. Furthermore, the pollution and climate change represent undesirable side effects of global concern. To meet these major challenges, it is needed to shift from carbon-based non-renewable resources to carbon-neutral renewable sources of energy. The possible alternative renewable sources of energy are solar, hydroelectric, wind power, biofuels, etc. The major drawback in all these cases is that periods of peak energy production do not necessarily coincide with periods of peak energy consumption. Therefore a complete transition to such an alternative energy source relies on efficient capture, conversion and storage, which is currently being explored worldwide. In this context, Hydrogen has been considered as the fuel of the future and an environmentally friendly alternative to depleting fossil fuels. It can be created by splitting water into oxygen and hydrogen with many clean renewable energy sources and when used the products are energy and plain water again. The retrievable energy can be used in conventional combustion, powering cars, heating houses, etc. or be used together with fuel cells to produce electricity in large or small scale. Hydrogen has very high energy content per kilogram, almost three times higher than gasoline. Hydrogen can be an environmentally cleaner source of energy to end-users, particularly in transportation applications, without release of pollutants (such as particulate matter) or carbon dioxide at the point of end use. The technical obstacles in hydrogen economy are hydrogen storage issues and the purity requirement of hydrogen used in fuel cells – with current technology, an operating fuel cell requires the purity of hydrogen to be as high as 99.999%. Currently, global hydrogen production is 48% from natural gas, 30% from oil, and 18% from coal; water electrolysis accounts for only 4%.

Hydrogen exhibits the highest heating value per mass of all chemical fuels. Furthermore, hydrogen is regenerative and environmentally friendly. There
are two reasons why hydrogen is not the major fuel of today’s energy consumption. First of all, hydrogen is just an energy carrier and, although it is the most abundant element in the universe, it has to be produced, since on earth, it only occurs in the form of water and hydrocarbons. This implies that we have to pay for the hydrogen energy, which results in a difficult economy. The second difficulty with hydrogen as an energy carrier is its low critical temperature of 33 K (i.e. hydrogen is a gas at ambient temperature). For mobile and in many cases also for stationary applications the volumetric and gravimetric density of hydrogen in a storage material is crucial.

2.2 The storage and transportation of hydrogen remains a major challenge in realizing hydrogen economy. Different strategies for hydrogen storage have been developed.

Hydrogen can be stored using six different methods and phenomena: (1) high-pressure gas cylinders (up to 800 bar), (2) liquid hydrogen in in dewars or cryogenic tanks (at 21K), (3) adsorbed hydrogen on materials with a large specific surface area adsorbents (Zeolites, Carbon materials and porous coordination polymers or Metal-Organic Frameworks) (at T<100 K), (4) absorbed on interstitial sites in a host metal (at ambient pressure and temperature), (5) chemically bonded in covalent and ionic compounds (at ambient pressure), and (6) through oxidation of reactive metals, e.g. Li, Na, Mg, Al, Zn with water.

Hydrogen storage can broadly be divided into two categories, 1. Physical Storage and 2. Chemical Storage. The physical storage, i.e., storage of hydrogen in molecular form, includes storage in the form of compressed gas, hybrid tanks and liquid/cryogenic storage (Figure 2.1). The chemical storage involves reversible methods main metal hydrides, whereas the other non-reversible chemical storage forms are reformed, hydrolyzed or decomposed fuel (Figure 2.1). Table 2.1 gives a comprehensive list of different hydrogen storage technologies.
Table 2.1: Various Hydrogen Storage Technologies and Their Main Characteristics (Handbook of Hydrogen Energy, CRC Press, 2015)
However, no system reported so far has met the targets set by US DOE for on-board applications of H₂.

2.3 The recent study "The Future of the Hydrogen Economy" analyzes the physics of the Hydrogen Economy. In particular, the energy required to package, distribute, store and transfer hydrogen is assessed. A particularly daunting
challenge facing its use in transportation, however, is the development of a safe and practical storage system. As opposed to stationary storage, in which the tank volume and mass are less of a concern, storage of large quantities of \( \text{H}_2 \) in a passenger car, for which volume, mass, and heat exchange are of utmost importance. The molecular hydrogen has very high energy density on a mass basis, because of its low molecular weight, as a gas at ambient conditions it has very low energy density by volume. If it is to be used as fuel stored on board the vehicle, pure hydrogen gas must be pressurized or liquefied to provide sufficient driving range. Increasing gas pressure improves the energy density by volume, making for smaller, but not lighter container tanks. Achieving higher pressures necessitates greater use of external energy to power the compression. Alternatively, higher volumetric energy density liquid hydrogen or slush hydrogen may be used. However, liquid hydrogen is cryogenic and boils at 20.268K (–252.882°C). Cryogenic storage cuts weight but requires large liquefaction energies. The liquefaction process, involving pressurizing and cooling steps, is energy intensive. Liquid hydrogen storage tanks must also be well insulated to minimize boil off. Ice may form around the tank and help corrode it further if the liquid hydrogen tank insulation fails. Currently most common method of on board hydrogen storage in today’s demonstration vehicles is as a compressed gas at pressures of roughly 700 bar (70 MPa). The mass of the hydrogen tanks needed for compressed hydrogen reduces the fuel economy of the vehicle. Hydrogen tends to diffuse through any liner material intended to contain it, leading to the embrittlement or weakening of its container. In all cases, the containment vessel contributes at least 90% of the system mass, but there is still room for improvement with respect to the maximum pressure that can be maintained (operation at 825 bar is now being demonstrated or the minimization of liquid boil-off in cryogenic systems).

2.4 Hydrogen as an energy carrier

Hydrogen is an energy carrier rather than a primary energy source. It is
therefore not generally suited for an efficient utilization based on a “well to wheel” basis. Though hydrogen is available in plenty in nature around us and constitutes almost 75% of matter in the universe, it exists invariably in a form which is combined with other elements. We lost the element hydrogen in the early part of the Earth’s evolution due to the molecular velocity of the heated hydrogen being higher than what the Earth’s gravitational field could hold.

If hydrogen were to be used in the combined form that it is available in nature, the oxygen or carbon or the other elements in water, hydrocarbon, etc. needs to be first isolated or removed and the hydrogen could be employed as an energy source. Work is therefore pursued to generate hydrogen from water by different processes and so far they have been somewhat energy intensive. Hydrogen combined with carbon as hydrocarbon is a very good energy source since both the hydrogen and the carbon in it contribute to energy. However, carbon in hydrocarbon leads to pollution and formation of global warming CO₂. This is especially true if the bonds between the hydrogen and carbon atom in the hydrocarbon gets to be more complex than the simple single or double bond. If hydrogen can be isolated from the hydrocarbon and used to generate energy by its oxidation to water, the product water could be reused again to from more hydrogen. We therefore have hydrogen as a renewable energy. Care should be taken that the temperature of the oxidation process of hydrogen is kept rather low such that oxides of hydrogen especially N₂O, which is even a stronger global-warming gas and pollutant than CO₂, is not formed.

Hydrogen is a clean source of energy, if burnt with air at relatively low temperatures or if used to generate power directly using fuel cells. The latter is particularly attractive considering the near reversible process and relatively higher thermodynamic efficiencies. The energy so generated can be used for doing work in different propulsive applications or simply for generating power.
Hydrogen is an energy carrier like electricity and we can think of generating hydrogen at a source from water, hydrocarbon or other substances containing it and transporting it to the place where energy is required. The energy carrier hydrogen is stored at the point of its production, moved or transported to the point of application where it delivers its energy. It has one advantage over electricity as an energy carrier in that it can be stored. In fact, the excess electrical energy generated from hydroelectric power generation in Quebec in Canada has been used to generate hydrogen. Similarly the excess wind energy which is available during some seasons can be used to produce hydrogen which thereafter can be used to generate power.

When power requirements are phenomenal but the high power is required only for a short period of time, hydrogen comes to the rescue. The hydrogen generated over a prolonged period is used up in a short period of time during which the energy requirements are very intensive.

### 2.5 Storage and transportation of hydrogen

Hydrogen formed by different means say the “reforming” of hydrocarbon or electrolysis of water or any other biochemical process or otherwise is invariably produced as a gas. The gas is very light with a density of 0.084 kg/m$^3$ which is about $1/10^{th}$ of the lightest hydrocarbon gas methane. The energy available per unit volume of the stored hydrogen gas is compared with crude oil and other low grade fuels such as dry wood in the Table 2.2.

Table 2.2: Volumetric energy content per cubic meter of some fuels

<table>
<thead>
<tr>
<th>Substance</th>
<th>Energy in MJ/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen gas at ambient pressure and temperature</td>
<td>10</td>
</tr>
<tr>
<td>Crude oil</td>
<td>37,000</td>
</tr>
<tr>
<td>Coal</td>
<td>42,000</td>
</tr>
<tr>
<td>Dry wood</td>
<td>10,000</td>
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</tbody>
</table>
The very low volumetric energy content of hydrogen demands extremely large volumes of gas holders at the source of its production if any meaningful storage of energy is desirable at ambient pressure. Even if stored at very high pressures of about 50 MPa (about 500 bars) and room temperature, the energy available is less than that in dry wood. The storage of hydrogen at high pressures is also not straightforward due to hydrogen embrittlement of materials used in the construction of pressure vessels; it becomes necessary to use special alloys or composite fiber reinforced cases.

Compressed gas storage also poses issues of high potential energies and safety hazards due to explosion. However, it is possible to institute necessary safety practices with suitable blast walls and monitors/sensors and ensure compatible and safe high pressure storage bottles. Storage and transportation of hydrogen in liquid or solid state may be simpler and advantageous especially from safety aspects.

2.6 Targets for storage capacity

Onboard hydrogen storage for transportation applications continues to be one of the most technically challenging barriers to the widespread commercialization of hydrogen-fueled light-duty vehicles. The DOE Office of Energy Efficiency and Renewable Energy (EERE), Fuel Cell Technologies (FCT) Program’s hydrogen storage activity focuses primarily on the applied research and development (R&D) of low-pressure, materials-based technologies to allow for a driving range of greater than 500 km while meeting packaging, cost, safety, and performance requirements to be competitive with comparable vehicles in the market place. While automakers have demonstrated progress with some prototype vehicles traveling greater than 500 km on a single fill, this driving range must be achievable across different vehicle makes and models and without compromising customer expectations of space, performance, safety, or cost.
The DOE Hydrogen Program website and the FCT Program’s Multi-Year Research, Development, and Demonstration Plan contain further information on the Program and its objectives. The new “Ultimate Full Fleet” targets are similar in philosophy to the previous 2015 targets in that they represent the hydrogen storage system performance that is required for full vehicle penetration into the light-duty market across a broad range of makes and models. The “Ultimate Full Fleet” targets also approximate current gasoline ICE vehicle systems for packaging volume across the most demanding vehicle platforms. While the “Ultimate Full Fleet” targets allow increases in weight and volume compared to current vehicle fuel tank systems, these increases are manageable across the range of light-duty vehicle platforms. Storage systems that can meet the “Ultimate Full Fleet” targets would therefore have driving ranges that are competitive with most of the current ICE vehicle fleet. The DoE targets are given in the Table 2.3.

Table 2.3 : US DoE Targets for Hydrogen Storage

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Target Year</th>
<th>2010</th>
<th>2015(old)</th>
<th>2015(new)</th>
<th>2020*</th>
<th>Ultimate Full Fleet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Capacity</td>
<td></td>
<td>2.0 kWh/kg</td>
<td>3.0 kWh/kg</td>
<td>1.8 kWh/kg</td>
<td>1.8 kWh/kg</td>
<td>2.5 kWh/kg</td>
</tr>
<tr>
<td>(Specific energy)</td>
<td></td>
<td>0.060 kg H₂/kg</td>
<td>0.090 kg H₂/kg</td>
<td>0.055 kg H₂/kg</td>
<td>0.055 kg H₂/kg</td>
<td>0.075 kg H₂/kg</td>
</tr>
<tr>
<td>Volumetric Capacity</td>
<td></td>
<td>1.5 kWh/L</td>
<td>2.7 kWh/L</td>
<td>1.3 kWh/L</td>
<td>1.3 kWh/L</td>
<td>2.3 kWh/L</td>
</tr>
<tr>
<td>(Energy Density)</td>
<td></td>
<td>0.045 kg H₂/L</td>
<td>0.081 kg H₂/L</td>
<td>0.040 kg H₂/L</td>
<td>0.040 kg H₂/L</td>
<td>0.070 kg H₂/L</td>
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<tr>
<td>Storage system cost</td>
<td></td>
<td>$4 /kWh</td>
<td>$2 /kWh</td>
<td>To be decided</td>
<td>$10 /kWh</td>
<td>To be decided</td>
</tr>
<tr>
<td>System Cost:</td>
<td></td>
<td>$ 666</td>
<td>$ 333</td>
<td>To be decided</td>
<td>$ 333</td>
<td>To be decided</td>
</tr>
<tr>
<td>Refueling rate</td>
<td></td>
<td>1.5 kg H₂/min</td>
<td>2.0 kg H₂/min</td>
<td>1.5 kg H₂/min</td>
<td>1.5 kg H₂/min</td>
<td>2.0 kg H₂/min</td>
</tr>
<tr>
<td>Refueling Time</td>
<td></td>
<td>3.3 min</td>
<td>2.5 min</td>
<td>3.3 min</td>
<td>3.3 min</td>
<td>2.5 min</td>
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HYDROGEN STORAGE TECHNOLOGIES
HYDROGEN STORAGE IN GASEOUS STATE
3.0 HYDROGEN STORAGE IN GASEOUS STATE

3.1 Introduction

3.1.1 Storage of gaseous Hydrogen at elevated pressure is indeed a necessity, as a primary or supporting storage, given the fact that almost all energy conversion applications of the fuel requires that the fuel is available in gaseous state. The well-known industrial gas storage at around 150 bar in heavy steel / aluminium cylinders is indeed the method in vogue currently. With the advent of storing large quantities of hydrogen for multitude of applications including on-board automobiles, methods which are much better in terms of volumetric and gravimetric considerations have gained urgency and importance. The most successful technological product that has emerged in the past decades in this regard is composite high pressure cylinders. In fact, this has made hydrogen based vehicles of equivalent traveling range to that use gasoline feasible, without the need for a cryogenic storage on-board.

3.1.2 When taken in the free-state and placed under standard conditions, hydrogen is a colourless, odorless, and tasteless gas having a density of 0.084 kg/m3. The latter means that 1 kg of hydrogen occupies a volume of 11 m^3. When in gaseous state and under any pressure, hydrogen possesses an energy lower than that of natural gas, methanol, and propane, to say nothing of gasoline (per unit volume). Liquid hydrogen (at a temperature of 20 K) occupies 1/700th of the volume it takes in the gaseous state. When placed under a pressure of 80 MPa, gaseous hydrogen becomes virtually equivalent to liquid hydrogen in specific content of energy per unit volume and mass. This has driven the world to look for pressurized storage of gaseous Hydrogen at pressure levels of 700 to 800 bar. The success in the design and development of technologies on composites as well as seamless thin pressure vessels together have yielded the composite pressure vessels known today.
3.1.3 Enhancing the capabilities further, cylinders without the metal liner has also become a reality. These cylinder with advanced polymeric liners are the so called type IV class cylinders and offer significant weight advantages.

3.2 Composite high pressure vessel Type III – features and details

3.2.1 Configuration: High pressure gaseous hydrogen tanks of Type III class, generally used up to 700 bar, are carbon fibres filament-wound tanks of cylindrical shape with an inner metal liner of steel or aluminium layer. The construction details of the cylinders are which are shown in the Figure 3.1(a) and 3.1 (b):

![Figure 3.1(a): Composite high pressure container](image)
Figure 3.1(b): Composite high pressure containers
3.2.2 **Key features of typical composite pressure vessels** that are available today are as follows:

- Non-permeable, seamless, aluminum liner
- Metallic liner guarantees high impact resistance
- Fast-fill capability without fill restrictions
- Excellent resistance to heat exposure
- Single and dual port configurations available
- As a component to be plugged on board vehicles, they are also reported to be assembly-line ready, Lightweight and are easily accessible for maintenance and inspection

3.2.3 **Protective measures:** The following procedures are generally recommended to prevent injury to personnel or damage to cylinder:

- Cylinder shall be handled only under depressurized condition
- There should not be any damage to the carbon fiber or the aluminum liner.
- Safety shoes shall be used and hands shall be free of grease, grit and oil to avoid possible damage to
- Cylinder shall not be handled by their valves, fittings, pipings or pressure devices.

3.2.4 **Typical storage procedures** are as follows:

- Cylinders shall be restrained from moving / rolling and no impact shall be permitted
- Appropriate plastic plugs shall be used whenever necessary and entry of dirt, water inside the cylinder shall be strictly prevented
- Cylinder shall be protected from excessive heat, UV radiation (direct sunlight) and corrosive environment
- Rubber strips shall in place between cylinders and appropriate tools and accessories shall be used while lifting and moving cylinders; possibility of incurring any kind of damage to the fibers must be avoided
3.3 Environmental considerations

Generally, typical automobile environment is acceptable. Exposure to highly corrosive acids and bases should be avoided. No protective coating shall be applied and the thin transparent epoxy coating on the vessels is sufficient to protect the fibers, and at the same time, revealing the health of the fibers readily. Surface of the vessel shall not be subjected to any kind of abrasion, from gravel or debris. Tap water or ordinary water shall not be allowed to enter cylinders. Temperature of the medium (hydrogen gas) can be in the range of -40 °C to 65 °C. Typical cylinders available in market specify Hydrogen gas composition complying with ISO 14687.

3.4 Service Life

Typically, service life is specified in terms of number of cycles as well as years. Cylinders have a maximum service life of 15 – 20 years, from the final manufacturing inspection date. But, the actual date for decommissioning is related to the number of cycles per year specified in the standard for the country where it is used. Number of cycles specified for the cylinder (typical spec, more than 1000 x service life in years) or service life in years, whichever is occurring earlier, shall be the criteria for removing the cylinder from service.

3.5 Inspection & retesting

Periodic visual inspection at pre-determined intervals is very essential for all cylinders in service. These inspections shall be done in accordance with applicable standards and regulations of the country of use. Generally ISO 19078 is followed along with other standards specified for each country. In case a hydraulic pressure test is mandatory, as part of the retest, only specially treated shall be used and the exposure time shall be minimum.
3.6 Cylinders after collision or fire

Cylinders involved in collisions shall be subjected to detailed inspection by authorised agency. If found unaffected, that there are no impact damage, the same shall be returned to service. The cylinders subjected fire shall be removed from service since it is possible that fire / heat could cause serious damage even without any visible damage.

3.7 Installation and mounting

This shall be done only according to the prescribed procedure and guidelines by the manufactures. Strict control shall be exercised and care shall be taken to avoid any damage to the cylinder surface / structure. All essential safety devices viz., pressure relief valve, rupture disc etc shall be in place.

3.8 Protection and shielding

The cylinders shall be provided with sufficient protection and shielding, especially for those mounted in a vehicle, to prevent possible damages from, debris from road, contact with vehicle cargo and exposure to vehicle heat, harmful liquids such as break-fluid and radiation (sun light). At the same time, care shall be taken to avoid direct contact between shielding fuel storage tanks, trapping of solid debris/liquid between the same and contact with vehicle components such as frame members, brake lines, body panels and exhaust systems. Generally open mesh type shielding is preferred as it avoid collection of water and other liquids and enable easy access for inspection etc. There should be a permanent electrically conductive connection between the cylinder and the vehicle to prevent static charge build-up.

3.9 Basic design aspects
The cylinders have a distinct three layer configuration. A thin walled aluminium (AA6061) liner forms the basic structure. This is uniformly and completely intimately covered with carbon fibres, but for the openings. This layer is provided with a wrapping by epoxy resin matrix.

The selection of the materials of construction of the vessel is based on the detailed assessment of their compatibility with the Hydrogen as well as the mechanical properties. Brief details regarding selection of the materials are given in Table 3.1.

3.10 **Major tests and certification requirements**

Important tests that the composite pressure vessels shall be subjected and certified for shall include,

i) Hydrostatic burst test  
ii) Ambient pressure cycle test  
iii) Environmental  
iv) Acid environment  
v) Bonfire  
vi) Laminate flaw tolerance  
vii) Extreme temperature cycle  
viii) Accelerated stress rupture  
ix) Aluminum tensile  
x) Laminate shear strength  
xi) Glass transition

The tests shall be carried out in accordance with international standards and findings shall be made available.
3.11 **Key issue to be addressed**

Because of the low cycle fatigue associated with frequent filling and emptying of tanks, present day composite tanks would require periodic replacement. This is indeed a constraint to be overcome since the traditional fuel tanks last as long as the vehicle lasts.
In Indian context, this is an issue which requires special attention. There has to be a robust mechanism in place that the vessels in use are tracked and periodically inspected during its life time. More importantly, the vessels that reach its life must be removed from service, recovered and disposed safely and should not be allowed to remain in public domain. There has to be a technological-regulatory-fiscal frame work well in place to enforce this before the vessels are allowed/put into use.

3.12 Type IV cylinders

This cylinder is the latest entrant in the high pressure gas storage systems. For Hydrogen storage, though it could make significant weight saving, widespread use is limited to the Type III category. This is mainly due to the associated testing and certification requirements of enhanced nature to establish mandatory safety levels. They are generally,

- 70% lighter than steel cylinders
- Certified to NGV2-07 & ISO 11439
- Capable of service pressure 3,600 psi (typ)
- With life of 20 years (typ)
- Safe, durable, and reliable

3.13 International Status - Technology and manufacturing

Today, globally, the technology of the cylinders is commercially ready. Major manufacturers include M/s Quantum Technologies, M/s Luxfer Gas Cylinders and M/s Dynetek Industries Limited. Cylinders are available in various capacities. While there are many more manufacturers under this category, capability to supply cylinders for Hydrogen gas of the high pressure levels generally required for the present purpose that too with all mandatory safety tests results, needs to be ascertained? Generally, the cylinders are made available with due certifications and clearances. User level clearances in the country of
use alone is mostly left out. Large number of cylinders from the above manufacturers are already in use on-board automobiles across the globe. Good amount of data is already available with regard to their performance under typical service environments. More importantly, they have been involved in accidents and their behaviour under such conditions have been closely studied and recorded.

3.14 National Status

The technology for realizing the carbon composite with aluminum liner cylinder, type III, detailed above is not readily available in the country. Currently, the cylinders are being imported for various applications of non-energy in nature and, mostly, with air. The more popular, metal liner with Kevlar fiber wound type are the kind which are widely used in the country. The agencies/personnel who use such items today include ISRO, DRDO, Aviation industry, Medical Institution for emergency oxygen, divers etc. Use of carbon composite wrapped metal liners have also been initiated. The authority for certifying pressure vessels in the country, CCoE, already has the clearance protocols in place for such items. In-house developed technology for Kevlar composite titanium bottles for space application is already there with VSSC-ISRO which are used typically with Helium gas. Design, manufacturing, testing and use of these are already established well.

Globally, Type IV cylinders are also available on commercial scale. Still its use in the country is yet to start. Essential certifications/ clearance mechanisms for this type is also understood to be in the evolving stage.

3.15 Work plan for India

India shall have a sound technological-regulatory-fiscal frame work in place to track the composite bottles in service and replace and recover that
crosses the stipulated life period/cycles, on priority. Tracking of the numerous cylinders that are going to be on-board automobiles and ensuring that they recovered as and when each one crosses its life term is indeed new and complex task requiring special attention.

a) Relevant policies, with regard to import/duties, shall be reviewed and made ready for making the carbon composite-metal liner cylinders readily available for various applications and use in the country.

b) Development of the same with a view to manufacturing it in the country cost effectively, shall be pursued on priority.

c) Familiarization, certification and development of Type IV cylinders shall also be taken up in the country concurrently to reap in benefit of this new technology early.
HYDROGEN STORAGE IN LIQUID STATE
4.0 HYDROGEN STORAGE IN LIQUID STATE

4.1 About liquid hydrogen

4.1.1 The density of liquid hydrogen is 70.85 kg/m$^3$ which is again small since hydrogen is a quantum fluid. The zero point energy (835 J/mole) becomes significant for the quantum hydrogen at the low temperature of 20 K with the result that it is not possible to bring the atoms near to each other. If the hydrogen is frozen or a mixture of liquid and solid hydrogen known as slush hydrogen is formed at a temperature of about 15 K, the density does not significantly increase. The gain is less than 10%. However, if very high pressure of the order of Giga Pascal is applied one could get a high density solid hydrogen known as metallic hydrogen. This is not yet reliably achieved though it is claimed to be available in plenty in the gravitationally compressed interiors of planets Jupiter and Saturn.

4.1.2 The only alternative to storing hydrogen as a gas is in the liquid form. Slush or metallic hydrogen is not a contender for large storage. However, the slush hydrogen has a high value of specific heats and is therefore as excellent regenerative fuel for cooling and may be applicable in future for space propulsion. Figure 4.1 taken from Krainz in “Automotive applications of hydrogen” shows the higher energy density of liquid hydrogen as compared to high pressure compressed hydrogen.

4.1.3 In order to liquefy hydrogen gas, it needs to be pre-cooled below its maximum inversion temperature of 200K for the simple Linde Hampson or Claude liquefaction process. Further, the temperature must be reduced below the critical temperature of 33 K for the liquefaction. At 1 atmospheric pressure, the temperature got to be reduced to about 20.2 K. The energy required to liquefy 1kg of hydrogen is about 47 MJ when the initial condition of the gas is 300 K at a
Fig. 4.1 Energy Density of compressed hydrogen gas and liquid hydrogen

pressure of 1 atm. The energy also is dependent on the size of the plant. With improved technologies and small plants involving magnetic regenerative liquefaction about half of this energy may be adequate. An ideal process would require energy levels about a quarter of the present demands of energy for liquefaction. Hence with technology improvements one could aim for energy levels of the order of 13 to 14 MJ for the liquefaction process. However, since the liquid hydrogen is mainly in the para-form while the gaseous hydrogen is in the ortho-form and since the liquid phase reactions at the lower range of temperatures are slow, catalysts and auxiliary cooling with liquid nitrogen or otherwise become essential.

4.1.4 The lower calorific value of hydrogen is 120 MJ/kg. The present demand of energy to produce 1 kg of liquid hydrogen is about half this value which suggests that the use of hydrogen in the liquefied form may be difficult. However, with improvements in the liquefaction strategies, only about 10 to 15 % of the lower calorific value which could be generated from hydrogen would be spent in
the liquefaction process. On the other hand, the energy required in an ideal and reversible isothermal compression, if hydrogen is stored as a high pressure gas at 500 atm. is 7.8 MJ. With non-idealities in the compression process, efficiencies of the compressors and cooling of the gases during the compression, the energy required would be of the order of 10 MJ/kg. This is only marginally lower than the energy requirements for the liquefaction.

4.1.6 In summary, the requirements of energy are about 10 to 20% of the lower calorific value of hydrogen for bulk storage and transport hydrogen gas at high pressures and for cryogenic liquid hydrogen. The other methods of storage such as metal hydrides cannot cater to the large volume requirements involving energy related applications.

4.1.7 The embrittlement problems associated with gas storage are present for liquid storage also. As long as FCC materials of construction are used with good insulation systems comprising double walled vacuum vessels, opacifiers and MLI insulations which are developed, it is possible to store and transport hydrogen in the liquid form.

4.2 Safety aspects of using hydrogen as a liquid

4.2.1 Since the flammability limits of hydrogen with air is very wide between 4% and 75% of volume of hydrogen in the mixture, the chances of the mixture catching fire is always a matter of concern. Further, at the stoichiometric conditions, the energy required to ignite the mixture is extremely small at about 0.02 mJ which is less than can be produced by a stray electrostatic spark. In fact the frictional energy dissipated by hydrogen gas flow over surfaces gives energy of this magnitude. Hence well mixed hydrogen air mixture spontaneously catches fire. However, the ease of ignition is a blessing in disguise since the hydrogen burns away as soon as it encounters an electric spark. It does not accumulate as
does LPG and other hydrocarbon gases while waiting for a sufficiently larger ignition source and this accumulated when ignited results in an explosion.

4.2.2 The diameter of hydrogen molecule is very small at $1.372 \times 10^{-10}$ m and the hydrogen is very susceptible to leak out of very small crevices. It also has a higher value of diffusivity of about $1.13 \times 10^{-3}$ m$^2$/s. The high diffusivity prevents the formation of a flammable mixture under different conditions of atmospheric stability. This is also an advantage. Handling hydrogen gas in a confined geometry is therefore not desirable since we do not allow it to escape. The interaction with confinement often results in a detonation or an explosion.

4.2.3 Hydrogen gas if handled carefully is safer than most hydrocarbons. The same applies for liquid hydrogen. The problems of low temperature burns, asphyxiation, dense vapor generation and formation of flammable mixtures are present. However, no major accident has been reported in its usage so far.
HYDROGEN STORAGE USING LIQUID ORGANIC HYDRIDES
5.0 HYDROGEN STORAGE USING LIQUID ORGANIC HYDRIDES

5.1 Introduction

5.1.1 Liquid organic hydrides consisting of various cycloalkanes are the potential candidates for transporting hydrogen effectively from hydrogen production facility to fuelling stations. The approach is of particular interest due to associated advantages namely higher storage capacity for hydrogen (more than 6 wt% and 60 kg/m$^3$), supply of clean hydrogen, transportation at near ambient conditions and use of simple infrastructure such as Lorries. Particularly, the approach of using cycloalkanes is most useful to transport the hydrogen from centralized generation facilities to fuelling stations. Hydrogen produced at centralized production facility is used for hydrogenation of toluene and product methyl cyclohexane is transported to a fuelling station. At the fuelling station a subsequent dehydrogenation reaction supplies hydrogen to fuel cell vehicles and recycles back the toluene to the hydrogen production facility. The efficient catalytic systems are developed and being up-scaled presently at National and International level. A diagram of Liquid organic hydrides is shown in Figure 5.1.

![Diagram of Liquid organic hydrides](image_url)

Figure 5.1 A diagram of Liquid organic hydrides
5.2 International Status

5.2.1 On International level pioneering work on Liquid Organic Hydride (LOH) was carried out in Japan at two different laboratories. In addition to Japan a group in US EPA has worked on LOH. Subsequently several laboratories started working on the various aspects of hydrogen storage and delivery using LOH. A list of laboratories is given below:

- Catalysis Research Center, Hokkaido University, Sapporo, Japan
- Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, Tokyo, Japan
- Department of Energy, USA and associate laboratories
- Chemical Engineering Department, Swiss Federal Institute of Technology, Universitiiitstr, Zurich, Switzerland
- Swiss Federal Laboratories for Materials Research and Testing, Switzerland
- Department for General Energy Technology, Paul ScherrerInsitut, Switzerland.
- Instituto de Carboqui´mica (C.S.I.C.), Miguel LuesmaCasta´n, Zaragoza, Spain
- Petroleum Research and Studies Center, Kuwait Institute of Scientific Research, Kuwait.
- Environmental Technology Centre, School of Chemical Engineering and Analytical Science, The University of Manchester, UK.
- School of Chemical Engineering and Technology, Xian Jiaotong University, China.
- Chemical and Environmental Systems Organization, GE Global Research, NY, USA.
- Department of Chemistry, University of Rochester, NY, USA

5.2.1 Industrial Efforts

- R&D Centre, Chiyoda Corporation, Japan
• Sekisui Chemical Co., Ltd., Japan
• Exxon Research and Engineering Company, Annandale, USA

Status of the some of the LOH work at bench and pilot level from Japan as reported in open literature and elsewhere is as following Table 5.1:

Table 5.1  Details of International Status of some of the LOH Work

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Country</th>
<th>Storage medium</th>
<th>Stage of operation</th>
<th>Maximum Conversion (%)</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sekisui Chemical Co., Ltd., Japan</td>
<td>Methyl Cyclohexane (MCH)/Decalin</td>
<td>15 L / single type reactor producing 5500 - 6000 mL min⁻¹ of H₂</td>
<td>80</td>
<td>2004</td>
</tr>
<tr>
<td>2</td>
<td>Public demonstration at Sapporo Sato-Land, Japan</td>
<td>Decalin</td>
<td>30 L / parallel-7 type reactor producing 13 L min⁻¹ of H₂</td>
<td>76</td>
<td>2004</td>
</tr>
<tr>
<td>3</td>
<td>Sapporo Science Center, Hokkaido, Japan</td>
<td>Decalin</td>
<td>196 L / boxer-11 type reactor producing 200 L min⁻¹ of H₂</td>
<td>40</td>
<td>2006</td>
</tr>
<tr>
<td>4</td>
<td>Chiyoda Corporation, Japan</td>
<td>Methyl Cyclohexane (MCH)</td>
<td>Demonstration plant (50 Nm³/h), 3000 hrs tested</td>
<td>95</td>
<td>2013</td>
</tr>
</tbody>
</table>

5.3 National Status

On National Status pioneering work has been carried out by National Environmental Engineering Research Institute (NEERI), Nagpur. The work has been on laboratory level under MNRE sponsored project from March 2007 to March 2010. This work has resulted into development of several active and selective dehydrogenation catalyst, a specific catalytic reactor to handle
endothermic reactions and a complete process flow sheet. The salient results of this work are catalytic system with 20NL/h flow of hydrogen with one step catalytic efficiency of 98% conversion. The stability of the reaction was tested till 200 h. The national and international patents for the process has been filed. Presently Cleaner Technology Centre, NEERI is working on development of a pilot plant for hydrogen storage and delivery through LOH. The targeted scale of the plant is 100Nm3/h of hydrogen delivery at usage point. The work is expected to be completed by 2019.

5.4. Action Plan

In Indian context hydrogen production is possible at refineries and recovery of hydrogen from chloroalkali industries. Whereas the methods for transportation of hydrogen to delivery points either for vehicle applications (fuel stations) or to stationary applications required to be developed. Hydrogen storage in LOH and transportation at near ambient conditions is a potential method of hydrogen storage and delivery to long distance. Following action plan may be considered;

- Liquid organic hydrides and other liquid hydrocarbons are having high hydrogen storage capacity (both gravimetric and volumetric). An intensive research may be taken up by setting a Center of Excellence on Liquid Hydrides with financial support from MNRE
- Under proposed center of excellence, a few more laboratories and industries working in the field of chemical process development may be networked under lead of NEERI for rapid development of pilot plants. Petroleum industry may be networked to support the pilot runs
- R&D projects on further development of selective and stable catalysts may be funded
- International collaborative projects in mission mode with industrial participation from both sides may be supported
A demonstration project is proposed to establish feasibility of the hydrogen storage through Liquid Organic Hydrides by setting up the facilities near a refinery and providing hydrogen to telecom towers in the range of 50 to 100 kms. The project should demonstrate uninterrupted operation for at least one year.

5.5 The National Environmental Engineering Research Institute, Nagpur has received the financial supported from MNRE for the following projects on Liquid Organic Hydrides:

a) Development of catalytic materials for storage and supply of clean hydrogen liquid organic hydrides with Project Duration from March 2007 to February, 2010 with Project Cost of Rs.29 lakhs

HYDROGEN STORAGE IN SOLID STATE
6.0 HYDROGEN STORAGE IN SOLID STATE

6.1 Hydrogen storage is the stumbling block in harnessing hydrogen, be it the use of Hydrogen in cold combustion in Fuel Cells or hot combustion in I.C. Engine or Turbines.

Hydrogen is already produced to the tune of 50 Million Tonne per year worldwide by a variety of methods. This level of production can be easily extended. Thus if storage issue is solved, it will mark the coming of Hydrogen in market place. Therefore, vigorous R&D on storage aspects is being carried out. Decades of research has revealed that the solid state storage in the form of hydrides is the most efficient as well as safest storage mode. In view of this the highest priority is in search of hydrides with requisite characteristics. Basic parameters of hydrogen storage materials as decided by Dept. of Energy: DUE, USA are given in Table 6.1.

<table>
<thead>
<tr>
<th>Target</th>
<th>2010 (new)</th>
<th>2010 (old)</th>
<th>2015 (new)</th>
<th>2015 (old)</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Density (% wt)</td>
<td>4.5</td>
<td>6</td>
<td>5.5</td>
<td>9</td>
</tr>
<tr>
<td>System Volumetric Density (g/L)</td>
<td>28 (0.9 kWh/L)</td>
<td>45 (1.5 kWh/L)</td>
<td>40 (1.3 kWh/L)</td>
<td>81 (2.7 kWh/L)</td>
</tr>
</tbody>
</table>

6.2 The early R&D efforts on hydrogen storage materials have been focused on intermetallic hydrides typified by AB₅ (LaNi₅) AB₂ (ZrV₂), A₂B (MgNi₂) and AB (FeTi). However even though volumetric storage capacity and reversibility for these hydrides are excellent and meet the DOE limit, their gravimetric storage capacity is at best upto about 2.0 wt% (highest being 2.4 wt%). Thus even though R&D on Intermetallic Hydrides are still being carried out, the new hydrides namely (a) elemental hydrides (b) complex hydrides & (c) altogether
new upcoming hydrides. These hydrides have received boost in R&D after realizing the catalyzed hydrogen sorption (dehydrogenation/hydrogenation).

Generic energy system concept that incorporates chemical hydride hydrogen storage is illustrated in Figure 6.1. The leading design consideration of this system is to meet or exceed the “Grand Challenge” goals for hydrogen storage. This technical approach results in the selection of base materials that have a high enough hydrogen storage potential to allow for the inclusion of necessary supporting hardware and auxiliaries in resulting systems. The concept intends to optimize the performance of the onboard hydride processor through the use of energy convertor byproducts and to develop efficient, economical off-board reprocessor and refueling concepts. This approach combines technology that has the potential to improve hydrogen yields, with first-order system analyses that identify critical technical issues for hydride processors, product reprocessors, and hydride feed systems for fuel cell and combustion engine convertors. Results of this analysis will provide valuable insights into the raw potential of chemical hydride systems to produce hydrogen and into the overall performance that can be achieved when these chemical hydride systems are coupled with candidate convertors in practical power systems.

Figure 6.1: Energy System Concept Using Chemical Hydride Hydrogen Storage
There are four fundamental tenets associated with the generic technical concept.

(i) That the source chemical hydrides can be delivered to the on-board storage tank in their near-solid storage densities.

(ii) That water and other products of the convertor will be available to the hydride processor to maximize its efficiency.

(iii) That the products can be collected in a form that will permit easy transfer to the off-board reprocessor station at the time of refueling.

(iv) That the resulting products can be economically returned to source metal hydrides at the off-board station.

6.3 Candidate Chemical Hydrides

Table 6.2 shows the primary reaction equation and associated hydrogen storage properties of some well-known chemical hydride materials, including lithium hydride, LiH; sodium hydride, NaH; calcium hydride, CaH$_2$; magnesium hydride, MgH$_2$; lithium aluminum hydride, LiAlH$_4$; titanium hydride, TiH$_2$; lithium borohydride, LiBH$_4$; and sodium borohydride, NaBH$_4$. The physical, chemical and safety properties of these reactants and products suggest that they could be used in a complete hydride-based storage system.

Table 6.2: Candidate Hydride Reactions and Hydrogen Storage Properties.
Typically, hydrogen can be generated from chemical hydrides via two mechanisms: through a direct reaction with water or through thermal decomposition. While both mechanisms are possible for most materials, only one is likely to be practical for this system concept. Thus, LiH, NaH, CaH$_2$, LiAlH$_4$, LiBH$_4$, and NaBH$_4$ were assumed to react with water, while MgH$_2$ and TiH$_2$ were considered to undergo thermal decomposition. The water reactions also assumed low-to-moderate temperatures, which results in hydroxides being formed rather than oxides as predicted by standard chemical equilibrium analyses used at ARL. As will be shown later, however, elevating the reaction temperature will produce metal oxide products rather than hydroxides in some cases (e.g., Li$_2$O rather than LiOH), which in turn could decrease reprocessor energy needs.

The best way to use LiH is in the slurry form. This is 60% lithium hydride in mineral oil with a dispersant to maintain the slurry properties. The viscosity of the slurry is about 2000 cp. This slurry is stable for several weeks or more. This slurry is transportable and can be used in the present gasoline dispensing infrastructure. The vision of this energy concept is shown in Figure 6.2.

Figure 6.2: Vision of the Energy System Concept
6.4 The advantages of this energy system concept include:

- The potential to achieve high hydrogen storage density and attain storage goals for 2015
- The ability of hydride processors to utilize products from an energy convertor (for example, water and waste heat from a fuel cell) to maintain high efficiency
- The use of hydride materials that are generally nontoxic and stable until combined with water or thermally decomposed
- The ability to produce a low pressure, non-venting source of hydrogen that can be regulated according to hydrogen demand
- The application of a system-level approach that attempts to integrate all components associated with chemical hydride-based storage in order to maximize efficiency
- The primary technical issues associated with its development include:
  - Achieving high hydrogen yield from a compact hydride processor
  - Developing efficient and cost competitive hydride reprocessing technologies
  - Developing effective and reliable methods of delivering hydride and removing products
  - Matching operational characteristics of the hydride reprocessor with the energy convertor
  - Developing compact, economical, reusable, and durable system hardware
  - Ensuring a high level of safety in both the operational system and the refueling process

6.5 Elemental Hydrides (EH)

Out of the two elemental hydrides envisaged to be studied in the proposed studies namely AlH$_3$ and MgH$_2$, we have at present stage focused on MgH$_2$. 
This is due to the fact that whereas MgH$_2$ is a stable phase at ambient conditions, AlH$_3$ is not (it is at best metastable). Also Mg (density 1.58 g/cc) is lighter than Al (density 2.3 g/cc). Yet another reason is that Mg deposits in Earth’s crust are plentiful (Figure 6.3). It should be mentioned that whereas it is possible to synthesize MgH$_2$ with the help of catalyst through hydrogenation of Mg, but the same has not been possible for AlH$_3$. Salient features of Mg/MgH$_2$ are given below:

**Advantages**

- Large deposit in earth crust.
- Low cost
- A very Light metal hydride
- High gravimetric storage capacity (7.6 wt%)
- High Volumetric Storage capacity (110 kg/m$^3$)

**Issues:**

- High desorption Temperature above 400$^0$C (desired ~150-200$^0$C).
- High desorption activation energy ~97 kJ/mol.
- Slow Kinetics.

![Percent composition of different elements in Earth’s crust.](image)

Figure 6.3 Percent composition of different elements in Earth’s crust.
6.6  

Mg/MgH\textsubscript{2} Storage System

MgH\textsubscript{2} is considered to be one of the most favorable candidates due to its high H\textsubscript{2} storage capacity of 7.6 % by weight, availability, low-cost, reversibility and non-toxicity. Owing to above said properties, Mg has attracted extensive research in the last few decades. Since, magnesium (Mg) has a very strong affinity to hydrogen and forms a very stable Mg-H bond due to which MgH\textsubscript{2} has two disadvantages. First is its very large decomposition enthalpy (~75 kJ mol\textsuperscript{-1} H\textsubscript{2}) which means that a very high temperature (~300-400\textdegree C) is required for desorption and the second limitation is its slow de/rehydrogenation kinetics which is not acceptable for on-board applications. To overcome these two limitations, several efforts like alloying, nano-structuring, making composites, using metal catalysts such as Zr, Ti, V, Mn, Co, Pd, Fe, Ni etc and oxide catalysts like, MmO, Nb\textsubscript{2}O\textsubscript{5}, V\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, Mn\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4} etc. have been employed. Out of all the oxide catalysts, transition metals and their oxides shows excellent effects on the hydrogen sorption, especially TiO\textsubscript{2} which shows potential as a catalyst for improving the hydrogen sorption properties of different H\textsubscript{2} storage materials as it can undergo reduction in hydrogen atmosphere and also has the same tetragonal structure with the lattice parameter close to that of MgH\textsubscript{2}. It is found that 5 wt. % of 50 nm TiO\textsubscript{2} catalyst showed better catalytic effect in rehydrogenation among 7, 25, 50, 100 and 250 nm sizes of TiO\textsubscript{2} catalyst as a catalyst with MgH\textsubscript{2} system.

MgH\textsubscript{2} (98% Alfa Aesar with lattice parameter of a= 4.517 Å & c=3.020 Å) and 5 wt.% of 50 nm TiO\textsubscript{2} rutile tetragonal phase (lattice parameter a= 4.593 Å, and c=2.959 Å) were used as the starting material and were ball-milled using a planetary ball-miller (Retsch. PM400). The ball to powder ratio of samples was kept 30:1 by weight. The sample was ball-milled under 5 atm of H\textsubscript{2}-pressure at an operating rotational speed of 170 rpm for 24 hrs in a stainless steel vial. This resulted in the formation of MgH\textsubscript{2} catalyzed through 5wt% of TiO\textsubscript{2} i.e. MgH\textsubscript{2}/(TiO\textsubscript{2})(5wt%). For admixing the carbon nanostructures (CNS) namely,
SWCNT (MK Impex, Canada) was used as-received and graphene was synthesized by thermal exfoliation method. Before using graphene-nano sheets (GNS), residual gas analysis (RGA) treatment was performed at 150°C. 2 wt.% of SWCNT and graphene (after RGA treatment) were admixed with MgH$_2$/TiO$_2$ sample in a locally fabricated admixer. Admixing of 2 wt% each of graphene and SWCNT to MgH$_2$/TiO$_2$ (5wt%) was done through the admixer.

Ball-milling MgH$_2$ with 5 wt.% of TiO$_2$ reduced the onset desorption temp. of MgH$_2$ to ~312°C but on admixing carbon nanostructures (SWNT & graphene) in the sample, desorption temperature further gets reduced to ~295 & 280°C respectively. In rehydrogenation study at 250°C under 30 atm, MgH$_2$/TiO$_2$ (5wt%)/GNS (2wt%) sample absorbed ~5 wt.% and MgH$_2$/TiO$_2$ (5wt%)/SWCNT (2wt%) absorbed ~4.4 wt.% of H$_2$. In our findings, admixing of graphene shows more beneficial effects in regards to kinetics as compared to the admixing of SWCNT in MgH$_2$/TiO$_2$ (5wt%). This enhancement in the sorption property is attributed to the co-catalytic effect produced by both the catalysts i.e. TiO$_2$ and graphene. This can be explained by the fact that TiO$_2$ undergoes reduction thereby enhancing its ability as a catalyst, also the graphene provides better platform for homogeneous distribution of reduced TiO$_2$ np.

6.7 MgH$_2$ catalyzed through a new catalyst: Leached Quasi Crystalline alloy Al$_{65}$Cu$_{15}$Fe$_{20}$

It is known that for making MgH$_2$ a viable hydrogen storage material, new catalyst is being searched interestingly. In an effort of this type, we have developed an altogether new catalyst which has not been used so far by any group. This new catalyst as will be shown in the following turns out to be the best known so far for catalyzing MgH$_2$. The quasicrystalline (QC) material was discovered by Prof. Dan Shechtman et.al. in 1984. The QC corresponds to a new material phase which is neither crystalline nor amorphous. Its potential application as a catalyst for reformation of methanol was first reported by
Nosakiet. al.in 1998. Since, quasicrystals (QCs) are stable, hard, brittle, high specific surface area and several of them are stable up to high temperatures. The thermally stable icosahedral phases Al-Cu-Fe leached with NaOH aqueous solution shows excellent activity for steam reforming of methanol (SRM). Recently, the reason for the excellent performance of the QC as a catalyst is credited to the formation of a homogenous leached layer generated by leaching Al bearing QC materials. More recently, leaching has been carried out on the surfaces of oriented single grain icosahedra Al-Cu-Fe, decagonal Al-Ni-Co and polygrain Al-Pd-Re quasicrystalline materials.

To check the reversibility of the sample, cycling experiments were performed on MgH$_2$ catalyzed with LBACF received over 51 sorption cycles with fairly minor kinetic degradation. It may be pointed out that the use of QC Al$_{65}$Cu$_{2e}$Fe$_{15}$ as a catalyst for making hydrogen sorption amenable in MgH$_2$ is a new landmark research, not done earlier anywhere. Salient features are given below:

**Role of leaching AlCuFe**

On leaching Al-Cu-fe alloy, Al atoms gets leached by chemical reaction followed by dissolution leaving individually Cu & Fe atoms alone. Cu-Fe are attached to Al-Cu-Fe base matrix so, it is expected that they will not agglomerate. **Temperature programmed desorption:** In TPD profile, the onset desorption temperature for MgH$_2$ catalyzed with leached ball-milled Al-Cu-Fe QC alloy gets lowered to ~210°C

**Rehydrogenation:** This system exhibits faster rehydrogenation kinetics by absorbing ~6 wt. % of H$_2$ in just 30 seconds under 20 atm H$_2$ pressure at 250°C, this research is a record for MgH$_2$ and has been done for the first time for the material MgH$_2$. 
It has shown better hydriding kinetics even at lower temperatures of 200°C & 150°C by absorbing ~ 5.5 wt. % within 1 minute and ~5 wt. % at 100°C in 30 minutes under the same condition of H₂ pressure.

**Cyclic stability:** The sample received over 51 sorption cycles with fairly minor kinetic degradation. Further cycling experiments are going on to check the reversibility upto 500 and 1000 cycles.

6.8 Effects of Ti-based catalysts and synergistic effect of SWCNTs-TiF₃ on hydrogen uptake and release from MgH₂

To improve the sorption behavior of Mg/MgH₂, several catalysts have already been used such as metal oxides, composite with intermetallic compounds, transition metals and their compounds. Also the significant catalytic effect of different carbon based nano structures has already been described by the different research groups. Our earlier work on MgH₂ also shows the beneficial effect of different shaped carbon nanofibers on derehydrogenation characteristics of nanocrystalline MgH₂. Through the numerous studies, it is now well understood that transition metals and their compounds are one of the most effective catalysts for MgH₂. Recently we have also investigated the co-catalytic effect of the most effective transition metals Fe, Ti and Ni (for the case of MgH₂) on de/rehydrogenation characteristics of nanocrystalline MgH₂. In the light of the above, the aim of the study is to investigate the catalytic effect of Ti and Ti-based compounds such as TiO₂, TiCl₃ and TiF₃ on sorption behavior of MgH₂. Out of all the Ti additives, TiF₃ is found to be most effect catalyst. Promising catalytic effect of TiF₃ in MgH₂ was first observed by Ma et al. According to Ma et al., the main problem of MgH₂-TiF₃ system is the decrease of hydrogen desorption capacity with cycle. To address the problem of cycling, we have admixed SWCNTs as an additive in MgH₂-TiF₃. The cyclability of the MgH₂ catalyzed with TiF₃ is improved by the deployment of SWCNTs. The synergistic effect of SWCNTs and TiF₃ have described in details. The presence of SWCNTs in Mg/ MgH₂ matrix reduces the
agglomeration of nano grains by providing support to nanoparticles and improves the cyclability and kinetics of MgH₂ catalyzed with TiF₃.

6.9 Catalytic effect of carbon nanostructures on the hydrogen storage properties of MgH₂-NaAlH₄ composite.

Among the solid-state storage mode of hydrogen, elemental hydride (like MgH₂) and alanate-based complex metal hydrides (like NaAlH₄) are the promising candidates as a hydrogen storage material. The promising elemental hydride MgH₂ desorbs hydrogen in a single step and releases 7.6 wt% (<410°C) of hydrogen. MgH₂ has already been studied by using various types of catalyst including carbon nanostructures (CNS) (i.e. SWCNT, Multi wall carbon nanotubes (MWCNT), planar graphitic nanofibre (PGNF), helical graphitic nanofibre (HGNF) etc). Rodenaset. al. studied the beneficial effects of different CNS on hydrogen desorption from MgH₂. Amirkhiz et. al. and BHU have also found that addition of CNS as catalyst in MgH₂ improves the de/rehydrogenation properties of MgH₂. Key issues related with MgH₂ like sluggish kinetics of H₂ uptake and release, high de/rehydrogenation temperature & poor cyclability at an appropriate temperature are still not completely solved.

Among light metal complex hydrides, NaAlH₄ has been studied extensively for practical application. NaAlH₄ releases hydrogen through 3 sub steps having 7.2 wt.% (<500°C) out of which 5.5 wt% (< 300°C) is considered to be useful for practical application. Studies on NaAlH₄ get picked up after the work of Bogdanovicet. al which shows reversibility in NaAlH₄ upon doping with Ti. After this discovery of Bogdanovicet. Al., many research groups studied NaAlH₄ using different types of catalysts including metal, metal halide, metal oxide. NaAlH₄ has also been studied using carbon nanostructure (CNS). Selvanet. al. used carbon nanotubes (CNTs), to lower the hydrogen desorption temperature of NaAlH₄. Hudson et.al. have also used various types of carbon nanostructures to improve the de/rehydrogenation characteristics of NaAlH₄. Theoretical and experimental
studies on NaAlH$_4$ by Berseth et al. also shows the beneficial effect of CNS on de/rehydrogenation properties of NaAlH$_4$. Recently, some other groups also studied the promising effect of CNS on hydrogen sorption properties of NaAlH$_4$. Despite all these extensive efforts, the use of NaAlH$_4$ is greatly hampered by thermodynamic limitation and slow diffusion of hydrogen from NaAlH$_4$.

In the light of the above, it will be opportune to study composite of MgH$_2$-NaAlH$_4$ (optimized composition is 2:1 molar ratio of MgH$_2$-NaAlH$_4$). This composite catalyzed through carbon nanostructures (which have various microstructures are stable and light weight catalysts) has not been studied so far. Therefore, the present investigation is focused on sorption (de/rehydrogenation) studies of carbon nanostructures catalyzed MgH$_2$-NaAlH$_4$ composite.

Researchers at BHU have investigated the de/rehydrogenation behavior of 2:1 molar ratio of MgH$_2$-NaAlH$_4$ composite, which offers beneficial hydrogen storage properties as compared to pristine MgH$_2$ and NaAlH$_4$. Relating amount of 2wt% of CNS namely SWCNT and GNS have been used as catalyst to improve the de/rehydrogenation properties of MgH$_2$-NaAlH$_4$. The GNS + SWCNT (1.5 + 0.5) wt.% is found to be most effective catalyst for de/rehydrogenation from MgH$_2$-NaAlH$_4$. This can be attributed to co-catalytic effect of GNS and SWCNT in 2M-N 1.5 wt% GNS /0.5 wt.% SWCNT composite. SWCNT hinders the re-stacking of GNS layer. This makes it more effective as micro-confinement agent. The synergistic effect between GNS + SWCNT provides better thermal conductivity and dispersive properties to GNS + SWCNT as compared to GNS & SWCNT when used alone. This affirms that GNS + SWCNT is a better catalyst as compared to GNS and SWCNT.

6.10 Effect of carbon nanofibres and titanium halide on hydrogen sorption (dehydrogenation/rehydrogenation) properties of MgH$_2$-NaAlH$_4$ composite.
The present study describes the synthesis of nano MgH$_2$-NaAlH$_4$ and its hydrogen storage. It may be pointed out that in addition to carbon nanostructures, halides of transition elements e.g. TiF$_3$ has also been used for catalyzing MgH$_2$ and NaAlH$_4$. Keeping this in view and also the fact that out of various possible carbon nanostructures, BHU has already employed two of them namely SWCNT and graphene nanosheets, Synergistic effect of catalyzing MgH$_2$ with TiF$_3$and carbon nanofibres (CNFs) has been investigated. Handling of samples was performed in an argon filled glove box (mBRAM MB10 compact) with H$_2$O and O$_2$ ≤ 1 ppm. The MgH$_2$-NaAlH$_4$ composite in which admixing of 2 wt.% PGNF was done will be labeled as 2M-N PGNF. Similarly, the other composite will be labeled as 2M-N HGNF, 2M-N TiF$_3$ and 2M-N TiF$_3$ + HGNF. 2:1 molar mixture of MgH$_2$ and NaAlH$_4$ was ball milled and found to have beneficial hydrogen sorption properties as compared to pristine MgH$_2$ and NaAlH$_4$. Out of different CNS, HGNF shows better hydrogen sorption properties due to more active carbon sites owing to its curved structure. Among CNS and halide, TiF$_3$ shows pronounced effect on Hydrogen sorption properties of TiF$_3$ + HGNF (due to well-known electronegative properties of fluoride). Synergistic effects of TiF$_3$ + HGNF is found to be beneficial for hydrogen sorption from 2M-N as compared to TiF$_3$ and HGNF catalyzed 2M-N alone.

6.11 Investigations on another complex hydride: corresponding to Li-Mg-N-H system [Mg (NH$_2$)$_2$ + LiH]

In addition to MgH$_2$ Alanates typified by NaAlH$_4$ another complex built in hydride is the system Li-Mg-N-H. It shows storage capacities between 5 and 6 wt%. One difficulty with this system is that the usual route for synthesis corresponding to ball milling MgH$_2$ and LiNH$_2$ leads to only partial formation of the desired phase Mg (NH$_2$)$_2$/LiH. Unreacted amide/imide and some MgH$_2$ gets left behind even after prolonged ball milling, it has tried to use several transition metal, compounds and alloys as catalyst for synthesis of pure phases. It has been found that out of several catalysts studied, Zr Fe$_2$ is the optimum one. It
does not get hydrogenated and dehydrided at temperatures and pressures used for dehydrogenation/re-hydrogenation temperatures use for Mg bearing amides/imides. The other advantage is that it is harder (hardness ~8mho) than MgH₂ (hardness ~4 mho) LiAlH₂ (hardness ~6mho). This Zr Fe₂ will have a pulverizing effect and it will get ball milled in the form of a fine powder. It will, therefore, get uniformly disturbed on Mg (NH₂)₂/LiH catalytic effect of Zr Fe₂ will be due to the transition nature of both Zr and Fe. We have been able to get pure Mg(NH₂)₂ / LiH phases with hydrogen storage capacities of ~ 5 wt%. Further R&D for making this complex hydride system is being made.

6.12 Work in Progress

(i) MgF₂ catalyzed MgH₂
(ii) Synthesis of Mg starting from magnesium
(iii) QC catalyzed NaAlH₄
(iv) ZrFe₂ catalyzed Magnesium amide
(v) Exploratory studies on other types of hydrides including intermetallic hydrides
(vi) Studies of improving recyclability of elemental and complex hydride through co-catalyzation and encapsulation of hydride.

As already stated, there are various ways of Hydrogen Storage. These are High pressure gaseous storage, Storage as liquid hydrogen, Storage in intermetallic hydrides, Storage in complex hydrides, Nanomaterial based hydride Metal Organic Complexes, Clatherate H₂-(H₂O)₂ and Hydrate H₂-(CH₄), Storage in glass microspheres, Storage as liquid hydride (e.g. cyclohexane), Storage in zeolites, Storage in aerogels, Storage in ammonia and ammonium compounds, Storage in depleted mines (underground storage). Nearly State of the Art Storage Modes: (a) High Pressure Gaseous Storage (b) Liquid Hydrogen (c) Metal / alloy based Hydrides.
6.14 Storage of Hydrogen in different conditions and forms are given in Table 6.3.

Table 6.3 Storage of Hydrogen in different conditions and forms.

<table>
<thead>
<tr>
<th>Mode</th>
<th>wt%</th>
<th>Volumetric Capacity</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed H(_2) (\sim 200 \text{ bar})</td>
<td>&lt;1</td>
<td>~20</td>
<td>Risky, Inefficient</td>
</tr>
<tr>
<td>Compressed H(_2) (\sim 400 \text{ bar})</td>
<td>3</td>
<td>~30</td>
<td>Very Risky, Inefficient</td>
</tr>
<tr>
<td>Liquid H(_2) (with super-insulated container)</td>
<td>~4</td>
<td>~40</td>
<td>Risky, Not Viable for Vehicular Transport in India</td>
</tr>
<tr>
<td>Intermetallic Hydride (near RT)</td>
<td>2 to 3</td>
<td>~60</td>
<td>Safe, Efficiency better than GH and LH, Further R&amp;D required</td>
</tr>
<tr>
<td>Nanomaterial Hydride</td>
<td>~5-6 wt%</td>
<td>Volumetric storage capacity to reach the required value of ~60Kg/m(^3).</td>
<td>Safe, Efficient R&amp;D Required</td>
</tr>
<tr>
<td>Complex Hydrides</td>
<td>~5 to ~11 wt%, R&amp;D in regard to Reversibility and required kinetics.</td>
<td>Volumetric storage capacity to reach the required value of ~60Kg/m(^3).</td>
<td>Safe, as outlined R&amp;D Required</td>
</tr>
<tr>
<td>Zeolite</td>
<td>0.34 wt% at 298K and 10MPa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal Organic Framework</td>
<td>Upto 2-7 wt% at Liq. Nitrogen temp.</td>
<td>45Kg/m(^3)</td>
<td>R&amp;D required to achieve higher vol. capacity (60Kg/m(^3) at room temp.)</td>
</tr>
<tr>
<td>Liquid Hydride</td>
<td>Upto 6.5 wt%</td>
<td></td>
<td>Needs R&amp;D dehydrogenation of liq. hydride such as cyclohexane is difficult and full dehydrogenation is</td>
</tr>
</tbody>
</table>
Presently unexplored and unknown storage modes e.g. (KSiH$_3$) can reach from ~5 to ~9 wt% R&D required not achievable so far

| Presently unexplored and unknown storage modes e.g. (KSiH$_3$) | Can reach from ~5 to ~9 wt% R&D required | ≥60 Kg/m$^3$ | Safe, R&D required |

All the above methods have some disadvantages, but the most promising is solid state route of hydrogen in the form of reversible hydrides appears to be hydrides. Liquid hydrogen storage meets volumetric and gravimetric requirements, but 'boil off' and refueling present safety hazards. In addition, liquefaction requires significant energy. Storage as high-pressure gas will not meet volumetric density requirements even at pressure of 650 bar; (at R.T. employing HPG storage mode for storing 2 kg of hydrogen at atm. pressure, occupies a volume of ~45 meter cubes ~a balloon of 3m diameter; this is apparently not a practical solution for a hydrogen fueled vehicle where the volumetric storage capacity is crucial. Besides significant energy is required for compression; and the high flammability of hydrogen presents hazards in collisions. In Japan hydrogen cylinder with gas at ~400 atmospheres or higher is not allowed in road transport. However, for large vehicles like buses, trucks hydrogen storage in the form of compressed gaseous form may be viable both for IC Engine and Fuel Cell based transport.

6.15 International and National Efforts and Technology Gaps

International and National status of storage of hydrogen technology in different conditions and forms and technology gaps are given in Table 6.4.

Table 6.4 International and National status of hydrogen storage technology in different conditions and forms and Technology Gaps.
<table>
<thead>
<tr>
<th>Aspects of Hydrogen Energy</th>
<th>International Status</th>
<th>Indian Status</th>
<th>Gap Areas to be Bridged</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium and Magnesium Hydride MgH₂</td>
<td>Leading groups: (a) C.M. Jenssen (USA) (b) Y. Kojima (Japan) (c) L.L.aversenne (France) (d) Luca Pasquini (Italy) (desorption of 6.5 wt% at temperature ~ 325°C and absorption ~ 200°C)</td>
<td>1. B.H.U. CNF catalyzed NaAlH₄, LiAlH₄, Mg (AlH₄)₂ at 200°C to 250°C absorption of 6 wt% at 300°C within 1 hour. Rajasthan university, Mg₂Ni absorption / desorption of 3.5 wt%. TiF₃, catalysed MgH₂</td>
<td>The efforts are now focused on further lowering of desorption temperature and improvement in cyclability of magnesium and magnesium based hydrides.</td>
</tr>
<tr>
<td>Amide-Hydride Mixture</td>
<td>(a) P. Chen (China) (b) Hui Wu (USA) (c) Ping Wang (China) (d) El K. Stefanakos (USA) (e) S Nayebossadri (UK) (Desorption of 5 wt% at temperature 140°C)</td>
<td>2. BHU Mg-Li-N-H complex hydride.</td>
<td>The major limitations of Li-Mg-N-H system is poor rehydro-genation kinetics and liberation of ammonia with cycles. The acceptable amount of weight loss during cycling is 10% after 1000 cycle. For this case the weight loss with cycling is found to be 20%. Further R&amp;D is required.</td>
</tr>
<tr>
<td>Alanates MAIH₄ (M = Na, Li, Mg)</td>
<td>(a) Yuepeng Pang (China) (b) B. Bagdanovic (Germany) (c) A.C. Dillon (USA) (Level : ~ 3.5 to 5.0 in catalyzed NaAlH₄ reproducible capacity at ~ 150°C)</td>
<td>BHU, IIT (M), ARC (Hyderabad), Jaipur University - ~ 2.4wt% by BHU in AB₅, Mg based composite</td>
<td>The potential of NaAlH₄ as a kind of practical on-board hydrogen storage material is hindered owing to the high kinetic barriers of the dehydrogenation / hydrogenation reactions.</td>
</tr>
<tr>
<td>Hydrides</td>
<td>Metal and alloy hydrides. Large R&amp;D efforts in Japan, USA and several other countries. Some</td>
<td>BHU, IIT (M), ARC (Hyderabad), Jaipur University - ~ 2.4wt% by BHU in AB₅, Mg based composite</td>
<td>The development of indigenous hydride synthesis technology is a must for hydrogen powered economy. Hydrides not only store</td>
</tr>
</tbody>
</table>
leading research groups are those of (i) Dr. E. Akiba (Japan), (ii) Dr. A. Zuttel (Switzerland), (iii) Dr. H. Itoh (Japan) and (iv) Dr. R. Schulz (Canada). ~ 1.5 wt% to 2 wt% for ambient condition storage ~ 5 to 6 wt% for high temperature. materials ~ 5 to 6 wt% hydride being developed at BHU. BHU is carrying out mission mode programme on ‘Hydrogen Storage in Hydrides (elemental, intermetallic, complex hydrides). Innovative results on Al$_{65}$Cu$_{20}$Fe$_{15}$catalyzed MgH$_2$ have been obtained by BHU. Hydrogen absorption to the time of ~ 6 wt% is obtained within ~ 1 minute and desorption to 5.6wt% is obtained within ~ 30 minutes. These are record features. IIT (M) is carrying out a Mission Mode programme on hydrogen storage in various forms of carbon. NEERI (Nagpur) is carrying out work on liquid hydrides, NFTDC Hyderabad is doing work on ball milled and alloy catalyzed MgH$_2$ hydrogen but also heat energy and can be used in a variety of applications e.g. hydrogen storage for vehicles and power generating system, hydrogen compressors, hydrogen cookers, hydrogen based air-conditioners, Ni-MH battery etc. Low level support as compared to other countries including China and Japan for basic R&D in this area. R&D efforts to be strengthened and supported. Large scale hydride production

<p>| High pressure gaseous storage | Several companies e.g. Quantum (USA); Dynatejk Industries (Canada); Power Tec | No high pressure gaseous storage technology exists in the country (recently in 2004) | High pressure gaseous storage efforts to be strengthened and supported. The development of |</p>
<table>
<thead>
<tr>
<th><strong>Liquid Hydrogen</strong></th>
<th>Space Organizations like NASA (USA), AIREN (Europe)</th>
<th>Liquid H₂ plant is installed near Trivendrum; No R&amp;D efforts to test liquid H₂ for vehicular transport or power generation have been made so far.</th>
<th>Efforts on development of Liquid Hydrogen Storage for vehicular transport to be developed by ISRO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unusual routes</strong></td>
<td>Efforts being made on several unusual routes such as storage in zeolite, glass microsphere, chemical hydrides, storage in depleted mines (underground storage) are being investigated</td>
<td>Hardly any efforts in these areas in India are being made</td>
<td>R&amp;D efforts to be initiated and strengthened</td>
</tr>
<tr>
<td><strong>Leading Groups:</strong></td>
<td>(a) C.M. Jenssen (USA) (b) W. Schutz (Germany) (c) B. Bagdanovic (Germany) (d) A.C. Dillon (USA) (e) RTK Baker and N. Rodriguez</td>
<td>KSiH₃</td>
<td>R&amp;D in new materials to be strengthened and strongly supported since this route holds significant promise (solid state, storage modes and safest and also possess highest efficiency storage features) and at international level high priority R&amp;D efforts are going on relating to hydrides, particularly complex and intermetallic and new hydrides.</td>
</tr>
</tbody>
</table>
Solid metal hydrides have been studied for many years, particularly for understanding the process of metal embrittlement upon absorption of hydrogen at interstitial sites. After surface adsorption, molecular hydrogen may dissociate into atoms that form a solid solution of a hydride phase in the metal or alloy or generate an intermetallic region. The uptake of hydrogen continues at nearly constant pressure until the pure hydride phase is formed, which may have volumetric densities of 150 kg H\textsubscript{2} per m\textsuperscript{3} (Mg\textsubscript{2}NiH\textsubscript{4}). In favorable cases this process is reversible and cycling can occur at desirable pressures (1–10 bar). For materials with a significant capacity for hydrogen, however, desorption usually occurs at a higher temperature than the targeted conditions. Improving the uptake/release kinetics and retention of cycling capacity are currently the major areas of materials research. The disadvantages of these compounds include high cost, susceptibility to impurities, and low reversible gravimetric capacity (typically less than 3 wt%). To circumvent some of these issues chemical hydrides (also called complex or covalent hydrides) such as NaAlH\textsubscript{4} have been studied and shown to reversibly cycle hydrogen on doping with a catalyst. Other alanates and boro hydrides of Groups 1, 2, and 13 elements have large gravimetric capacities (>7 wt%), but the extent to which their hydrogen sorption is reversible requires continued investigation. Hydrolysis of alkali metals and their hydrides is also a convenient route for hydrogen release, but requires off-board recycling of the decomposition products. Most of these chemical methods still require demonstration of both physical and economic viability. Current barriers to practical storage schemes stem from the high pressure and temperature conditions needed for hydride formation and hydrogen release. For many potential systems hydriding and de hydriding kinetics and heat management are also issues that need to be overcome. Another approach is to adsorb molecular hydrogen on the surface of a solid storage material. Suggested adsorbents include activated carbon, nano structured carbons (including CNTs), MOFs, and hydrogen clathrate hydrate.
The storage methods presently under the most consideration are physisorbents and chemical and metal hydrides. In addition to total storage capacity, the kinetics and thermodynamics of release and recharging must be considered. Undesirable kinetics and thermodynamics can not only limit the release and recharging rate, but may also add unnecessary weight and volume to the vehicle because of the need for extra heat exchangers—this leads to consideration of the heat of formation of the hydrogen-carrying species or heat of hydrogen adsorption of sorbents, ΔH_f or ΔH_ads, when evaluating a potential storage method. Chemisorption techniques, involving the formation of hydrides, suffer from binding hydrogen too tightly, i.e., ΔH_f too large—ranging from 50 to over 200 kJ mol. For metal hydrides, such as LaNi_{5}H_{6}, the storage system must operate above ambient temperature (often 400 K) in order to release the hydrogen fuel, while refueling liberates large amounts of energy. The thermodynamics of chemical hydrides (such as LiNH_{2}, LiBH_{4}) are such that there are questions regarding the reversibility of the hydrogen uptake and release, while the chemical reaction which releases hydrogen only occurs at elevated temperatures; additionally, the energy input to create the hydride reduces the overall efficiency of the system. As a contrast, most physisorption techniques, including carbon nanotubes and other porous materials (activated carbon, zeolites, etc.), suffer from the opposite problem: ΔH_ads is typically small, less than 10 kJ/mol, and appreciable adsorption can only be achieved at very low temperatures (typically, 10^0 K).

Unfortunately, commercial hydrides such as FeTiH_{2} and LaNi_{5}H_{6} suffer from a low gravimetric efficiency, typically lower than 2wt%, while innovative hydrides such as MgH_{2} and alanates present slow absorption and desorption kinetics also at high temperatures. The need for a material able to overcome these limits at practical operative conditions of pressure (1–10 atm) and temperature (30–100°C) has stimulated the interest of many research laboratories. An important step in the experimental research is the analysis of the H_{2} storage efficiency of the new materials and the study of their absorption and
desorption kinetics. In favorable cases this process is reversible and cycling can occur at desirable pressures (1–10 bar). For materials with a significant capacity for hydrogen, however, desorption usually occurs at a higher temperature than the targeted conditions. Improving the uptake/release kinetics and retention of cycling capacity are currently the major areas of materials research. The disadvantages of these compounds include high cost, susceptibility to impurities, and low reversible gravimetric capacity (typically less than 3 wt%). To circumvent some of these issues chemical hydrides (also called complex or covalent hydrides) such as NaAlH4 have been studied and shown to reversibly cycle hydrogen on doping with a catalyst.

The Department of Atomic Energy has set a number of short-term goals against DOE targets for on-board hydrogen storage systems: 6.0 wt% and 45 g L-1 by the year 2015, but current materials fall far short of this goal. These goals should be met at near-ambient temperatures and applicable pressures (less than 100 bar), and any storage technology must minimize weight and volume contributions to the potential fuel-cell powered vehicle.

6.16 Hydrogen Storage as chemical and metal hydrides and in Metal-Organic Frameworks

Metal hydrides have been considered as potential candidates for reversible on-board hydrogen storage and release at low temperatures and pressures. Complex metal hydrides such as NaAlH4 have the potential for higher gravimetric hydrogen storage capacities in the operational window.

\[
\begin{align*}
\text{NaAlH}_4 & = \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \\
\text{Na}_3\text{AlH}_6 & = 3 \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2
\end{align*}
\]

But the main limitations of NaAlH4 are due to its slow uptake/release kinetics and high hydrogen desorption temperature. The development of enhanced hydrogen sorption by Ti-doped alanates opened up an entirely new
prospect for lightweight hydrogen storage. These materials have nearly ideal equilibrium thermodynamics, high capacities, and moderate kinetics. However, while the hydrogen capacity is 2 to 3 times better than commercial low-temperature hydrides, it does not meet the DOE storage capacity targets. Thus, other higher capacity reversible complex hydrides must be developed. At the same time, Na alanates continue to provide a good working model to better understand reversible hydrogen sorption in complex hydrides. Sandia’s direct synthesis process and new Ti-doping methods have led to a dramatic improvement in the reversible hydrogen capacity and hydrogen absorption and desorption rates. These methods will be employed to seek out advanced complex hydrides with larger hydrogen storage capacities and better performance.

Neat NaAlH₄ desorbs 70% of its H₂ at T ≈ 250 °C, this higher value of desorption temperature has been reduced by incorporating it into a MOF material. Allendorf and coworkers have infused the MOF, HKUST-1, \((\text{Cu}_3(\text{BTC})_2)_n\), with 4 wt% NaAlH₄ and due to the uniform particle size (formed in the rigid framework) and favorable chemical environment the sample was able to desorb 80% of the total H₂ at 155°C. These reports are promising for developing new systems utilizing MOFs combined with metal hydrides for reversible storage of hydrogen for on-board applications. Besides complex hydrides, amino-borane \((\text{NH}_3\text{BH}_3)\) has received much attention as promising hydrogen-storage material because of its satisfactory air stability, relatively low molecular mass \((30.7 \text{ g mol}^{-1})\), and remarkably high energy-storage densities (gravimetric and volumetric hydrogen capacities are 19.6 wt% and 140 g L⁻¹, respectively). However, the direct use of pristine \(\text{NH}_3\text{BH}_3\) as a hydrogen energy carrier in onboard/fuel-cell applications is prevented by its very slow dehydrogenation kinetics below 100 °C and concurrent release of volatile by-products such as ammonia, borazine, and diborane. Towards increasing the dehydrogenation kinetics by reducing the high temperatures required, amino-borane has been incorporated into porous MOF and its dehydrogenation behavior has been
studied. Interestingly, NH$_3$BH$_3$ incorporated within the MOF-74(Mg) has showed clean and dramatically improved H$_2$ release properties compared to pristine NH$_3$BH$_3$. This is a promising result for future development of hydrogen storage materials.

6.17 Metal Hydrides for reversible Hydrogen Storage Devices as DAE targets.

The purpose of this project is to focus on complex metal hydrides with high reversible hydrogen storage capacities and novel approaches to on-board hydrogen storage. The storage capacity of materials identified on the basis of reversible hydrogen storage capacity of 6 wt% or higher is shown in Table 6.5.

**Table 6.5**

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Reversible H$_2$ storage reaction</th>
<th>Heat of reaction (ΔH)</th>
<th>H$_2$ storage capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li$_3$N + 2 H$_2$ → LiNH$_2$(s) + 2 LiH(s)</td>
<td>28-30 kJ/mol H$_2$</td>
<td>11.5 wt%</td>
</tr>
<tr>
<td>2</td>
<td>LiNH$_2$(s) + 2 LiH(s) → Li$_2$NH + 2H$_2$</td>
<td>28-30 kJ/mol H$_2$</td>
<td>7 wt%</td>
</tr>
<tr>
<td>3</td>
<td>LiNH$_2$ + MgH$_2$ → LiMg N + 2H$_2$</td>
<td>30-32 kJ/mol H$_2$</td>
<td>8.19 wt%</td>
</tr>
<tr>
<td>4</td>
<td>LiBH$_4$ + LiNH$_2$ → Li$_2$BN$_2$ + 4 H$_2$</td>
<td>22-24 kJ/mol H$_2$</td>
<td>11.9 wt %</td>
</tr>
<tr>
<td>5</td>
<td>2 LiBH$_4$ + MgH$_2$ → MgB$_2$ + 2LiH + 4H$_2$</td>
<td>24-26 kJ/mol H$_2$</td>
<td>11.56 wt %</td>
</tr>
</tbody>
</table>

6.18 Hydrogen storage materials in the Li–Mg–N–H system:
Li–N–H complex hydrides are promising novel solid-state hydrogen storage materials currently under investigation. By using lithium amide and hydride (LiNH$_2$ and LiH) as a hydrogen storage medium, demonstrated the reversible absorption and desorption of hydrogen via the formation of lithium imide (Li$_2$NH) in reaction 6.1:

$$\text{LiNH}_2 + \text{LiH} \rightarrow \text{Li}_2\text{NH} + \text{H}_2$$  \hspace{1cm} 6.1

This reaction has a theoretical gravimetric density of 6.5 wt.%. The measured enthalpy of reaction ($\Delta H$) is 66 kJ/mol H$_2$, a value that is too high for near-ambient reactions and translates to undesirable operating conditions involving high-temperatures (and/or low-pressures).

Therefore, more efforts have focused on overcoming the thermodynamic and kinetic barriers associated with the LiNH$_2$/LiH system. The hydrogen desorption temperature lowered by the substitution of LiH with MgH$_2$ in Eq. (1). Specifically, this substitution results in an effective decrease in the hydrogen desorption temperature from 280 °C (Li–N–H) to 180 °C (Mg–Li–N–H) extrapolated to 1 bar hydrogen atmosphere via the reaction 6.2:

$$2\text{LiNH}_2 + \text{MgH}_2 \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2$$  \hspace{1cm} (6.2)

which contains a theoretical 5.5 wt.% H$_2$. The intermediate phases Mg(NH$_2$)$_2$ and LiH are formed upon heating ball milled starting materials under a hydrogen atmosphere. In practice excess of MgH$_2$ is also incorporated into the storage mixture to circumvent the formation of ammonia arising from decomposition of LiNH$_2$. Importantly, based on the measured plateau pressures of reaction at various temperatures, the corresponding van’t Hoff plot reveals that the enthalpy of this reaction (39 kJ/mol H$_2$) now approaches a thermodynamic value that is suitable for on-board hydrogen vehicle applications. The Molten State Process,
MSP, was used to develop new hybrid amide compounds by combining or “alloying” together different complex hydrides compounds.

The reversible storage capacity in wt% of different metal hydrides against DOE targets are shown in Figure 6.4.

![Metal hydrides against DOE targets](image)

**Figure 6.4:** Reversible storage capacity in wt% of different metal hydrides against DOE targets.

The diagram for molten phase synthesis of Li₃N hydrogen storage materials from and Li-Mg-N systems are shown in Figure 6.5.
The PCI measurements were performed and used to evaluate and confirm the $\Delta H$ as 41.6 kJ/mol $H_2$ for the reversible hydrogen storage reaction. Although the hydrogen release temperature is projected to be 90 °C to 1 bar, measurements reveal that the reaction is kinetically limited, and is quite slow at 180 °C, absorbing <2 wt. % in 8 h at 110 bars. Additional work is required to develop and incorporate an effective catalyst to overcome the current kinetic barriers and further decrease the hydriding/dehydriding reaction temperatures to their thermodynamically predicted values. Experimental realization of such theoretical values would increase the practical feasibility of the Li–Mg–N–H system for on-board storage applications.

### 6.19 Thermodynamics:

The reaction enthalpy ($\Delta H$) and entropy ($\Delta S$) for reaction were characterized by measuring the PCI at 210, 220, 230, and 240 °C. The corresponding van’t Hoff plot derived from the desorption PCI measurements. Here, the observed $\Delta H$ is calculated to be 41.6 kJ/mol $H_2$, a value that is consistent with the other reported by Luo (39 kJ/mol $H_2$).
6.20 Kinetics:

It is additionally assessed the hydrogen absorption kinetics for this storage system at 180 and 220 °C in a hydrogen atmosphere of 110 bar. From these data, it can be seen that the hydriding process is complete after 4.5 h at 220 °C, with a corresponding 4.3 wt.% hydrogen uptake. However, the absorption process is considerably slower at 180 °C, absorbing < 2 wt.% in 8 h. According to measured thermodynamic values of $\Delta H$ and $\Delta S$, the LiH and Mg(NH$_2$)$_2$ mixture has an expected theoretical hydrogen desorption temperature of approximately 90 °C to 1 bar pressure, conditions that approach those that would be practical for on-board storage applications. However, although the thermodynamics of this reaction appears to be promising, it is clear from the data that this reaction is kinetically hindered. Current experiments indicate that a much higher temperature is required to provide the necessary activation energy for the reversible reaction between Li$_2$Mg(NH)$_2$, Mg(NH$_2$)$_2$ and LiH to occur.

6.21 Metal organic frameworks (MOFs):

These are presently under substantial investigation due to their attractive properties as a new class of porous materials suitable for broad range of industrial applications such as gas storage [hydrogen storage], liquid absorption, liquid or gas separation, catalysis, etc. Hydrogen storage in solids which involve the use of high surface area sorbents are required to be studied for identifying compact, safe, cost effective storage medium for hydrogen. The MOFs with the combination of metal clusters and organic linkers offer great flexibility in the unique structure design and porosity. Those 3D networks often contain accessible pores and therefore they are ideal candidates for gas sorption. The current research efforts will mainly focus on the following issues for high wt% storage of hydrogen at ambient conditions (a) to develop porous MOF materials with narrow pore sizes based on light metal ions, such as, Be, Mg, Al, etc. (b) to enhance the heat of adsorption b/n H$_2$ and the material by utilizing kubas-type interactions. (c) to investigate the incorporation of metal hydrides, complex
hydrides into porous MOFs and study their \( \text{H}_2 \) desorption kinetics, and also notably, to a process for preparing it.

The synthesized metal–organic frameworks should be investigated for Hydrogen adsorption by molecular simulation. The simulated and experimental adsorption isotherms of pure \( \text{H}_2 \) are needed to be compared. The simulation study will provide quantitative microscopic insight into the adsorption mechanism in MOFs. Novel chemistry approaches should be adopted for predicting crystal structures and Non-Stoichiometry, crystal binding energies and decomposition path ways to synthesize compounds for more easily reversible addition of gases. Modeling, and simulation should be used to enhance our understanding of known systems and enable the design of new hydrogen storage materials and of catalysts to effect easy release and addition of \( \text{H}_2 \) and also to obtain thermodynamic and kinetic information to develop new methods and materials in hydrogen storage. The selectivity of gases (isotopes) in MOFs increases with increasing pressure and finally reaches a constant at certain pressure. Hence pressure effect on interactions between above gases and the framework also need to be investigated. In comparison to chemical storage (chemisorption) of \( \text{H}_2 \), physisorption in highly porous materials such as, Zeolites, Carbon materials and porous coordination polymers or metal-organic frameworks (MOFs) has attracted much attention due to the advantageous of non-activation, fast kinetics and reversibility of hydrogen storage and release. Among the porous materials, MOFs or porous coordination polymers have gained much attention due to their ultra-high surface areas for high wt\% \( \text{H}_2 \) storage applications. MOFs are crystalline solids with infinite network structures obtained by connecting the metal ions (nodes) or clusters (SBU) with multifunctional organic spacers (linkers). The main advantageous of MOFs over other traditional porous materials such as zeolites is that the pore size, dimensionality, and functionality can be tuned by a judicial choice of organic linkers. The use of rational design approach from suitable building blocks has resulted MOF materials with unique properties for a wide range of potential applications including catalysis, gas storage, nonlinear
optics, and sensing. The distinct features of MOFs are (a) Highly ordered crystalline nature (b) Tunable morphology with suitable functionality (c) Structural diversity (d) Flexible framework (e) Thermal stability, etc. Another interesting feature of MOFs is the gated adsorption which depends on the flexibility of the framework; that is, on hydrogen adsorption the framework structure expands and shrinks upon desorption. This property can be used to load hydrogen at high pressures and release at lower pressures. Although some MOFs store large amounts of hydrogen (6-9.05 wt%) at low temperatures (77 K) but at room temperature the hydrogen storage capacities reduce to 1 wt% or less. Hence, there is an urgent need for efficient and cost-effective materials with high hydrogen storage capacities at ambient conditions for realizing hydrogen economy.

6.22 Theoretical studies to understand the experimental results and for better design of storage material

It is very essential to understand the factors responsible for high storage capacity of H₂ with any materials. Understanding the nature of interaction between material and the gases is crucial for improving the interaction energy (heat of adsorption of H₂) with the matrix. Hence, theoretical simulations shall be carried out to understand the observed H₂ storage capacities of the materials synthesized and for further improvement in the design. First principles calculations can predict thermodynamic properties. For known system, periodic DFT will be used while for new system exhibiting weak van der Waal's interactions, quantum molecular cluster methods and Monte Carlo methods will be used.

Solid metal hydrides are a promising class of materials for hydrogen storage. They have attracted a lot of interest in recent years. However, many questions remain concerning their thermodynamic behavior that is critical for further improvement of their performance. In BARC we have recently developed
theoretical and computational capabilities to perform first-principles calculations of thermodynamic properties of solid metal hydrides. Most energetic calculations reported in the literature are performed at absolute zero temperature (i.e., 0 K). However, practical mobile applications of such materials will inevitably involve finite (even quite high) temperature and pressure. It is therefore critical that the thermodynamic behavior of hydrogen storage materials be examined and understood. Also completed an extensive computational study of the thermodynamic properties of lithium amides. The obtained thermodynamic functions are in excellent agreement with available experimental data. The full set of calculated thermodynamic functions provides a reliable basis for the construction of the pressure-temperature phase diagram of these materials. It allows the examination of the hydrogen adsorption and desorption processes under realistic operating conditions in anticipated applications. We have implemented such calculations and examined the stability and reversibility of hydrogen storage in several lithium amides and identified the phase boundaries for reversible hydrogen storage.

6.23 Challenge in designing Hydrogen Storage Systems

The main challenge in all hydrogen storage systems design is to meet three basic requirements, high safety, high efficiency and cost effectiveness at the same time. a) **The weight and volume** of hydrogen storage systems are presently too high, resulting in inadequate vehicle range compared to conventional petroleum-fueled vehicles. *Materials and components are needed that allow compact, lightweight hydrogen storage systems while enabling greater than 300-mile range in all light-duty vehicle.* b) **Energy efficiency** is a challenge for all hydrogen storage approaches. The energy required to get hydrogen in and out is an issue for reversible solid-state materials. The energy associated with compression and liquefaction must be considered for compressed and liquid hydrogen technologies. c) **Durability** of hydrogen storage systems is inadequate. Materials and components are needed that allow hydrogen storage systems with
a lifetime of 1500 cycles. d) **Refueling times** are too long. There is a need to develop hydrogen storage systems with refueling times of less than three minutes, over the lifetime of the system. e) The **cost** of on-board hydrogen storage systems is too high, particularly in comparison with conventional storage systems for petroleum fuels. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods. f) Applicable **codes and standards** for hydrogen storage systems and interface technologies, which will facilitate implementation/ commercialization and assure safety and public acceptance, have not been established.

### 6.24 Sievert’s-type apparatus for the study of hydrogen storage materials and systems

Setting up a Sievert’s-type experimental apparatus for the study of hydrogen storage materials and storage systems (Figure 6.6) has been completed at Chemical Technology Division in BARC. The apparatus is realized by only using commercial components. Sievert’s-type apparatus allows the study of pressure–composition ($P–C$) isotherms of the metal–hydrogen system in a wide temperature range, 300–773 K and H$_2$ pressure in the range 1–160 bar and the hydrogen absorption and desorption kinetics. The H$_2$ storage efficiency can be measured with a good accuracy of 3%. The experimental errors in the hydrogen absorption and desorption kinetics are of 1% and 6%, respectively.

There are two kinds of experimental approach followed. (a) Thermo gravimetric techniques, (b) Volumetric techniques. The accuracy of volumetric techniques is potentially greater compared to that of thermo gravimetric techniques since large changes in gas pressure are measured rather than small changes in the mass. In the volumetric devices the H$_2$ gas pressure in the reaction chamber is maintained constant during the experiment by mass flow controllers, in the hydriding path of the reaction chamber. Sievert’s-type apparatus consists of Hydrogen gas purification columns, Fully automated and
computer controlled Hydrogen Gas Boosting and Distribution System, High pressure high temperature hydriding reactors, secondary containment, High vacuum system, Gas analyzer, Mass flow controllers and meters; sample chamber; reservoir chamber; admission chamber; thermocouple controlled temperature programmable heater for reactors; variable leak valves; pneumatic on–off valve; manually operated valve; strain pressure gauge; mechanical pump.

Figure 6.6: Sievert’s-type apparatus for the study of hydrogen storage materials and storage systems

6.25 Hydrogen storage and a Van’t Hoff’s plot

The Hydrogen concentration in the M-H phase \([C_H]\) is a strong function of pressure, obeying a near square root pressure dependence called the Sievert’s Law which is shown in equation 6.3.

\[
C_H = k p^{0.5}
\]

(6.3)

where \(k\) is constant dependent on temperature.
The equilibrium H$_2$ pressure ‘p’ related to absolute temperature ‘T’ by a Van’t Hoff equation.

Van’t Hoff equation relates the plateau hydrogen pressure $P_{eq}$ (bar) to absolute temperature $T$, of the hydride, enthalpy change $\Delta H$, Entropy change $\Delta S$, and universal gas constant $R_u$.

The equilibrium H$_2$ pressure ‘p’ related to absolute temperature ‘T’ by a Van’t Hoff equation which is shown in equation 6.3.

\[
\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad \ldots \ldots \quad (6.4) ; \quad \text{where } R \text{ is the gas constant.}
\]

A plot of $\ln p$ Vs $1/T$ [Van’t Hoff's plot], will be straight line. The slope of which gives $\Delta H$ and intercept [1/T =0] gives the value of $\Delta S$. The value of $\Delta H$ can vary widely from metal to metal and is a measure of strength of the M-H bond. This will control hydriding and dehydriding properties of materials.

### 6.26 Hydrogen safety

Hydrogen has one of the widest explosive/ignition mix range with air of all the gases with few exceptions such as acetylene, silane, and ethylene oxide. That means that whatever the mix proportion between air and hydrogen, a hydrogen leak will most likely lead to an explosion, not a mere flame, when a flame or spark ignites the mixture. This makes the use of hydrogen particularly dangerous in enclosed areas such as tunnels or underground parking. Pure hydrogen-oxygen flames burn in the ultraviolet color range and are nearly invisible to the naked eye, so a flame detector is needed to detect if a hydrogen leak is burning. Hydrogen is odorless and leaks cannot be detected by smell.

Hydrogen codes and standards are codes and standards for the safe handling and storage of hydrogen. Codes and standards have repeatedly been identified as a major institutional control in deploying hydrogen technologies and developing a hydrogen economy. To enable the commercialization of hydrogen
in consumer products, new model building codes, equipment and other technical standards are to be developed and recognized by governments.

One of the measures on the roadmap is to implement higher safety standards like early leak detection with hydrogen sensors. Hydrogen safety issues are addressed in the Design and assembly of equipment, the integrity of the primary container of Hydrogen is ensured for all normal operations, anticipated operational occurrences, and withstand for the design basis accidents. Hydrogen leak prevention, detection, containment/exhaust.

6.27 Solid State Hydrogen in Metallic and Metallic + Carbon composite materials

Solid state storage of Hydrogen has been attempted by exploiting the mechanism of physisorption, chemisorption (metastable proton + materials) of hydrogen and inorganic compound formation such as alanates, clathrates and metallic hydrides. The four important vectors of R & D have been on (i) phenomena and mechanism; (ii) materials and performance (iii) design and engineering of devices and (iv) energy economics, viz., energy cost of hydrogenation plus dehydrogenation vs hydrogen caloric value realizable from a material. This corresponds to the walking the technology readiness levels (TRL-1 to 7). The status of various options and realization can be mapped to the technology readiness levels.

6.28 Physi-sorption Phenomena and Carbon Based Materials:

Physio-sorption of hydrogen relies more on pressure and limited charge transfer between hydrogen molecule/atom with the host material. From a fundamental scientific point of view, feasibility of weak hydrogen and van der Waals bond formation dictate the use of these materials for H2 storage. The biggest advantage is lower desorption temperature and less energy input for
absorption & desorption. Many carbon based materials such as (a) natural graphite, (b) expanded forms of graphite such as exfoliated graphite, (c) carbon foams derived from natural polymers and agri based systems such as seeds, husk ash (d) synthetic carbon forms such as MWCNT and (e) graphenes. The cost of these materials varies from very low for Expanded Natural Graphite (ENG) to very high for MWCNTs. Gravimetric storage of these materials vary from as low as 3% to as high as 30% in thin films. However, it is the lower end materials such as expanded graphite and graphite foams that have reached commercialization to a limited extent.

6.29 National Scene in Carbon based systems:

Two research groups studied in detail solid state storage using carbon based materials in India. IIT M and partners studied all forms of carbon based storage while NFTDC studied the process technology for obtaining various carbon forms in bulk quantities which will enable scale-up not only for H2 storage but also for other applications. The carbon materials and processes have to be taken together and summary of results are given hereunder.

6.30 Process Technologies for Carbon Based Materials

Process flow sheets for carbon based materials are simpler and are summarized subsequent paragraphs.

6.31 Expanded carbon forms from natural graphite

For materials starting for natural carbon, the principal issue is the level of inorganic oxide impurities, volatiles and sulphur in carbon. The separation processes for removal of inorganics by acid /alkali leaching followed by thermal treatment at 300-400°C in air environment which activates the atomic sites. Oxidants such as dichromates are used to expand along c-axis following the
thermal treatment. The trade secrets of many companies lie in the oxidant additives. Fundamental studies on such synthesized carbon show graphene foils in worm like structure together with glassy amorphous carbon and hexagonal platelet carbon. The volume phase fraction of these forms vary in a wide range depending of the process and the oxidant used which is the reason for such a divergence in the H2 sorption percentage. The processes are being standardized to obtain a repeatable phase fractions with an aim to increase the graphene content. The technology readiness level is TRL 3 and very few demonstrations have reached alpha prototypes (TRL-4)

6.32 Meso porous foams of carbon from natural materials

The natural materials comprise a wide range of polymers and agricultural products. Natural polymers are a good source of carbon, particularly short carbon fibres. Carbon - Carbon composites are derived from lignin obtained in these natural polymers. Agro-waste is a potential effective source for obtaining meso porous forms of carbon. Coconut shell, coir pith and corn cobs have been investigated. Seeds of many fruits (e.g. tamarind) have a potential. The important scientific knowledge that has been extracted from these studies show the role played by other impurities such as Si, Fe, Mg, K, N, P and B in enhancing H2 sorption characteristics. Of these, P and B seem to have the maximum effect. Taking cue from these naturally occurring systems, it is now possible to engineer such dopants.

The Process technology in general involves (i) crushing of solids after external wash; (ii) chemical activation using zinc chloride, phosphoric acid or sulphuric acid which remove the starchy matter and moisture to reveal basic carbon scaffold; (iii) thermal treatment around 300-400 C in absence of air (note in contrast natural graphite was thermal treated in air) which is similar to pyrolysis to remove volatile hydrocarbons. Any dopant can be introduced in the taking cognizance of chemical activating agents mentioned above. The dopant should
be part of the scaffold structure as potential sites. The technology and trade secrets lie in the chemical agents to get the carbon scaffold. Large surface area with highly active sites are achieved in these steps.

**6.33 Chemisorption and Metal Hydrides**

While the aforementioned carbon based systems are based on weak hydrogen bonding with the host scaffold, metal hydrides and meta stable metal - hydrogen systems (below the critical point in phase diagram depicting miscibility gap) have been investigated over the last two decades. Rare earth systems based on La, transition metals based on Ti and of late light metal based such as Mg have been the candidates. Two crucial parameters determine the performance metrics of metal hydrides, namely gravimetric percentage and desorption temperature. As metal hydrides form a mixed bond with lattice structure such as in MgH2, the chemical bond strength of M-H bond is high and therefore, higher energy inputs are required to release the hydrogen. In other words, higher the enthalpy of formation of hydride, higher is the temperature of desorption. Of the metal hydrides investigated by various groups across the world, two systems stand out, namely (i) La Ni5 with additions of Ce and Al to tune the desorption temperature from as low as 40 C to 140 C, with maximum storage of 1.2wt% H2 and (ii) Mg based materials with as high a storage as 6wt% with penalty on desorption temperature of 250 - 300C. The lowest desorption temperature achieved is 210C with 3.5 wt% storage capacity.

**6.34 National Scene in Mg based systems.**

Two research groups, one in NFTDC, Hyderabad and the other in BHU studied the metal hydride based solutions. A gravimetric storage capacity of close to 5 wt % and 270C desorption temperature was achieved with Mg-Expanded Graphite composite. It is possible to reduce the desorption temperature down to 200 - 250 C if we go down to nano size and fine tune the structure and dopants in expanded carbon additive. Other systems studied have
shown a gravimetric storage capacity ranging from 4 – 6 wt % with catalyst additive such as metals and metal plus oxides such as Cr2O3, Nb2O5. Reactive milling too has been carried out to obtained nano structured MgH2 with dispersants such as Mg2Ni, LaNi5; NFTDC also developed the process flow sheet and all the special purpose equipments within India such as Mg melting under Ar pressure, attritor mill for nano Mg production, thus enabling scale - up possibilities.

BHU group has done work on Mg based hydride with additives such as SWNT, CNT, carbon aerogel, graphene, misch metal, oxides such as CeO2, metallic additives such as Ti, Ni and quasi crystals of Al-Fe-Cu system. The quasi crystal additives have been reported to have given lowest desorption temperature of 200 °C. The following figure summarizes the performance metrics of many metal hydrides.

![Graph showing performance metrics of metal hydrides.](image)

6.35 International Scenario

**Mg + carbon composite Materials**

Magnesium competency centre, Stuttgart, Germany is the world leader in the investigations pertaining to these category of materials. They have
investigated a large number of Mg-X-H compounds as the target to achieve lower desorption temperatures as early as 2000. The present trend throughout seems to be add both carbon based materials to Mg materials to achieve an intermediate desorption temperature around 200°C. These systems are suitable for applications where waste heat or solar thermal is available close to usage point. NFTDC’s Mg + 5%ENG also follows the same pattern of composites.

Commercial Systems for large Applications

At present there are two companies involved in commercialisation of technologies related to magnesium based solid state hydrogen storage. They are

(i) Mc Phy, France (Mg based) Storage and industrial applications of hydrogen
(ii) Hydrexia, Australia (Mg based), developed hydrogen storage device

McPhy uses Magnesium based materials in powder form together with expanded natural graphite (ENG) to achieve a gravimetric storage capacity of 6wt %. Hydrexia uses milled flakes from cast Mg-Ni alloy to obtain low cost manufacture. During activation the flakes break down into smaller particles and subsequently sinter during cycling to form a solid porous material. McPhy energy solution involves a hydrogen generator based on water electrolysis, solid state hydrogen storage and equipment as required for converting hydrogen to electricity. McPhy’s hydrogen storage has two technologies namely,

a. ‘HDS technology’ which uses available heat (such as waste or solar) and
b. HES series (adiabatic storage) – Cartridges surrounding the storage material are surrounded by phase change material.

Hydrexia’s has come out ground storage products which use a scalable skid based design for industrial energy requirements at customer site to serve as an autonomous H2 storage system and the company also integrates Balance of
Plant. The capital costs are lower and four times storage capacity in Mg based systems compared to compressed gas bottles is achieved at lower pressures of only 10 bar thus providing an added advantage of safety.

**Small portable Storage Devices based on LaNi5 systems**

Small portable H2 canisters made of Al alloy for light weight and storing up to 1.2wt% Al in LaNi5 is available in the international market from a few companies. These canisters are now used for (i) camp sites and off grid to generate small amount of power using PEMFC for lighting and communication devices; (ii) one 2 wheeler EV vehicle in Taiwan (Asia Pacific Fuel Cell Technology) company has even integrated these canisters with PEMFC and motor to get 80 km range.

**International Status on Materials Research**

International efforts are focussed on size reduction with catalyst additives to enhance the kinetics and there are innumerable reports similar to BHU and NFTDC investigations. A noteworthy report of recent origin is from a team of California Institute of Technology modelled Mg-H clusters and shown that MgH2 particles with sizes lesser than 2 nm show remarkable trend of lowering stability due to modifications in thermodynamics. While, another group from Curtin University of Technology has experimentally shown that thermodynamic tuning can be achieved even for sizes up to 7 nm. In order to achieve absorption and desorption small clusters are being impregnated on scaffolds which offer durability and thermal stability. Alternative process such as severe plastic deformation and accumulative roll bonding, equi channel angular pressing of magnesium based alloys are also emerging.
Technology Readiness Levels: Materials, Processes, Devices in Solid State H2 Storage

The details of different Materials, Processes, Devices in Solid State Hydrogen Storage are given in Table 6.6.

Table 6.6: Details of different Materials, Processes and Devices in Solid State Hydrogen Storage.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Material</th>
<th>Gravimetric Storage Capacity Wt%</th>
<th>Desorption Temp</th>
<th>Process Technology Readiness (Scale Up)</th>
<th>Basic Product Development</th>
<th>Product dovetailing to load</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Expanded Graphite</td>
<td>~3%</td>
<td>~40 - 60 C</td>
<td>Easy</td>
<td>Not Done</td>
<td>Not Done</td>
</tr>
<tr>
<td>2</td>
<td>Meso-porous Doped Graphite</td>
<td>~6-10%</td>
<td>~40 - 60 C</td>
<td>Medium Complexity at TRL-3</td>
<td>TRL 4-6 to be done</td>
<td>TRL 4-7 to be done</td>
</tr>
<tr>
<td>3</td>
<td>LaNi5 based</td>
<td>~1.2%</td>
<td>~50 C</td>
<td>National at TRL-4</td>
<td>International at TRL-7</td>
<td>International at TRL-7</td>
</tr>
<tr>
<td>4</td>
<td>Mg based</td>
<td>~5-6%</td>
<td>~250-300 C</td>
<td>Intl at TRL-7 National at TRL-3,4</td>
<td>International at TRL-7</td>
<td>International at TRL-7</td>
</tr>
<tr>
<td>5</td>
<td>Mg + C Composite</td>
<td>~5-6%</td>
<td>~200-250 C</td>
<td>Intl at TRL-7 National at TRL-3,4</td>
<td>International at TRL-7</td>
<td>International at TRL-7</td>
</tr>
</tbody>
</table>

6.36 Future Directions for India in Solid State H2 Storage

R & D efforts in India has so far been only on TRL 1 - 2 (basic) and occasionally at TRL -3 (critical function demonstration). TRL - 3 demonstration has been on gravimetric storage up to 6wt% in carbon and Mg + Carbon based materials. 6wt% is a good metric even for automotive applications while 3- 4 wt% is acceptable for scale up and device development.

TRL 4 - 6 is the real valley of death which calls for device development with appropriate engineering scale. At TRL - 5, one has to integrate the service
condition, in this case the load or the H2 consuming device such as fuel cell and prove it in long duration testing and validation in TRL - 6 to iterate out the device design and scale. At TRL - 7, we should go for pilot production of devices and field testing and evaluation in large scale power production or automotive propulsion or distributed power generation. The thrust of our next round of R & D should be TRL 3 - 6 with device development and deployment in TRL - 7.

6.37 Materials

With regard to materials, India should spend its R & D resources on three systems only, namely (a) processed carbon forms from natural graphite and agricultural waste source and (b) Mg + carbon composites and (c) La based materials which will serve both sorption cooling as well as H2 storage for small applications. The former is for lower Temperature desorption and later for large scale H2 storage. The aim should be to scale up the processes, achieve the required nano sizes, embedded clusters, mesoporous structures so as to serve the device developers. Process reactor design and engineering, process equipments at a pilot plant level and product testing equipments are to be streamlined in an end to end technology endeavour. Here again the aim should be to develop process technologies to get the materials and process equipment at system level design at TRL 4-6.

6.38 Device Development and dovetailing to load (materials to device to deployment)

Here one should take a top down approach and decide on three major platforms;
(i) for large scale static storage using Mg + Carbon based systems and H2 release using waste heat or solar thermal process heat (CSH) and electricity production using PEMFC or SOFC depending on the impurity levels in H2; Mg based materials H2 storage stack with SOFC coupling can utilize the exhaust
heat from SOFC at 500 - 600 C to release H2 at 250C, thus enhancing the overall efficiency of the system. The unused H2 from fuel cell is also recovered or used for methanol/CNG reformation for fuel cell.

(ii) Devices using Carbon based materials systems for portable applications to take advantage of light weight and lower desorption temperature. This has to be coupled to a PEMFC (not with an H2 IC engine) in an automotive platform. A two wheeler vehicle platform is a useful starting point.

(iii) Small portable device development using LaNi5 (1.2wt%H2) materials which will give 1 to 2 kWe power generation equivalence.

These exercises are system level developments and they necessarily involved crossing TRL 4-6 with design, engineering and rendering work. The team size has to be bigger and with multidisciplinary character. These product development vectors with specific end use platform will give a fillip to the backward integration of materials to device endeavours.

6.39 Conclusions and Suggested Action Plan

There are several methods of hydrogen storage, having advantages and disadvantages over the other methods. It is important to note that any method that is to be adapted should fit the present infrastructure to reduce the infrastructure cost of the technology. The storage methods could be based on the site and requirement; they can be segregated into bulk storage, small storage capacities and mobile/on board storage.

Currently, hydrogen is stored either in high pressure tanks or in liquid form in cryogenic tanks. These forms of storage are not suitable for widespread commercial application. The alternative is to use solid materials for hydrogen storage. But each of the solid materials being used or studied for hydrogen storage has their inherent limitations. Metal hydrides are reversible under ambient conditions but are too heavy. Simple chemical hydrides are reversible
but at very high pressure and temperature. Complex chemical hydrides have high hydrogen density but suffer from poor reversibility. Sorbent materials offer good reversibility but require very low temperatures. Theoretical calculations have predicted many promising cluster-based materials, but they are hard to synthesize. Nanostructured materials provide opportunities but are yet to emerge as practical materials. Considering the impact that a successful hydrogen economy can have on our energy needs and the progress that basic research has made in the past decade in addressing issues and challenges in hydrogen storage, it is imperative that the momentum of current research into a basic understanding of hydrogen interaction in materials be accelerated.

After studying merits and demerits of different types of hydrides viz. MgH$_2$, Mg$_2$NiH$_4$, NaAlH$_4$, other alanates, borohydrates (gravimetric hydrogen capacity of >7wt%), commercial hydrides such as FeTiH$_2$ and LaNi$_5$H$_6$, adsorbents like carbon, nano-structured carbons (including CNTs) MoFs and hydrogen clathrate hydrate were investigated for hydrogenation and dehydrogenation reaction conditions and their kinetics, retention of cycling capacity, and reversible capacities. MgH$_2$ has the advantage of being stable at ambient conditions.

The major areas of research are improving kinetics of hydrogen uptake / release and retention of cycling capacity.

It must be realized that any new energy technology takes few decades of time period to get established. This is true for changeover from horse/bullock to steam engine and then from steam engine to IC engine, based road transport. Another aspect which should be realized is that the new technology, be it steam engine or IC engine has not been cheaper to start with than the previous technology whom they have replaced.

Hydrogen energy technology is helpful to India in two crucial ways. One it provides relief from the very scant oil reserves in the country (whereas Russia
has ~ 13%, Saudia Arabia ~ 12%, USA ~10%, Iran ~ 5%, China ~ 5%, Iraq ~ 4% of world oil reserves, India has only 1.04%) and the second is relief from pressures exerted by developed countries on ‘Climate Change’.

For India to be slowly shifting to Hydrogen, the following steps are essential and should be taken:

(i) Certain cities where hydrogen expertise exists should be declared Hydrogen cities. Some such cities may be New Delhi, Varanasi, and Hyderabad to start with. In these cities hydrogen filling stations (preferably PV driven electrolysis) should be established. These cities should first establish fleets of hydrogen fueled vehicular transport (3 wheelers and cars say 100 in number). Whereas for car HPG storage mode should be tried, for 3 wheeler and small car hydride storage mode should be preferred.

(ii) After about 3 years a certain fraction of vehicular transport (3 wheelers and small cars), a certain fraction say 1 through 5 to 10% of total vehicular population of these cities should be run hydrogen.

(iii) Exercise similar to (i) and (ii) should be done for heavy duty transport like buses and trucks.

(iv) Zero emission / nearly zero emission laws should be passed say first for the above cities and then for other cities / whole country.

(v) Carbon tax laws similar to that in (iii) above should be passed.

(vi) Hydrogen (clean fuel) incentive laws should be invoked. As per these, special tax rebates, tax exemptions subsides etc. to all those who help bringing in Hydrogen Energy and to Industries, corporate bodies who support and are participating in R&D commercialization efforts.

The Hydrogen safety system design will ensure the safe operation of the equipment, within designed parameters like pressure, temperature, gas/liquid flow etc. and hence of preventing fire, explosion, release of toxic materials or criticality which may lead to loss of material and property. This is achieved by a
built-in safety system incorporated in the design to ensure that operating parameters are not exceeded beyond safety limits through interlocks which control process parameters and alert operating staff by audio-visual signals, or by action such as switching off power supply, cutting off feed etc.
HYDROGEN STORAGE IN NANO-MATERIALS
7.0 HYDROGEN STORAGE IN NANO-MATERIALS

7.1 Introduction

Nano-materials appears to be a new state of matter even though it may for all practical purposes can be considered as part of solid state. However, it has been realized for some time now that this state may have its own equation of state and also the thermodynamics and surface properties of these materials can be different from those observed with bulk solid state materials. In this state unusual mechanical, electrical, electronic, optical, magnetic, dielectric and surface properties have been reported. The high surface/volume ratio of these materials has significant implications with respect to energy storage. Both the high surface area and the opportunity for nanomaterial consolidation are key attributes of this new state class of materials for hydrogen storage devices. Nanostructured systems including carbon nanotubes, nano-magnesium based hydrides, complex hydride/carbon nanocomposites, boron nitride nanotubes, sulphide nano-tubes of titanium and molybdenum, alanates, polymer nanocomposites, and metal organic frameworks are considered to be potential candidates for storing large quantities of hydrogen. Recent investigations have shown that nanoscale materials may over advantages if certain physical and chemical effects related to the nanoscale can be used efficiently. The present write up focuses on the application of nanostructured materials for storing atomic or molecular hydrogen. The synergistic effects of nanocrystalinity and nanocatalyst doping on the metal or complex hydrides for improving the thermodynamics and hydrogen reaction kinetics are considered. In addition, various carbonaceous nanomaterials and novel sorbent systems (e.g. carbon nanotubes, fullerenes, nanofibers, polyaniline nano-spheres and metal organic frameworks etc.) and their hydrogen storage characteristics are considered.

Hydrogen as the future generation fuel has been realized for some time now for various reasons including its high combustion value and also the
possibility of generating the fuel from renewable sources like water through photo-electro-chemical or photo-catalytic routes. Various issues with respect to hydrogen economy have been considered. The essential criteria that have to be considered for selection of materials for hydrogen storage include (1) light weight (2) cost and availability (3) high volumetric and gravimetric density of hydrogen (4) fast hydrogen sorption kinetics (5) easy and quick regenerability of the materials and reversibility (6) low temperature operation and favourable thermodynamics of the process (7) long term cyclability and also durability. All these characteristics for an appropriate hydrogen storage material place considerable restrictions on the choice of materials for hydrogen storage application. Among the various possibilities that have been considered and evaluated, nanomaterials like nanotubes, nanofibres, nanohorns, nanospheres and nanoparticles have been examined for the hydrogen storage capacity to fulfill the specifications of DOE. In spite of these consistent and persistent efforts, these materials are yet to satisfy the required characteristics like storage capacity of around 6 weight percent, favourable and tuning thermodynamics around 30-55 KJ/mol of hydrogen and temperature of operation around 373 K with about 1000s of cycles of operation.

7.2 Nano Materials - Potentials and Possibilities

In addition to the unique surface properties of nano materials, dimensionality is one of the specific features of nano materials. One dimensional nano rods and nanotubes are particularly interesting since they can store hydrogen. However the possibility nano horns and other three dimensional architectures also open up wide scope for this application. Nano-scale processing have been used in a generic way to enhance the performance of known hydrides and also to develop entirely new systems. Exploitation of these techniques is still in its early days, and one may expect in the next few years to see a continued refinement even in of metal hydrides, with more and more materials being developed to meet specific performance criteria. Furthermore,
the underlying process ball milling is already used in industrial production, implying that upscaling the process to large volume should not present any insuperable obstacles. Solid state hydrogen storage has always been appealing though the other possibilities exist and have also been demonstrated. This is because new routes for the synthesis of new solid state materials with tailored and also patterned solids like mesoporous solids, templated materials, metal organic frameworks and functionalized materials like poly aniline where functional amino groups can hook on hydrogen can be designed and synthesized for examination and exploitation as hydrogen storage materials.

Relationship between type of materials and enthalpy of adsorption/desorption is shown in Figure 7.1.

Figure 7.1: Relationship between type of materials and enthalpy of adsorption/desorption in KJ.mol\(^{-1}\) H\(_2\).
7.3 The role of nano scale structure on hydrogen sorption

Nano structures materials are generally defined that type of material which has at least one of the dimensions in nanometer scale only. The issue that is not yet definite is the detailed mechanism of hydrogen diffusion in nano materials. However, there are unequivocal proof that the materials in nanostate is capable of sorbing higher quantity of hydrogen as compared to the conventional material.

Effect of grain size on hydrogen absorption of ball-milled Mg powder at 573 K no activation and on poly-crystalline and nanocrystalline Mg2Ni at 473 K Reproduced are shown in Figure 7.2(a) and Figure 7.2(B) respectively (Ref.8). In the capacity for hydrogen absorption on 50 and 30 nm at 573 K on Mg sample is shown. It is seen the sorption capacity on 30 nm sample is higher than that in 50 nm sample and also the equilibration time is also considerably reduced.

![Figure 7.2(a): Effect of grain size on hydrogen absorption of ball-milled Mg powder at 573 K no activation](image1)

![Figure 7.2(B): Rate of hydrogen absorption on poly-crystalline and nanocrystalline Mg2Ni at 473 K Reproduced.](image2)
To demonstrate this effect unambiguously, the kinetic of hydrogen absorption on Mg$_2$Ni at 473 K is shown wherein it is obvious that the rate is several orders of magnitude higher on nano state as compared to the bulk polycrystalline state. The points of relevance are:

(1) Poly crystalline samples required prior activation while in nano state the same material absorbed hydrogen in the first cycle itself.
(2) Higher quantities of hydrogen is sorbed as compared to that on polycrystalline samples. This observation has been consistently recorded in the literature.

These studies indicated that a carefully monitored homogeneous nano structured material is required and hence other techniques other than ball milling like vapour condensation or sputtering have to be resorted to for generating homogeneous nano structured materials without much imperfections. These materials showed remarkable recovery to the nano structure after hydrogenation-dehydrogenation cycles though they may or may not retain the nano structure in the hydrogenated state.

A more moderate approach would be to continue carbon work for a limited additional time. In this timeframe; the most reasonable specific R&D tasks seem to be to:

(i) Perform fundamental surface and electronic studies.
(ii) Continue theoretical modeling studies of H on carbon surfaces and in bulk. Determine if there is some new CH bonding mechanism possible and, if theoretically so, how to achieve it in practice.
(iii) Study carbon-metal composites capable of catalyzing H$_2$ dissociation and so-called “spillover”.
(iv) Calculate the high volume production costs for promising carbons (e.g., graphite nanofibers and nanotubes).
(v) Develop standard testing techniques for measuring H₂ uptake and release from small carbon samples.

(vi) Develop a carbon sample and activation procedure that can be used as an international standard for researchers in the field. (This sample should have a reversible room temperature capacity > 2 wt% H₂).

7.4 Activated Carbon

Environmental destruction has increased the urgency to develop technologies for the recycling of various materials. The disposal of biomass waste from agricultural activities is an environmental problem. One of the solutions to this problem is to produce functional and reusable materials from biomass resources. Activated carbons fabricated from biomass resource have been studied for use as functional materials. In particular, some activated carbons with nano-meter size pores, i.e., micropores, offer high performance because of their high specific surface areas. These activated carbon materials are prepared from various raw materials such as coal, palm shell, coffee waste, and rice husks. Such activated carbon materials are widely used because of their high adsorption properties. These approaches have been applied to hydrogen storage materials and adsorbent materials for gases.

From recent reports, it is apparent that various carbon materials made from carbon nanotubes, graphite nanofibers, and activated carbons are capable of storing hydrogen and have been considered for the next generation of energy systems. For example, porous carbons with a specific surface area of 3220 m²/g is capable of storing hydrogen of 1.3 wt% at room temperature. The reports suggest the influence of specific surface area on the hydrogen storage efficiency of the micro-pores. In activated carbons fabricated from biomass recourses, it was reported that activated carbons with micro-pores in the pore structure were fabricated from lignin. Lignin is product as of a residual material in the manufacture process of cellulose pulps. Some researchers have used potassium
hydroxide (KOH) for the activation. The micro-pore structure found in activated carbons fabricated with lignin following KOH activation is expected to be utilized as hydrogen storage materials.

At 298K, the stored hydrogen content of the activated carbons increases as the equilibrium pressure of hydrogen increases. The hysteresis of stored contents was observed at 298K and 77K. These hystereses at 298K and 77K indicate that a chemical sorption also slightly occurred by effect of KOH activation. There results suggest that the micro-pore of activated carbons may effectively act as the hydrogen adsorption site at 77K and can be used in solid state hydrogen storage.

7.5 Nano-scale catalysis for improved hydrogen sorption

It is well known that the presence of small quantity of catalysts only affects the kinetics of the process. However, this effect is perceptible only when the catalyst particles are well dispersed in the system. In this case the catalyst and sorbing material are all in nano scale and could be in intimate contact. In Fig 7.3, a demonstrative example is shown wherein LaNi$_5$ system showed remarkably higher sorption of hydrogen when the nano crystalline alloy is mixed with catalyst. The choice of the catalyst possibly depends on the basic hydrogen sorbing system. Various different methodologies have been adopted like introduction of hetero atoms in carbon material whose function can be considered to be to dissociate hydrogen molecule and also facilitate the sorption kinetics. The results shown in Fig.7.4 demonstrate the validity of these postulates. The points of relevance are:

(i) The actual mechanism of action is yet to be fully understood and also the choice and selection of catalyst materials for the sorbing system have to be delineated.

(ii) Efficient dispersion methodologies have to be developed for the catalyst.
(iii) One has to be able to recognise the role of catalyst and distinguish it from the conventional role of active component. The later systems have to be identified as composite materials.

![Graph](image)

Figure 7.3: Rate of hydrogen absorption by LaNi$_5$ (a) Polycrystalline (b) nanocrystalline, and (c) nanocrystalline with catalyst

![Graph](image)

Figure 7.4: Thermal desorption of a mixture of hydrides (65 weight percent MgH$_2$ and 35 weight percent of Mg$_2$NiH$_4$) at 10 degree per minute (a) untreated (b) after ball milling of the hydrogenated mixture
7.6  Nanocomposites

As stated before, nano composites are systems where more than one active component is simultaneously present. To demonstrate this effect one example is shown in Fig.7.4. In is seen from this figure, it is seen that desorption temperature is considerably reduced in the composite system Mg$_2$NiH$_4$ and MgH$_2$ composite system when it was subjected to ball milling. The points of relevance for this class of nano materials for hydrogen sorption are: (1) The nature of mutual synergistic effect is still intriguing and has yet to elucidated. (2) It has been usually assumed that desorption kinetic behvaiour of the composite system will be more like that the characteristic of the low temperature component. It is possible to build a cascade of components with maximization of the sorption capacity or improving the kinetics of the process or reducing the temperature of operation.

7.7  Functional Nano-composites

The meaning of functional nano composites exhibits special function other than catalysis or sorption capacity and the function improves the main property of the composite. It can be the second component can facilitate the thermal conductivity of the system, or facilitating the solid state reaction of the active component or alter the hydrogenation thermodynamics in such a way that the system can operate at lower temperature. This aspect has not yet been fully exploited. In fact our understanding of this effect is minimal at this stage and needs careful further intense investigation.

7.8  Nano Scale Reactions

There are two possibilities. In one case a normally non miscible two components can become miscible in the presence of hydrogen and thus generating a useful hydrogen absorption system. A second variation is a metallic
hydride and a non-absorbing system can give rise to a system as result of hydrogen desorption from the first hydride. These two cases can be expressed in terms of simple reactions.

(i) $mA + nB + \frac{x}{2}H_2 \rightarrow AmBnHx$
(ii) $AmHx + nB \rightarrow AMBn + \frac{x}{2}H_2$

Other variations of these reaction sequences are possible in nano-functional systems for the generation of hydrides.

7.9 Perspective Aspects

There are still a number of issues that have to be answered before nano systems and nano science can be exploited for formulating energy (hydrogen) storage systems. Some of them are listed below:

(i) Even though the enhancement of hydrogen absorption in the nano state is established unequivocally, the extent of enhancement and if it will reach the level specified by DOE can be realized are still questions to be answered.
(ii) The factors like surface to volume ratio and also residual surface tension forces are favourable for higher hydrogen absorption, the precise manner of operation and how to optimize these residual forces are not yet clearly delineated.
(iii) Hydrogen absorption itself is intriguing since it is the smallest atom, the storage is due to simple trapping by van der Waals forces or due to formation of specific bonds.
(iv) The optimum size of the nano materials and also the extent of dispersion of nano catalysts have to be established with respect to individual species.
(v) In the case of carbon nano materials the hydrogen storage may have many other implications as stated previously since dimensionality and also possibility of carbon nano tubes, nano rods, nano cones all of them can
present various active sites and thus show enhanced hydrogen absorption. These aspects have to be established unequivocally.

(vi) Various levels of theory have been employed at the level of DFT to understand and rationalize the hydrogen absorption in variety of materials and these will also be intensified to formulate and design new materials. It is possible there are other untrodden avenues for exploiting nano state for hydrogen storage.
DESIGN CONSIDERATIONS
8.0 DESIGN CONSIDERATIONS

While the characteristics, properties and limitations of a storage material are the initial considerations for any given application, numerous engineering factors impact the design and performance of the integrated hydrogen storage system. Reliable and safe containment of hydrogen is required over the entire range of operating pressure and temperature during the projected lifetime with adequate margins of safety. Hence, the materials used to fabricate the storage devices and the components exposed to hydrogen should not be susceptible to hydrogen embrittlement or other detrimental chemical reactions especially corrosion. In addition to the design for mechanical integrity, heat and mass transfer related issues must also be addressed.

The designs of cylinders and refueling stations for H₂ gas compressed to high pressures should provide for accommodating heat generated during both compression and the inverse Joule–Thomson effect under ambient conditions in order to achieve efficient filling of the cylinder.

The cryogenic storage of hydrogen as either liquid or cryo-compressed gas requires designs that provide efficient thermal insulation that can minimize loss of hydrogen by boil-off or excessive vaporization from extraneous heat leaks.

For hydrogen storage using physical adsorption on activated carbon or other high surface materials, the thermal conductivity within the sorbent bed also needs to be augmented by metallic foams, fins, or meshes to manage the heat of reaction during adsorption or desorption.

The reasonably high heats of reaction in the range of ~20–100+ kJ/mol for hydrogen absorption by the metal hydrides and complex hydrides necessitate improved thermal conductivity of the packed beds within the
storage devices. Due to complexity of reactions associated with chemical hydrogen systems where both the reactant materials and the products formed during decomposition must be processed and/or separated dynamically as hydrogen is released, extensive thermal management is needed for various components and auxiliary subsystems. Because metal hydrides are commonly known to have very poor thermal conductivities in powder form, extensive efforts have been made to develop hydride bed designs with various configurations that enhance the effective conductivity within the bed without seriously impacting filling capacity, bed mass, and internal gas flow.

The thermal engineering issues may be summarized as follows:-

- Heat transfer is the major sorption/desorption rate controlling factor in metal hydride beds.
- In order reduce the cycle time and to reduce the total weight, improvement in the heat transfer characteristics of the bed is the most desirable.
- The hydriding and dehydriding reactions occur in the entire bed. However, faster rate of reaction may be observed in a narrow region close to the heat transfer boundary.
- Reactor configuration and geometric parameters are important in obtaining the desired sorption / desorption performance from hydrogen storage devices.
- Hydrogen supply pressure and coolant temperature are important operating parameters in deciding the charging / discharging rates in hydride devices.
- While storage material properties (Sorption, Thermodynamic, Thermophysical) are important, the thermal design of the overall storage device is crucial.
- Thermal masses of the heat transfer tubes, container, filters, distributors, heat transfer fluid, etc have to be minimized.
In addition to meeting high degrees of safety, efficiency and cost effectiveness, the main challenge in all hydrogen storage systems design is to meet the following basic requirements:

a) The weight and volume of hydrogen storage systems are presently too high compared to conventional petroleum-fueled vehicles. Use of lightweight materials and components are needed to enable more than 300-mile range for the light-duty vehicles.

b) Optimized Thermal and Mechanical Design of the reactor ensures that the storage capacity and kinetics are well balanced for a given application. High efficiencies coupled with low total weights should be achieved by proper design practices.

c) Energy efficiency is a challenge for all hydrogen storage approaches. The energy required to get hydrogen in and out is an issue for reversible solid-state materials. The energy associated with compression and liquefaction must be considered for compressed and liquid hydrogen technologies.

d) Durability of hydrogen storage systems is required with a lifetime of 1500 cycles.

e) Refueling time may be targeted to less than three minutes.

f) Cost of on-board hydrogen storage systems is too high, particularly in comparison with conventional storage systems for petroleum fuels. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.

g) Applicable codes and standards for hydrogen storage systems and interface technologies, which will facilitate implementation / commercialization and assure safety and public acceptance, are to be established.
APPLICATIONS OF HYDROGEN OTHER THAN TRANSPORTATION
APPLICATION OF HYDROGEN FOR STATIONARY POWER GENERATION
9.0 APPLICATION OF HYDROGEN FOR STATIONARY POWER GENERATION

9.1 Introduction

Diesel is mainly used in the road transport, agriculture, industry and power generation sectors. The total diesel sold in the country during 2012-13 was 69,080 TMT and petrol 15,744 TMT. Diesel constitutes about 44% of total consumption of petroleum products in India.

Metal hydrides have been widely considered and investigated for storage and delivery of hydrogen for transportation applications. However, several other energy related engineering applications of MHs are of interest to extend the use of hydrogen. Properties of hydrogen and MH are exclusively suited for constructing thermal devices such as heat pumps, refrigerators, high intensity thermal storage, hydrogen compressors, etc. Some of these are summarized in Tables 9.1 and 9.2.

Table 9.1: Different Applications of Metal hydrides Required MH

<table>
<thead>
<tr>
<th>Application</th>
<th>Required MH\textsubscript{X} Attributes</th>
<th>Candidate MHs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stationary fuel storage</td>
<td>Pr. 1-10 bar, very low cost, use waste heat, H-capacity &gt; 2 wt%, safety</td>
<td>TiFe, V-alloys, Mg-alloys, AB2 alloys</td>
</tr>
<tr>
<td>Vehicular fuel storage (ICE/Fuel cells)</td>
<td>H-capacity &gt; 5 wt%, cost, Pr. 1-10 bar, use waste heat, fast kinetics, durability during cycling, safety, contamination</td>
<td>AB2, Mg-alloys, alanates</td>
</tr>
<tr>
<td>Electrodes/Ni-MH batteries</td>
<td>Cost, reversible energy capacity, power density, activation, Pd &lt; 1 bar</td>
<td>AB5,AB2,AB</td>
</tr>
<tr>
<td>Chemical heat pumps and refrigerators</td>
<td>Very fast kinetics, cost, H-capacity, Pr.1-5 bar, use waste heat</td>
<td>AB5,AB2,AB</td>
</tr>
<tr>
<td>Purification, chemical &amp; isotope separation</td>
<td>Kinetics, Activation, impurity contamination, reaction efficiency, stability, durability, safety</td>
<td>Pd, V-alloys, Zr-alloys (AB2,AB)</td>
</tr>
<tr>
<td>Reversible gettering (vacuum)</td>
<td>Very low pressure, kinetics, pumping speed, activation, durability</td>
<td>U, Zr-alloys (AB2, AB, AxBvOz)</td>
</tr>
<tr>
<td>Gas gap thermal switches</td>
<td>Pd &lt;0.05 bar, fast kinetics, low power (10 mW), durability during temperature cycling, contamination, reliability</td>
<td>ZrNi, U, Zr-alloys (AB2, AxByOz)</td>
</tr>
<tr>
<td>Compressors (up to 500 bar) for liquefaction or filling gas storage tanks</td>
<td>Thermal efficiency (i.e., high ΔP/ΔT ratio), fast kinetics, cycling stability, safety, cost</td>
<td>V-alloys, AB5, AB2, AB</td>
</tr>
<tr>
<td>Sorption cryocoolers (space applications)</td>
<td>Fast kinetics, cycling stability, constant Pr absorption plateau, power, reliability</td>
<td>LaNi4.8Sn0.2, V-alloys, AB5, AB2</td>
</tr>
</tbody>
</table>
Table 9.2: Details of Different Application areas of Metal hydrides features utilized and Engineering Systems

<table>
<thead>
<tr>
<th>Applications areas</th>
<th>Hydride features utilized</th>
<th>Engineering systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Systems</td>
<td>- High storage capacity&lt;br&gt;- Reversible reaction during sorption process involving heat</td>
<td>Compressor, refrigeration, heat pump, heat storage, thermal engine, sorption cryocooler, gas gap heat switch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Battery, fuel cells</td>
</tr>
<tr>
<td>Energy Systems</td>
<td>- Hydrogen storage&lt;br&gt;- Hydrogen supply at moderate pressure from certain hydrides</td>
<td></td>
</tr>
<tr>
<td>Actuation and Sensing</td>
<td>- Reversible high pressure hydrogen supply&lt;br&gt;- Temperature variation in presence of gas&lt;br&gt;- Ability of certain hydrides to switch between transparency to opacity in presence or absence of hydrogen</td>
<td>Actuators, gas sensors, smart windows</td>
</tr>
<tr>
<td>Process</td>
<td>- Reacting with hydrogen and forming hydride when exposed to a mixture of gases&lt;br&gt;- Absorption preference of certain metals to certain isotopes of hydrogen, eg. Palladium preferably absorbs protium than heavier deuterium</td>
<td>H₂ purification, isotope separation, catalysis</td>
</tr>
<tr>
<td>Semiconductors</td>
<td>- Electrical conductivity of several hydrides similar to n-type and p-type conductivities of semiconductors</td>
<td>Semiconducting hydrides for 'hydride electronics'</td>
</tr>
<tr>
<td>Biomedical</td>
<td>- Powder formation by repeated hydrogenation and de-hydrogenation&lt;br&gt;- Biocompatibility of such process</td>
<td>Pre-processing of implant material preparation</td>
</tr>
<tr>
<td>Nuclear</td>
<td>- High transmutation capability without generating helium gas</td>
<td>Neutron moderator, transmutation</td>
</tr>
</tbody>
</table>
9.2 Power generation Using Gen Sets

Diesel engine is the prime mover, which drives an alternator to produce electrical energy. In the diesel engine, air is drawn into the cylinder and is compressed to a high ratio (14:1 to 25:1). During this compression, the air is heated to a temperature of 700–900°C. A metered quantity of diesel fuel is then injected into the cylinder, which ignites spontaneously because of the high temperature. Hence, the diesel engine is also known as compression ignition (CI) engine. A diagram of Genet based Power generation is shown in Figure 9.1.

![Diagram of Genet based Power generation](image)

**Figure 9.1**: Diagram of Genet based Power generation

Most frequently used diesel engine sizes are between the range 4 to 15 MW. For continuous operation, low speed diesel engine is more cost-effective than high speed diesel engine. Different types of captive power plants based on different technologies have compared in Table 9.3.
Table: 9.3  Comparison of Different types of captive power plants.

<table>
<thead>
<tr>
<th>Description</th>
<th>Units</th>
<th>Combined GT &amp; ST</th>
<th>Conventional Steam Plant</th>
<th>Diesel Engine Power Plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Efficiency</td>
<td>%</td>
<td>40 – 46</td>
<td>33 – 36</td>
<td>43 – 45</td>
</tr>
<tr>
<td>Initial Investment of Installed Capacity</td>
<td>Rs./kW</td>
<td>8,500 – 10,000</td>
<td>15,000 – 18,000</td>
<td>7,500 – 9,000</td>
</tr>
<tr>
<td>Space requirement</td>
<td></td>
<td>125 % (Approx.)</td>
<td>250 % (Approx.)</td>
<td>100 % (Approx.)</td>
</tr>
<tr>
<td>Construction time</td>
<td>Months</td>
<td>24 – 30</td>
<td>42 – 48</td>
<td>12 – 15</td>
</tr>
<tr>
<td>Project period</td>
<td>Months</td>
<td>30 – 36</td>
<td>52 – 60</td>
<td>12</td>
</tr>
<tr>
<td>Auxiliary Power Consumption</td>
<td>%</td>
<td>2 – 4</td>
<td>8 – 10</td>
<td>1.3 - 2.1</td>
</tr>
<tr>
<td>Plant Load Factor</td>
<td>kWh/kW</td>
<td>6000 – 7000</td>
<td>5000 – 6000</td>
<td>7200 – 7500</td>
</tr>
<tr>
<td>Start up time from cold</td>
<td>Minutes</td>
<td>About 10</td>
<td>120 – 180</td>
<td>15 – 20</td>
</tr>
</tbody>
</table>

Diesel gen-sets are preferred over because of its lower initial capital requirement, lower gestation period, good part load performance, comparable thermal efficiency and ability to use various fuels from light distillates to residual fuel oils. The wide scale usage of diesel gen-sets implies increased diesel fuel requirement. It has resulted in twin problems,

(i) In India more than 70% of its petroleum demand is met by importing the crude petroleum. Hence wide scale usage of diesel gen-set effect countries FOREX position.

(ii) The emission from usage of gen-set predominantly like the Particulate Matter, NOx are also of serious concern.

(iii) The growing number of diesel engines is posing twin problems of fuel oil scarcity and environmental degradation due to diesel exhaust emissions.

Petroleum Planning and Analysis Cell (PPAC), an attached office of the Ministry of Petroleum and Natural Gas conducted study of Sectoral Demand of Diesel & Petrol in India and report was submitted in 2013. Consumption trend of diesel in India from 1970-71 to 2012-13 is shown in Figure 9.2.
Some significant features of the report are mentioned below:

The power shortage in India is of the order of about 9%: at peak periods it goes up to 18%. In some regions it is worse. The deficit is increasingly being met through power produced by diesel and heavy fuel oil-powered generating sets. The power backup market in India is growing at an annual rate of 10-15% to rising demand-supply gap, however varying within the three different segments – generators, UPS and inverters.

Break up of Diesel Consumption Amongst Non-Transport Sector is shown in Table 9.4. At an all India level, diesel consumption for the period July-September 2012, in the non-transport sector is the highest in the tractors category at 6.09%, followed by industry gensets at 4.46%. The genset for non-industry purpose accounts for 4.3%. It can be clearly concluded that the in non-transport application of diesel genset accounts for around 8.76% of diesel consumption.
In view of the emerging trend of increased energy requirement of country and economic growth, it is expected that the use of genset units will increase substantially. Under such circumstances the conversion or development of genset units running using renewable energy becomes more relevant as these units could address the twin issue of energy crisis (fuel starvation) as well as environmental degradation caused by exhaust pollutants emitted by gensets.

All India End Use share of diesel in retail and direct and All India aggregate in 2013 is given in Table 9.5.
Table 9.5: All India End Use share of Diesel in retail and Direct: All India Aggregate 2013.

<table>
<thead>
<tr>
<th>End Use Segment</th>
<th>Retail Sales Volume (TMT)</th>
<th>Direct Sales Volume (TMT)</th>
<th>Overall Volume (Retail and Direct) (TMT)</th>
<th>Overall % (Retail and Direct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARS/UVs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cars &amp; UVs - Private</td>
<td>2612.06</td>
<td>-</td>
<td>2612.06</td>
<td>13.15</td>
</tr>
<tr>
<td>Cars &amp; UVs - Commercial</td>
<td>1775.88</td>
<td>-</td>
<td>1775.88</td>
<td>8.94</td>
</tr>
<tr>
<td>3 Wheelers-Passenger/Goods</td>
<td>1269.21</td>
<td>-</td>
<td>1269.21</td>
<td>6.39</td>
</tr>
<tr>
<td>COMMERICAL VEHICLES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCV/LCV</td>
<td>5613.35</td>
<td>-</td>
<td>5613.35</td>
<td>28.25</td>
</tr>
<tr>
<td>Buses</td>
<td>1428.59</td>
<td>469</td>
<td>1897.59</td>
<td>9.55</td>
</tr>
<tr>
<td>OTHER TRANSPORT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aviation/Shipping</td>
<td>-</td>
<td>96</td>
<td>96.00</td>
<td>0.48</td>
</tr>
<tr>
<td>Railways</td>
<td>-</td>
<td>644</td>
<td>643.67</td>
<td>3.24</td>
</tr>
<tr>
<td>AGRICULTURE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tractors</td>
<td>1327.80</td>
<td>144</td>
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<td>Agri Pumps Set</td>
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<td>OTHERS</td>
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<td>Mobile Tower</td>
<td>305.27</td>
<td>-</td>
<td>305.27</td>
<td>1.54</td>
</tr>
<tr>
<td>Others (Genset for non-industry purposes) &amp; Others</td>
<td>703.92</td>
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<td>17261.75</td>
<td>2608.67</td>
<td>19870.41</td>
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9.3 Hydrogen Energy for Power generation Using IC Engine Route

Hydrogen, as a carbon-free energy carrier, is likely to play an important role in a world with stringent protocols in place on greenhouse gas emissions. Hydrogen has an unlimited supply potential, since the basic raw material needed is water which occupies a vast portion of earth's surface. Hydrogen is the simplest and most abundant element in the universe. It makes up about 75% of all matter in the universe. Hydrogen fuel is also promptly recyclable as the final product of its combustion is water vapour which ultimately goes back to the earth's water reserves. Moreover, hydrogen is a clean burning fuel. It does not
contain ingredients like carbon or sulfur and hence, its combustion products, unlike those of diesel oil, do not contain obnoxious pollutants such as carbon monoxide, hydrocarbons and oxides of sulfur, etc.

Hydrogen is generated as a by-product in significant quantities by the chemical industry. Production of chlorine, sodium chlorate and ethylene/styrene are the largest sources. Currently, chemical manufacturers put this by-product hydrogen to a variety of uses, like:

✓ As chemical feed stock
✓ Sell to hydrogen distributors
✓ Vent out

The by-product hydrogen can be used to produce clean, zero-emission electricity that is either sold back to the grid, through the electricity utility, or used to offset power demand on site.

Use of hydrogen as a CI engine fuel can thus go a long way to meet the challenge of the growing diesel fuel scarcity and also reduce the menace of diesel smoke emissions. However, the problems due to oxides of nitrogen in the exhaust needs to be carefully addressed.

There are several reasons for applying hydrogen as an additional fuel to accompany diesel fuel in compression ignition (CI) engine. Firstly, it increases the H/C ratio of the entire fuel. Secondly, injecting small amounts of hydrogen to a diesel engine could decrease heterogeneity of a diesel fuel spray due to the high diffusivity of hydrogen. This makes the combustible mixture better premixed with air and more uniform. It could also reduce the combustion duration due to hydrogen’s high speed of flame propagation in relation to other fuels. The laminar flame speed for hydrogen is 1.9 m/s at normal pressure and temperature, and it is almost five times higher when compared to 0.4 m/s for most hydrocarbon fuels. Better homogeneity of the combustible mixture would provide better conditions
for the complete combustion process. Additionally, faster combustion becomes closer to constant volume causing an increase of the indicated efficiency.

Hydrogen because of its wide flammability limits, minimum ignition energy, high calorific value and high flame velocity has a great prospect as fuel for use in CI engines which can be used for power generation and several other applications such as irrigation pump sets, domestic stoves, lawn mowers etc. Besides, it does not need any substantial modifications in the existing hardware of the conventional diesel engine to run in dual fuel mode. Moreover, it does not contain any carbon atom and thus eliminates emissions of CO2, unburnt and partially burnt hydrocarbons such as aldehydes and other greenhouse gases concerned with combustion. Hydrogen Gen Set Application for the generation of electricity is shown in Figure 9.3.

![Figure 9.3: Hydrogen Gen Set Application for the generation of electricity.](image)

However, use of hydrogen as a fuel in CI engines poses some problems which need to be carefully looked into. Hydrogen has a very low cetane rating. It’s high flame velocity results in rapid rate of pressure rise during combustion and rough running of the engine. Its high self-ignition temperature makes it very difficult to
ignite by compression alone in a conventional diesel engine. Practical solution to these problems is hinged upon the use of diesel oil as the ignition source and thereby establishing dual fuel operation. Hydrogen combustion in atmospheric air is easily ignited at concentrations from 4% to 75% by volume. Hydrogen can be used for a part diesel oil substitution without major engine modifications. The engine can be operated as a dual fuel engine with hydrogen-air mixture induction during suction and injection of a pilot diesel charge in the conventional manner to trigger combustion.

There are some typical properties of hydrogen which are extremely critical to engine operation and therefore must be looked at from application point of view. It has an exceptional low density, which necessitates a high-pressure injection to ensure sufficient fuel-masses within the cylinder even at high engine loads. The wide ignition limits of H2/air-mixtures from $\lambda = 0.14$ up to $\lambda = 10$, which allow for unthrottled operation within a wide operating range. Third, and for the use in a CI engine most important, is the high self-ignition temperature, which can be found to be $\approx 853$ K, which is significantly higher than the respective value of conventional Diesel fuels ($\approx 523$ K).

A stable and reliable ignition source is very important for compression ignition engines. There can broadly be two methods for hydrogen ignition, the hydrogen is first ignited following impingement on the continuously operated glow plug

a) Surface Ignition

b) Diesel Pilot Injection

**Surface Ignition**

In the surface system ignition a single fuel injection pulse is provided. The combustion evolution then sharply raises the chamber pressure and temperature, and once better auto-ignition conditions are globally reached within the chamber,
then all of the hydrogen jets emerging from the multi holes injector ignite just following the mixing with air. Assuming adequate glow plug surface temperature, combustion starts as soon as one of the hydrogen jets reaches the glow plug. Knock is avoided by the then quick combustion of the hydrogen already available one working with hydrogen only but requiring a surface ignition, and one working with a pilot Diesel injection preceding the main hydrogen injection. After the combustion start-up phase, the injection of hydrogen in high temperatures gases produces a combustion rate basically controlled by the rate of injection for the hydrogen that then burns almost instantaneously following mixing with air and temperature heating up.

**Diesel Pilot Injection**

Diesel fuel is delivered into the combustion chamber in its liquid phase which upon combustion act as the ignition source for hydrogen. Other than hydrogen, Diesel fuel consists of several groups of hydrocarbons. Volatile substances with low evaporation as well as ignition-temperatures help to alleviate the CI– process. Once endothermic chemical processes are started further heat is generated to evaporate and burn non-volatile substances within the fuel.

**Fuel Injection System**

Hydrogen has an exceptional low density, which necessitates a high-pressure injection to guarantee sufficient fuel–masses within the cylinder even at high engine loads. The application of hydrogen in CI engine require a source of ignition which is provided by the pilot injection of diesel as indicated earlier. The diesel oil direct injection system is usually made of a mechanical fuel pump and injectors. Hydrogen injection system needs to be specifically design for engine intake system. The hydrogen injection system location is chosen such that it does not cause any major interference on the intake system in case of engine
operation with diesel oil only. The hydrogen also needs to be uniformly
distributed in case of multi-cylinder engine. A typical fuel induction system is
shown in the Figure 9.4.

![Typical Hydrogen Diesel Injection System](image)

**Figure 9.4: Typical Hydrogen Diesel Injection System**

In a diesel engine operating with diesel oil and hydrogen the ignition delay
depends on cylinder pressure, temperature and hydrogen concentration. The
ignition delay of hydrogen is higher than that of diesel oil, due to the higher
octane number and self-ignition temperature of hydrogen. Other advantages
associated to the use of hydrogen as a partial replacement to diesel oil are
reduced ignition failure and faster burning speed.
Saravanan and Nagarajan investigated hydrogen–diesel co-combustion in a diesel engine. They worked with hydrogen doses as enrichment to the diesel fuel. Hydrogen was changed in the range from 10% to 90% by volume. They focused on emission and performance characteristics of the engine as functions of brake load at various hydrogen doses. They concluded that knock can occur if only the hydrogen enrichment equals 50% or more at full load of the engine. Additionally they found lower hydrocarbons (HC), NOx emission as far as exhaust emission was concerned. Reduced fuel consumption by the use of hydrogen in a diesel engine has also been reported.

The use of EGR combined with indirect injection of hydrogen can reduce diesel oil consumption while increasing combustion rate and effective engine efficiency. The use of EGR in diesel engines with direct or indirect injection of hydrogen further reduce NOx emissions. Reduced sulfur dioxide (SO2) and soot emissions have been observed by the use of hydrogen in diesel engines IIT Delhi has studied the application of hydrogen as fuel for internal combustion engines for both Transportation as well as Power generation.

A commercial 4.00 kW diesel engine genset was modified to operate as a dual fuel engine with up to 60% full load energy substitution by hydrogen without undue loss of power output and efficiency. Helium, nitrogen and water vapour were introduced as diluents into the intake manifold which proved to be very effective in improving the knock-limited engine operation, thereby increasing the optimum hydrogen energy substitution percentage. With neat hydrogen supplementation, the maximum achievable hydrogen energy substitution could be as high as 85%, considerable engine derating and efficiency loss was observed. Hydrogen Supplemented Diesel Engine Performance is shown in Figure 9.5.
The optimum performance parameters of Hydrogen Supplemented Diesel Engine are shown in Figure 9.6.

Figure 9.6: Optimum performance parameters of Hydrogen Supplemented Diesel Engine.
Results from diesel engines operating with hydrogen fractions from 5% to 50% at different loads show reduced combustion duration, reduced heat transfer rate to the cylinder walls and increased effective engine efficiency, with more convincing results obtained for hydrogen concentrations below 30%.

Computational studies show that hydrogen increases effective engine efficiency of a diesel engine mainly due to the differences of entropy between hydrogen and hydrocarbon fuel combustion.

**Hydrogen SI Engine Route for power generation**

The SI engines which are used for power generation currently run on natural gas, but they can be optimized to run on propane, gasoline, biogas, or LPG etc. CI engines conventionally operate on diesel fuel. In developed countries like US, European countries prefer to use SI engine for power generation rather than CI engine due to the emissions from the later particularly associated with NO\textsubscript{x} and PM. In India too SI engine operated power generation is on the rise with major gen-set suppliers providing the Si variant. SI engines can be operated in two modes

a) Pure Hydrogen Mode

b) In dual fuel mode

**Pure Hydrogen Mode**

Hydrogen is an excellent fuel for SI engines. Its wide ignition limits and hence the ability to operate with limited throttling losses, high flame speed that leads to near constant volume combustion and high thermal efficiency, good mixing characteristics that allow high speed operation and formation of a homogeneous mixture with ease, resistance to auto-ignition that allows relatively high compression ratios to be used without end gas knocking and ability to be
used with other fuels to enhance their performance. All over the world research work has indicated several advantages and challenges to be faced when hydrogen is used as an engine fuel.

Comparison of Power with speed of Hydrogen fuelled Multi-cylinder Engine is shown in Figure 9.7.

Figure 9.7: Comparison of Power with speed of Hydrogen fuelled Multi-cylinder Engine

**In dual fuel mode**

The performance of a gas fuelled spark ignition engine is enhanced when relatively small amounts of hydrogen are present with methane. This improvement in performance which is especially pronounced at operational equivalence ratios that are much leaner than the stoichiometric value can be
attributed largely to the faster and cleaner burning characteristics of hydrogen in comparison to methane.

Indicated power output variations with equivalence ratios when operating on methane hydrogen mixtures is shown in Figure 9.8.

![Figure 9.8: Indicated power output variations with equivalence ratios when operating on methane hydrogen mixtures](image)

Studies have shown that the addition of some hydrogen to methane in a SI Engine enhanced the performance particularly when operating on relatively low equivalence ratio mixtures. The optimum concentration of hydrogen in the fuel mixture for producing a power gain and avoiding knock appears to be about 20-25% by volume over the range of conditions.
Break power with engine speed for the methane and different hydrogen blends is shown in Figure 9.9. Changes in the break power with the methane and hydrogen blends due to its low specific energy content in terms of volume, hydrogen fuelled engine has less power output than CH4 fuelled one for the same engine size, especially at low speeds. This problem can be solved by supercharging.

![Break power with engine speed for the methane and different hydrogen blends](image)

**Figure 9.9:** Break power with engine speed for the methane and different hydrogen blends.

The percent variation in the BSFC with the CH4 and hydrogen (CH4–H2) fuel blends as reference to CH4 fuel is shown Figure 9.10. The brake thermal efficiency increased with the increase of hydrogen fraction in fuel blends when hydrogen fraction was higher than 20%. When excess air ratio was under 1.4, hydrogen addition was not beneficial to improve efficiency. But according to the HC emission presented in the paper, hydrogen addition lowered the unburned HC emission which meant improved combustion efficiency. Reasons for the phenomenon may be reduction of heat transfer due to fast burn speed can be cancelled out by the higher in-cylinder temperature and shorter quenching distance caused by hydrogen addition.
Fig. 9.10  Changes in the BSFC with the natural gas and hydrogen blends.

\[ \text{NO}_x \text{ emissions depend on temperature and oxygen concentration in the cylinder. NO}_x \text{ emissions increase with the increase of hydrogen addition fraction as it is shown in Figure 9.11.} \]

Figure 9.11: Changes in the NOx emissions with the natural gas and hydrogen blends.
At the same excess air ratios, the oxygen content is kept roughly the same for all hydrogen addition levels, but the peak in-cylinder temperature is enhanced after hydrogen addition. So NOx emissions increase with the increase of hydrogen addition level.

Changes in the CO emissions with the natural gas and different hydrogen blends are shown in Figure 9.12.

![Graph showing CO emissions with different hydrogen blends](image)

**Fig 9.12:** Changes in the CO emissions with the natural gas and different hydrogen blends.

Although excess air for complete combustion is present in the cylinder, the engine is not capable of burning the total fuel. It was expected that hydrogen fuelled engine must have zero CO emission. This is due to the burning of lubricating oil film inside the engine cylinder. As engine speed increases, CO emission tends to diminish. CO emission increases with hydrogen addition when the excess air ratio is around stoichiometric, but the decreases with the addition of hydrogen under lean conditions. The increased in-cylinder temperature after hydrogen addition also contributes to stimulating the oxidation reaction of CO into CO2.
Changes in the HC emissions with the natural gas and different hydrogen blends are shown in Figure 9.13.

![Figure 9.13: Changes in the HC emissions with the natural gas and hydrogen blends.](image)

It can be found that HC emissions gradually decrease with the increase of excess air ratio and markedly lessen with the increase of hydrogen addition fraction.

A qualitative synopsis of the performance and emission footprint of hydrogen diesel dual fuel combustion (w/o EGR) as derived from the literature survey is shown in Table 9.6.
Table 9.6: A qualitative synopsis of the performance and emission footprint of hydrogen diesel dual fuel combustion (w/o EGR) as derived from the literature survey.

<table>
<thead>
<tr>
<th>Study Reference</th>
<th>Parametric Details Of The Case Study</th>
<th>Effect on Emission Spectra</th>
<th>Effect on Performance Indices</th>
<th>Desirable</th>
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<tr>
<td>Vorde &amp; Frame (1964)</td>
<td>&lt;15% HES PART LOAD</td>
<td>PM NOx TURC CO2 BSFC / BSEC</td>
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<td>Jing-jing, L. et al. (2006)</td>
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<td>NC</td>
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<td>Lambe and Wotton (1992)</td>
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<td>Pundir &amp; Kumer (2007)</td>
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<td>Saravanan and Nagarajan (2008)</td>
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<td>McWilliam, Megenidis &amp; Zhao (2008)</td>
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<td>Base and Maji (2009)</td>
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<td>Roy, et al. (2010)</td>
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<td>Saravanan and Nagarajan (2010)</td>
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<td>High load</td>
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<td>8.2 %v/v H2-air High load</td>
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<td>Lieu et al., (2012)</td>
<td>&lt;7% v/v H2-air 10-70% Full Load</td>
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<td></td>
<td>50-100% Full Load</td>
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<td></td>
<td>2.4 %v/v H2-air 10-70% Full Load</td>
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 NC = NO CHANGE
Pilot diesel injection varied between 67.7 BTDC to 3.2 ATDC @1500 RPM
At 90% H2 induction duration at 5° ATDC at full load
w/o EGR
TUHC = Raw H2 content in emissions
13-mode ESC cycle test
<table>
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<th>Study</th>
<th>HES</th>
<th>Load</th>
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<tr>
<td>Leta, et al. (2012)</td>
<td>30%</td>
<td>High Load</td>
<td>70-100% Full Load</td>
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<td></td>
<td>Low load</td>
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<tr>
<td></td>
<td>&gt;30% HES</td>
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<td>Wang, et al. (2012)</td>
<td>60%</td>
<td>24.5% Full Load</td>
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<td>Singh Yadav et al., (2012)</td>
<td>40g/hr</td>
<td>80% Full Load</td>
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<td>NC</td>
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<td>Christodoulou and Megaritis (2013)</td>
<td>≥6% (v/v) H₂-air</td>
<td>Low load</td>
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<tr>
<td></td>
<td>≤6% (v/v) H₂-air</td>
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<td></td>
<td>2-3% (v/v) H₂-air</td>
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<td>Köse &amp; Cinivc (2013)</td>
<td>2.5% (v/v) H₂-air</td>
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<td></td>
<td>5% (v/v) H₂-air</td>
<td>Trends for increase in engine speed, 1000 to 2500 RPM</td>
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<td>7.5% (v/v) H₂-air</td>
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<td>Sandalci and Korogz (2014)</td>
<td>36%</td>
<td>1300 rpm @ 5.1 kW</td>
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<td></td>
<td>46% HES</td>
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<td>Zhou, Cheung and</td>
<td>0-40% HES</td>
<td>&lt; 70% Full Load</td>
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<tr>
<td>Leung (2014)</td>
<td>70%</td>
<td>90% Full load</td>
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<td>Deb, et al. (2015)</td>
<td>0% -42% HES</td>
<td>5.2kw@1500 rpm</td>
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<td>Hamdan, et al. (2015)</td>
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<td>1260 RPM</td>
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<td>4SLPM</td>
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<td>4SLPM</td>
<td>Advancing injection timing @1260 RPM</td>
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<td>Korogz, Y., et al. (2015)</td>
<td>30%</td>
<td>Port loads</td>
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<td></td>
<td>HES</td>
<td>Full load</td>
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</table>
DISTRIBUTED POWER GENERATION
10.1 DISTRIBUTED POWER GENERATION

10.1 Introduction

While considerable amount of work is focused on hydrogen for transportation, distributed power generation has not received much attention. This initiative is very relevant for India today. Population of more than 300 million in the world does not have access to the electrical grid, as it is expensive to provide grid connectivity to populations located in remote, isolated, and geographically difficult terrains. Unfortunately our country has largest such population. Such communities primarily have two types of energy requirements—first as electrical energy for lighting and for electrical appliances and secondly, for meeting their energy needs of cooking. Renewable energy based distributed generation is the right solution. To meet such types of energy demand through renewable (e.g. solar and wind) alone becomes expensive, particularly for cooking. The green power sources are renewable but not sustainable. These cannot give power round the clock. That is why storage is required and hydrogen is a good option of energy storage.

To make renewable energy sustainable, there is need to develop a reliable, green, sustainable, and economical ESS (Energy Storage System). There are several energy storage options are available but storage of excess electrical energy in for of hydrogen has several advantages. Details of Characteristics of different Energy Storage System are given in Table 10.1.

Table 10.1: Details of Characteristics of different Energy Storage System.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Extra Large Scale</th>
<th>Large Scale</th>
<th>Medium Scale</th>
</tr>
</thead>
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<td>Response time</td>
<td>&lt; 15 minutes</td>
<td>&lt; 15 minutes</td>
<td>1-30 seconds</td>
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<tr>
<td>Discharge</td>
<td>Days to weeks</td>
<td>Hours to days</td>
<td>Minutes to hours</td>
</tr>
<tr>
<td>duration</td>
<td>Storage technologies</td>
<td>Compressed air and pumped hydro</td>
<td>Batteries</td>
</tr>
<tr>
<td>----------</td>
<td>----------------------</td>
<td>---------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Application</td>
<td>Long lasting unavailability of wind energy</td>
<td>Load leveling, secondary reserve</td>
<td>Primary reserve, load leveling, peak shaving</td>
</tr>
</tbody>
</table>

Integration of renewable energy source with hydrogen storage shall be viable solution. The excess electrical energy shall be used to generate hydrogen through electrolysis. The generated hydrogen is stored in pressure vessels to meet thermal energy (cooking) needs of the isolated communities. Thus in such an envisaged system, electrical energy is used only for lighting and running electrical appliances and thermal needs - such as that for cooking - are met by burning clean – green – hydrogen fuel.

10.2 International Status (including commercialization efforts by industry)-

Several decentralized generating system in Germany, Canada etc are demonstrated at MW scale. In Mainz/Germany, within a government-funded EUR 17m research project, a pilot plant for combined green hydrogen production and power-to-gas (injection of hydrogen into the natural gas grid) will be erected and operated. It comprises PEM electrolysis (up to 6 MW peak capacity), a novel ionic compressor, hydrogen storage tanks (~10,000 Nm3), a trailer filling facility, and a natural gas grid injection facility. Project partners are Siemens, Linde, Stadtwerke Mainz and HochschuleRheinMain. Schematic diagram of the Distributed Power Generation system is given in Figure 10.1.
The main objectives of the project are management of local grid bottlenecks, testing and gaining operational experience with components as well as developing intelligent control and market integration concepts. So far, the plant concept and layout has been refined, HAZOP studies have been performed, engineering and production of the key components has started and the authority approval request has been filed. Next steps are the start of civil construction, followed by erection of the components and balance of plant and start of operation; the latter is planned for first half of 2015.

10.3 National Status (including commercialization efforts by industry)

MNRE sponsored a project to demonstrate technical feasibility of storage of hydrogen from wind power. Two 5 kW wind turbines (installed in ERDA, Vadodara, where 5-6 months in a year wind is available) were connected with the load and to the water electrolyser through a controller (designed by ERDA). The controller diverts power to electrolyser, whenever it is in surplus (including in off power time) to produce hydrogen. This hydrogen is stored in cylinders and whenever required, it is used to generate power through hydrogen gen-set. This
was demonstrated at a very low level in Vadordara. This demonstration encourages to scale up wind hydrogen system particularly for remote locations such as islands. India also can explore possibility of acquiring this technology where it is already proven.

Water electrolyser is key component to succeed the hydrogen mission. Among three electrolyser technologies, alkaline electrolyser is proven, economical and available at large ratings. There are half a dozen alkaline electrolyser manufacturers are available in India. However, there is need to improve performance of indigenous alkaline electrolyser technology by incorporation of feature to operate at higher pressure using new materials, making more economical and efficient.

10.4 Action Plan (could consist of the following to the extent possible)

Following actions shall be considered:

(a) Feasibility of Power to gas project in India collaborations with all stake holders such as ONGC, GAIL, and PGCIL, Utilities, CEA etc.
(b) Demonstration of hydrogen village where all energy requirement shall met through renewable based distributed generation having hydrogen as energy storage medium.
(c) Development of efficient, economical high pressure alkaline electrolyser technology in collaboration with Indian industries.
(d) Application of hydrogen in chlore alkali industries
(e) Demonstration of MW scale wind hydrogen system
METAL HYDRIDE BASED COOLING SYSTEMS
11.0 METAL HYDRIDE BASED COOLING SYSTEMS

11.1 While the hydrogen absorption-desorption property is used in applications like hydrogen storage and purification, the reaction enthalpy changes can be applied in making hydrogen compressors and thermal machines such as refrigerators, heat pumps, etc.

The simple metal-hydrogen-thermodynamic machine, shown in Fig.11.1, operated as a single-stage heat pump, consist of two reactors filled with different materials A and B between which hydrogen is cyclically exchanged. The machine is operated on three temperature levels (TD>T_M>T_C) and two pressure levels (P_H>P_L). It is driven by heat input to A at the high temperature T_D, thereby desorbing hydrogen. The hydrogen flows to metal B which absorbs it, thereby forming a hydride and releasing the absorption enthalpy at a medium temperature level T_M (first half cycle). In the second half cycle, there is heat input to hydride B at a low temperature T_C, e.g. from the environment or other low temperature source, upgrading this heat to a higher temperature level T_M by desorption of B, then hydrogen flow to A, absorption in A, releasing absorption enthalpy at T_M. Between the two half cycles there are transition periods, where the two reactors have to be cooled down/heated up. The sensible heating up causes thermal losses which can be (partly) compensated by internal heat recovery between respective reactors. In the case of heat pump, there is a quasi-continuous heat output from the cyclically operated machine.

In case of a refrigerator (T_C<T_A, T_M≈T_A) there is only one cold generating half cycle. The same holds for the thermodynamically reversed heat pump, the heat transformer; in which there is heat input at medium temperature in each half cycle, but heat output at high temperature only in one half cycle. In
the latter two cases quasi-continuous cold/heat output can be achieved by operating two pairs of reactors in parallel with a phase shift of a half cycle.

11.2 CASCADING SORPTION SYSTEMS

To improve the performance of thermally driven sorption systems, it has been proposed that two sorption systems, each operating with a different working pair, may be coupled together to form a cascades as shown in Fig.3. A TC (Topping Cycle) is either providing cold and one times heat for the BC (Bottoming Cycle) (a), providing no cold and two times heat for the BC (b) or providing cold and two times heat for the BC (c). Operating principle of a single stage heat pump is given in Figure 11.1.

![Diagram of cascading sorption systems](image)

Figure 11.1: Operating principle of a single stage heat pump

The COP for cooling of a cascading sorption system comprises of two parts. The first is the COP for cooling of the TC and the second is the COP for cooling of the BC multiplied with the COA for heating of the TC, thus leading to:

\[
\text{COP}_{CS} = \text{COP}_{TC} \cdot \text{COA}_{TC} + \text{COP}_{BC} \cdot \text{COA}_{TC}
\]

Not all metal hydride schemes can be used as a BC in a coupled system. Double-stage and double-effect systems need a minimum driving temperature of 160°C. Triple-effect or multi-hydride systems need at least 240°C. There are
some other sorption systems which can provide such temperatures, but their efficiencies for cooling as well as heat pumping are rather low. Therefore only metal hydride single-stage/single-effect systems are suitable for the use as a BC. Such single-stage/single-effect systems can be operated with driving temperatures between 90 and 130°C; the maximum COPs that can be obtained are in the range of 0.5 to 0.7. If the use of metal hydride systems as a TC is considered, the results are more promising. The requirements are a high temperature of the released heat and either a very good COP or a very good COA. In principle, every machine scheme can be used as TC. However, if a single-stage system is used, there are no hydrides available which can deliver high efficiencies for the typical thermal boundary conditions of refrigeration conditions, and at the same time operate at pressure levels below 10MPa. Multi-hydride systems have also some disadvantages. The heat is not released at a constant temperature and the maximum COPs are around 0.9. To get good COAs, the driving temperature has to be in the range of 400 to 500°C which is difficult to handle with oil as heat transfer fluid. However, double-effect, triple-effect and double-stage systems or their combinations can fulfill the requirements for TC.

11.3 Metal Hydrides for Bottoming Cycles: Zeolite-water, salt-ammonia or nitrate-water systems can be used as TC. A zeolite-water system with a driving temperature of 310°C, providing heat at a temperature of 100°C can reach a COP of 0.53 and a COA of 1.53. Coupling with an appropriate metal hydride system with a driving temperature of 95°C and a COP of 0.65 would result in an overall COP of 1.52. With the same metal hydride system, a salt-ammonia system with a driving temperature of 290°C, a COP of 0.25 and a COA of 1.17 an overall COP$^{CS}$ of 1.01 can be reached.

11.4 Metal Hydrides for Topping Cycles: If metal hydride systems are used as TC, silica gel-water or LiBr- water systems can be used as BC. For example, silicagel-water systems can be driven with a temperature between 80 to 100°C
providing a COP between 0.5 and 0.65, LiBr-water systems can reach COPs up to 0.75 within the same driving temperature range. A metal hydride double-stage system with a driving temperature of 280°C and a temperature of the released heat of 100°C can provide a COP of 0.95 and a COA of 0.85. With the above-mentioned silicagel-water BC (COP of 0.63 for a driving temperature of 95°C) an overall COP of 1.49 can be reached. With the LiBr-water system (COP of 0.7 at a driving temperature of 95°C) an overall COP of 1.55 can be reached. If instead of the double-stage metal hydride system a double-effect system is used with a driving temperature of 370°C, a temperature of the released heat of 100°C and COP=0.9 and COA=0.8, the overall COP of a coupled hydride-silicagel-water system would reach 1.4, and the overall COP of a coupled hydride-LiBr-water system would reach 1.45. If a triple-effect metal hydride system is used with a driving temperature of 360°C, a temperature of the released heat of 100°C a COP of 1.2 and a COA of 0.8, then it is possible to reach an overall COP of 1.7 for a silicagel-water BC and an overall COP of 1.75 for a LiBr-water BC. Various cascading possibilities is shown in Figure 11.2.

![Figure 11.2: Various cascading possibilities](image)

System configurations for topping cycles is given in Figure 11.3.
In Figure 11.3, a survey is given on six cascading systems, coupling different metal hydride TC to a LiBr-water BC. Depending on the temperature of the driving heat for the BC, a single-stage/single-effect or a double-effect/double-stage LiBr-water system can be used.

Metal hydrides are promising working materials for thermally driven sorption machines. In recent years various designs of thermodynamic machines have been successfully developed and demonstrated on a lab model or prototype scale. A novel development are advanced metal hydride systems as topping cycles in cascading sorption systems for stationary air-conditioning applications.

11.5 At IIT Madras, a prototype MH based cooling system was built and tested with the following specifications:

- Hydride pair (HT/LT): ZrMnFe/MmNi_{4.5}Al_{0.5}
- Mass of ZrMnFe: 700 g
Mass of MmNi\textsubscript{4.5}Al\textsubscript{0.5} : 800 g
Cycle time : 3 to 12 minutes
Heat source temperature : 110 to 130\,^\circ\text{C}
Heat sink temperature : 25 to 30\,^\circ\text{C}
Cold temperature : 5 to 15\,^\circ\text{C}
Cooling capacity : 50 to 100 Watts
Cooling COP : 0.2 to 0.35

Further studies at IIT Madras also showed that MH based systems can be used for small capacity portable freezers (e.g. vaccine or serum storage) of performance better than the thermoelectric freezers, as seen in Table 11.1.

Table 11.1: Performance of MH based systems.

<table>
<thead>
<tr>
<th>Hot Side MH / Cold Side MH</th>
<th>$T_{\text{hot}}$ ($^\circ\text{C}$)</th>
<th>$T_{\text{ambient}}$ ($^\circ\text{C}$)</th>
<th>$T_{\text{cold}}$ ($^\circ\text{C}$)</th>
<th>$P$ (atm)</th>
<th>COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi\textsubscript{4.9}Al\textsubscript{0.1} / MmNi\textsubscript{4.15}Fe\textsubscript{0.85}</td>
<td>127/107</td>
<td>45/30</td>
<td>-12/-25</td>
<td>24/1.4</td>
<td>0.49</td>
</tr>
<tr>
<td>LaNi\textsubscript{4.75}Al\textsubscript{0.25} / Ti\textsubscript{0.8}Zr\textsubscript{0.2}Cr\textsubscript{0.8}Mn\textsubscript{1.2}</td>
<td>132/112</td>
<td>45/30</td>
<td>-14/-26</td>
<td>14/0.6</td>
<td>0.50</td>
</tr>
<tr>
<td>LaNi\textsubscript{4.83}Al\textsubscript{0.17} / Ti\textsubscript{0.8}Zr\textsubscript{0.2}Cr\textsubscript{0.8}Mn\textsubscript{1.2}</td>
<td>130/110</td>
<td>45/30</td>
<td>-11/-23</td>
<td>14/0.7</td>
<td>0.53</td>
</tr>
<tr>
<td>ZrMnFe / MmNi\textsubscript{4.5}Al\textsubscript{0.5}</td>
<td>132/125</td>
<td>45/30</td>
<td>-15/-20</td>
<td>8/0.5</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Internationally, several types of MH based cooling systems have been built and tested for applications such as automobile airconditioning, freezer food storage, etc. While Israel has run buses with MH airconditioners, in Japan several food freezer stores are in operation. Tokai University of Japan has developed a MH freezer of 2 kW cooling capacity at 0\,^\circ\text{C} using alloys of “Ti-Zr-Mn-V-Fe-Al” (36 kg x 2 for H.T. and 30 kg x 2 for L.T.) with a single abs/des cycle taking 7.5 hours. Cooling water from ground water and high temp (200\,^\circ\text{C}) waste heat from a steel factory were used.

Another Japanese study has shown that huge benefits in energy conservation and CO\textsubscript{2} reduction can be achieved with MH based systems. For cooling capacity of 10 kW at -30\,^\circ\text{C}, typical vapour compression freezer consumed about 7 kW electric power, whereas the MH based freezer consumed only about 2.3 kW in addition to about 20 kW of heat (which can be solar or waste heat) leading to a significant reduction of CO\textsubscript{2} emission by over 70 percent.
11.6 ACTION PLAN

Within the Country, capability exists to design and develop MH reactors of wide-ranging specifications (capacities, temperatures, pressures, kinetics, etc.). Specific application areas where MH based cooling systems would be beneficial need to be identified. Automobile air conditioning wherein hydrogen storage devices readily exist is a possible area. Food storage (both freezer and cooler) is another application deserving attention. In addition to being environment friendly, these systems can utilize waste heat from process industries and also solar thermal energy.
CHEMI-SORPTION THERMAL ENERGY STORAGE WITH METAL HYDRIDES
12.0 CHEMI-SORPTION THERMAL ENERGY STORAGE WITH METAL HYDRIDES

12.1 Introduction

A major advantage of reversible thermochemical energy storage systems is that the products are stored as stable chemicals, preferably at ambient temperatures. Hence, they can be stored indefinitely without incurring thermal losses, thereby greatly increasing overall system efficiency. Another advantage is that the heat is released at a constant temperature if the heat can be removed fast enough to prevent self-heating.

Metal hydrides provide an attractive possibility for thermal energy storage. Compared to conventional thermo-chemical reactions, metal hydride based systems offer several favorable features such as:

• Wide range of temperatures and kinetics are possible by tailoring the alloy compositions
• Temperature upgradation of the heat source can be achieved by heat pump/heat transformer effects
• Better heat and mass transfer characteristics and amenable to augmentation techniques
• Comparable gravimetric / sometimes better volumetric energy storage densities
• Cycling degradation (both physical and chemical) is minimal.
• Volume changes during absorption – desorption are minimal.
• Corrosion, toxicity, etc are avoided. Generally environment friendly. Flammability of H2 is an issue but can be easily handled.
• Cost is not prohibitive if one chooses suitable components and also designs optimally. Sizing is an important issue.
A typical MH based thermal energy storage system is shown in Figure 12.1.

![Diagram of MH based Thermal Energy Storage System]

Figure 12.1. Typical MH based Thermal Energy Storage System

**12.2 National Status**

Chemi-sorption based thermal energy storage work is rather scarce in India. However, over the past three decades, extensive studies on heat and mass transfer of metal hydride based hydrogen storage alloys have been reported in the country. At IIT Madras, extensive works on the design, development and testing of metal hydride based hydrogen storage devices. Such studies are also extensively reported from IIT Kharagpur, IIT Guwahati and IIT Indore in recent years. Even though all these works emphasize on the hydrogen storage aspects of metal hydrides, the results can also be extrapolated for thermal energy storage. However, at IIT Madras and IIT Guwahati some preliminary studies on the property requirements of metal hydrides for heat storage have been carried out. Currently, a DST project on development of MH based thermal storage systems suitable for CSP is ongoing at IISc Bangalore.
12.3 International

Several studies are reported which deal with the effect of geometric and operating parameters on the performance of the metal hydride based storage device. Even internationally, metal hydride based chemi-sorption heat storage studies are scarce. Yonezu et. Al. demonstrated heat storage system using coupled metal hydride beds with heat pipes in beds of CaNi$_5$ and LaNi$_5$. CaNi$_5$ operates in the temperature range of 40 to 100°C for heat storage and LaNi$_5$ operates in a temperature range 20 to 40°C to collect and store the hydrogen discharged from the CaNi$_5$ hydride during heat storage phase. The stored heat is recovered by reversing hydrogen transfer direction from LaNi$_5$ to CaNi$_5$. Later the same group developed Zerconium based hydrides, ZrMn$_{2-x}$Co$_x$Al$_y$ alloy with $x = 0.4$ to 0.7 and $y<0.1$ for use in temperature range of 100 to 200°C and ZrMn$_{1.92-x}$Co$_x$V$_{0.08}$ ($0.2<x<0.4$) for the temperature range 200 to 250°C. For high temperature (300 to 500°C) heat storage applications Bogdanovic and his coworkers studied Ni doped Mg/MgH$_2$ systems. The system developed by them is shown in Figure 2. Reiser et al. studied different Mg based systems for energy storage. They found that Mg-Fe and Mg-Co systems exhibit low dissociation pressures and these systems are of special interest for metal hydride based cooling systems.

12.4 ACTION PLAN

Within the Country, capability exists to design and develop MH reactors of wide-ranging specifications (capacities, temperatures, pressures, kinetics, etc.). Specific application areas where MH based thermal storage systems would be beneficial need to be identified. Several industrial processes (Food, Chemical, Pharmaceutical, etc.) which utilize and also reject heat at various temperatures are potential users of this technology. Concentrated solar power (CSP) systems, especially of small capacity distributed type, can benefit from the use of MH based thermal storage systems.
A Typical Heat Storage Device Using Metal Hydrides developed by Bogdanovic is shown in Figure 12.2.

![Diagram of a heat storage device using metal hydrides](image)

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of storage material (Ni-doped Mg)</td>
<td>14.5 kg</td>
</tr>
<tr>
<td>Volume of the pressure vessel</td>
<td>19.4 dm³</td>
</tr>
<tr>
<td>Weight of the pressure vessel</td>
<td>26 kg</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.75 g cm⁻³</td>
</tr>
<tr>
<td>Maximum operational pressure</td>
<td>50 bar</td>
</tr>
<tr>
<td>Maximum operational temperature</td>
<td>450 °C</td>
</tr>
<tr>
<td>Total weight</td>
<td>40 kg</td>
</tr>
<tr>
<td>Amount of stored heat / total weight</td>
<td>0.25 kWh kg⁻¹</td>
</tr>
<tr>
<td>Maximum power output</td>
<td>4 kW</td>
</tr>
<tr>
<td>Amount of water to be vaporized at the power output of 4 kW</td>
<td>6 kg h⁻¹</td>
</tr>
<tr>
<td>Maximum steam temperature</td>
<td>ca. 400 °C</td>
</tr>
<tr>
<td>Maximum steam pressure</td>
<td>40 bar</td>
</tr>
</tbody>
</table>

Figure 12.2: A Typical Heat Storage Device Using Metal Hydrides developed by Bogdanovic
APPLICATION OF HYDROGEN FOR COOKING
13.0 APPLICATION OF HYDROGEN FOR COOKING

13.1 Introduction

Future energy technology will utilize hydrogen with an increasing trend in steady as well as unsteady combustion processes. Hydrogen allows particularly low polluting processes without the necessity of taking care of in and out house pollution. This contribution presents a short survey about the state of the art of hydrogen combustion technology with particular emphasis as cooking source replacing LPG and CNG. The necessary research and development effort will be pointed out for the field of using H$_2$ as cooking gas. Hydrogen is advantageous over the conventional hydrocarbon fuels in the ease of catalytic ignition at low temperatures. The feasibility of adoption of inexpensive wide range of catalysts. However, it suffers from considerable non-uniform temperature distribution over the catalyst surface in the diffusive mode of combustion. A special design of fuel distribution would be required for reasonable mixing of hydrogen with ambient air entering at the bottom of the catalyst body. Therefore, a catalytic burning of the hydrogen in the home cooker is the best way to use the hydrogen for cooking. The hydrogen can be used separately with preheated catalyst as well as LPG–H$_2$ mixed with preheated air in cooking burner. The H$_2$ addition with LPG leads to a reduction in flame length and the flame length is observed to be reduced with increasing reactant temperature. However, the flame length is increased by increasing H$_2$ addition with constant LPG, which might have caused due to decrease in the Hydrogen and Carbon ratio in the flame. The flame temperature decreases with increasing LPG ratio in H$_2$/LPG mixture.

13.2 Technical Issues

(i) **Hydrogen Combustion:** The combustion / burning of hydrogen in open or nearly open ambience is a difficult exercise. This is due to the fact that self-
combustion / ignition energy of Hydrogen is extremely low. It is 0.02 mJ whereas for LPG it is 0.29mJ. Thus, a hydrogen source can get ignited even by an electrical spark or lightening. Therefore, controlled combustion of hydrogen in open ambience is difficult. This combustion is quite different from confined combustion of a certain fixed quantity of hydrogen as in cooker. The other difficulty is that on combustion hydrogen produces a colorless flame. Therefore, the effect of hydrogen burning in open ambience will be felt only when one enters the invisible hydrogen fire.

It is in the light of the above that no other group in India (and very few groups in the world) are doing any R & D and commercialization of device like Hydrogen based cooker. Hydrogen Energy Group at B.H.U. has therefore, undertaken the challenging project on “Development and Demonstration of Hydrogen Catalytic Combustion Cooker” and has successfully completed the first phase of the project.

(ii) The Hydrogen in Replacement of LPG: In India where most of the urban population has switched over to LP instead of wood fuel, the consumption of LPG has increased significantly. Thus whereas in 1980-81 the total requirement of LPG was about 405 TMT, in 2000-2001 it rose up to 6,613 TMT and now in 2015 it has touched the gigantic figure of more than about 10,000 TMT. It may also be pointed out that there is considerable subsidy on LPG. Thus at present whereas the market price of LPG is ~Rs. 296 per cylinder, there is a subsidy of Rs. ~316 (Real total price is Rs. 612/- per cylinder). Because of public reaction, the GOI generally does not increase price of LPG even when there is a rise of price on petrol and diesel. Finding substitute of LPG in Indian conditions appears more urgent than for petrol and diesel. Another factor, which makes replacement of LPG by clean fuel imperative, is the health aspect. According to WHO, Chulhas using coal, wood and animal dung as fuel and the resulting indoor air pollution has claimed 5 lacs lives in India in 2007. This is possibly the highest number of deaths due to indoor air pollution.
(iii) **The Hydrogen Based Catalytic Combustion Cooker:** The first part of investigation done in the BHU present project has been on determining the conditions, which prevents kindling of Hydrogen in Air. Unlike LPG, this situation arises due to altogether different physical properties of hydrogen. It has been found that when the velocity of hydrogen air mixture is greater than the combustion velocity of hydrogen, the combustion is not maintained and the flame is blown out. With high combustion velocities of hydrogen-air mixtures (e.g. ~3m/sec.), it does not appear feasible to maintain the necessary flow velocity over the completely catalytic surface which is the desired complete combustion condition.

To circumvent the above difficulty, we kept the hydrogen-air mixture outside the combustion limits. For this, we took hydrogen content of less than ~5 vol%. The catalyst surface is kept at a temperature lower than the self-ignition temperature of hydrogen. It should be recognized that due to peculiar property of hydrogen relating to the fact that it has a positive Joule Thomson coefficient, the temperature rises in the gas at pressures higher than the atmospheric pressure.

In view of the above said criterion we kept, the surface of the catalytic burner was optimized so that rate of heat generation did not exceed the dissipation rate of heat. The optimum surface area corresponded to ~20cm$^2$.

It should be realized that catalytic hydrogen cookers are pre-mixing burners where the reaction rate and temperatures are dependent on the catalyst. The basic difference between the catalytic combustion and direct combustion is that the final temperature in the former can be varied. In the catalytic combustion, cookers the envisaged temperatures are between ~200 to ~500$^\circ$C. The desired temperature is kept in between ~200 to ~500$^\circ$C (temperature range suitable for cooking) by controlling the feed rate of hydrogen. It should be pointed out that in the cooker when the source of hydrogen is hydride there is no
danger of starting fire even when the temperature of the system is high (~e.g. 500°C).

(iv) The Catalyst and Catalytic Action in the Present Project (Catalytic Combustion Cooker): Let us first outline the general considerations for catalysts and catalytic action. The fault with the statement that man has had trouble with combustion since Elijah and the burning bush lies in the fact that problem probably arose long before then. The production of energy by oxidation has always been desirable but has never been without difficulty. As a result, it seems to be an unnecessary complication to involve a catalyst in the process. Nevertheless, it has been found that advantages can be gained even though, as expected, further problems arise.

Combustion itself is hard to control, occurs only within specific fuel: air ratios and often produces pollutants. It is inefficient and energy recovery can be difficult. The introduction of a heterogeneous catalyst allows better control of oxidation over wider fuel: air ratios and produces less pollutants. On the debit side, catalysts may poison under extreme operating conditions.

The principle of catalytic combustion is simple. Mixtures of fuel and air are passed over a catalyst. Reaction occurs, liberating energy and oxidized products: for organic fuels, these are carbon dioxide and water, which may be discharged into the atmosphere. The reaction may be operated to generate energy (catalytic heaters, catalytic boilers, and catalytic gas turbines) or to remove pollutants (car exhaust clean-up catalysts etc.) In the case of hydrogen catalytic cookers, reaction between hydrogen and oxygen occurs, producing heat energy and steam/water which is non-polluting combustion.

There are several studies relating to catalytic combustion. The catalyst is used to break hydrogen molecule in hydrogen atoms, which then burns with atmosphere oxygen producing heat and steam/water. We may recall a well-known similar
catalytic reaction in ammonia synthesis. It is now well known that when a mixture of nitrogen and hydrogen gas is passed over the catalyst, ammonia is formed. When nitrogen molecules interact with iron atoms on the surface, they dissociate at relatively low temperatures. Iron catalyses the dissociation of N₂, in other words it lowers the energy barrier so that two nitrogen atoms (of the molecule) will separate easily. The iron atoms accomplish this by donating electrons to the nitrogen molecule. As a result the iron atom forms a chemical bond with the nitrogen molecule, and in a reciprocal manner, the bond between the two nitrogen atoms in the molecule is weakened. The weak nitrogen-nitrogen bond corresponds to a low energy barrier and facilitates N₂ dissociation. This process is typical of how catalysts work. The iron atom besides helping in dissociation of iron performs two other important functions in the synthesis of ammonia. First when hydrogen molecules H₂ interact with the iron surface, the hydrogen-hydrogen bond is weakened. Hydrogen atoms are thus easily freed and bind to the surface so that they may react to form NH, NH₂ and finally NH₃, ammonia the desired product.

Similar to the case of N₂, there are several catalysts, which can dissociate H₂. Some of Cu, Zn these are Fe, Ni, Co, Ti some alloys like Co-Mn-Ag, storage alloys like MmNi₅, ZrFe₂ etc. Of course Pt is known optimum catalyst for hydrogen dissociation but it is ~100 to ~1000 times more expensive than the above mentioned other catalysts. Unlike the use of Pt in hydrogen fueled comparatively expensive devices like vehicles, for much cheaper devices like hydrogen fueled cookers, use of Pt catalyst may not be feasible. Although we used Pt derived from chloroplatinic acid, we have been using the following less expensive but viable catalysts. Thus, the catalysts used correspond to Pt, Fe, Cu, Zn and ZrFe₂. There are two catalytic techniques which are relevant to hydrogen fueled catalytic cookers. One is use of porous ceramic plate embedded with platinum in pores. This produces flameless situation. Such as approach has been followed by our chemical engineering group. A great disadvantage of this method is the use of platinum (a very expensive and scarce
metal). The other catalytic technique relevant to hydrogen fueled cooker is based on suggestions of Roger billing according to which for hydrogen, “flame assisted catalysis” can also be produced. Thus when hydrogen air mixture is initially ignited high temperature (> 1200°C) flame is produced. Now if the metal around the nozzle when heated with this flame the metal will start producing catalytic action. Because of the catalytic action the burning temperature will come down (e.g. 300 to 500°C). We have followed this strategy for our hydrogen based cooker. Keeping in view the cost and ready machineability, we used brass metal for fabrication of nozzle system of specific hole size. Some of these are stainless steel, and copper. These were used in the form of wire mesh (2004) mapped around the nozzle of the cooker.

13.3 INTERNATIONAL STATUS (INCLUDING COMMERCIALIZATION EFFORTS BY INDUSTRY)

Several research groups all over the world are continuously working on the catalytic combustion of hydrogen. The Government Industrial Research Institute of Osaka, Japan, research group has done extensive work in the experimental catalytic combustion of hydrogen. Their experimental study was 168tiliza on the effect of fundamental conditions of hydrogen fuelled catalytic burners on their operating properties. In diffusive combustion, Pd-power coated Ni foam with relatively large pores could offer the highest combustion efficiency, however, it suffered from considerable non-uniform distribution of surface temperature. It was demonstrated that a ceramic foam coated with Co-Mn-Ag oxide was practically utilizable for catalytic appliances operating on hydrogen fuel, although it required a little preheating for initiating combustion. Premixing of air to a 40% stoichiometric amount with hydrogen was effective in improving combustion efficiency. The same group was also fabricated and tested two prototype heaters operating on hydrogen. A prototype heater in which hydrogen was introduced only from the bottom proved to yield inferior test results. This burner had appreciable
temperature non-uniformity and suffered from flame ignition invoked by hot spots at the bottom of the catalyst. A modified prototype heater in which hydrogen distribution was deliberately arranged exhibited relatively good test results in temperature uniformity and overall combustion efficiency of hydrogen. It could be operated at heat ratings from zero to 1.5 kcal cm$^{-2}$h$^{-1}$ with sufficiently high combustion efficiencies. A notable difference in performance was observed when Pt-impregnated nickel foam was replaced by the oxide-coated one. However, combustion efficiencies exceeding 96% were obtained up to a heat input of 1.0 kcal cm$^{-2}$h$^{-1}$. Other group from State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, People's Republic of China has done experimental study on the laminar flame speed of hydrogen/carbon monoxide/air mixtures. They have demonstrated the laminar flame speeds of H2, CO and H$_2$/CO in a Bunsen burner at normal temperature and pressure. The calculation of the laminar flame speeds was based on the reaction zone area instead of the unburned flame area. The good agreements among experimental results, and numerical simulations, and previous works have validated. Other group from State Key Laboratory for Turbulence and Complex Systems, Peking University, Beijing, China has studied the effects of hydrogen addition on the propagation of spherical methane/air flames. An experimental and numerical study on laminar burning characteristics of the premixed methane–hydrogen–air flames was conducted at room temperature and atmospheric pressure. The unstretched laminar burning velocity and the Markstein length were obtained over a wide range of equivalence ratios and hydrogen fractions. Moreover, for further understanding of the effect of hydrogen addition on the laminar burning velocity, the sensitivity analysis and flame structure were performed. The methane-dominated combustion regime and the methane-inhibited hydrogen combustion regime, the laminar burning velocity increases linearly with the increase of hydrogen fraction. However, in the transition regime, the laminar burning velocity increases exponentially with the increase of hydrogen fraction in the fuel blends.
Enhancement of chemical reaction with hydrogen addition as the increase of H, O and OH radical mole fractions in the flame was also deliberated. Research group from Department of Mechanical Engineering, University of Maryland, USA has done R&D work on combustion characteristics of a lean premixed LPG–H$_2$ combustor. Other USA research group from Combustion and Flame Dynamics Laboratory, School of Aerospace and Mechanical Engineering, University of Oklahoma, has shown the effect of elliptic burner geometry and air equivalence ratio on the nitric oxide emissions from turbulent hydrogen flames. German Aerospace Research Establishment, Stuttgart, has also done extensive R&D work on hydrogen combustion. Other German group from Fachhochschule Stralsund, Komplexlabor Alternative Energie, Zur Schwedenschanze, Stralsund, has established a non-stationary hydrogen cooker with portable hydride storage and catalytic hydrogen burner. They have shown that for normal use the design of the cooker was not favourable, so that the most important task is to adapt a hydride material for the storage, which only requires the heat of the surrounding air for dehydriding, but also has an acceptable mass-specific capacity. Then the cooker could be constructed in two pieces, which makes the replacement of the relatively heavy hydride storage easier. Furthermore, the cooker must be constructed in a secure way, which both excludes any hazards in its use and wrong operations of the cooker by the user.

A second way in the development of the cooker could be to construct geometrically relatively small hydride storages, which are arranged underneath the burner, to directly use the downward directed radiation. The UNIDO has also considered the requirements for the installation of the autonomous zero-emission energy supply system based on hydrogen as an energy carrier in developing countries

13.4 NATIONAL STATUS (INCLUDING COMMERCIALIZATION EFFORTS BY INDUSTRY)
In India, mainly four R&D groups are working in the area of application of hydrogen for home cooking is being done mostly at our group at Banaras Hindu University – Varanasi supported by MNRE. The main aim of this R&D was on considerations/optimizations of hydrogen catalytic combustion, development of catalysts including new catalysts for hydrogen catalytic combustion cooker, synthesis and development of hydride of choice, development and optimization of hydrogen catalytical combustion cooker, optimization of safety aspects of hydrogen catalytic combustion cooker, feedback from users of hydrogen catalytic combustion cookers. Where, the General considerations for development of Hydrogen Catalytic Combustion Cooker have been worked out. Catalysts have been identified. The Hydrides of choice for hydrogen storage for catalytic combustion Hydrogen cooker have been selected. Some catalytic combustion cookers have been fabricated and tests are being done. As outlined earlier strategy of flame assisted catalyst has been used. This permits one to use inexpensive catalyst. For a viable use of hydrogen cooker by general masses, one rather serious issue has to be resolved. This relates to the fact that hydrogen flame in the catalytic cooker, is nearly invisible. This is in one way quite risky. Since it is difficult to see the hydrogen flame, one gets a feeling of it through entering for example by the heating sensation it produces when you touch the flame. The flame temperature for flame assisted catalytic hydrogen burning is between 500 to 700°C and thus direct contact will produce burns and will be injurious. One possible way out of it will be of use some sodium chloride NaCl to burns with Brine. This turns invisible hydrogen flame visible by producing yellow NaCl will dissociate when put to burn with the hydrogen flame. The Na ions will emit yellow color. BHU R&D group looked into details of the flame developing yellow color in order to optimize this way of making hydrogen flame, colored to become visible and to find some better way of making the hydrogen flame visible. When NaCl powder is placed around the burning port, it vaporizes producing Na and Cl atoms (ions). The sodium vapor produces D line with a wavelength of ~589.5nm. This is one of the classified Fraunhofer lines observed in the visible spectrum of sun. This wavelength corresponds to transitions in atomic sodium in
which the valence-electron transitions from a 3p to 3s electronic state. Closer examination of the visible spectrum of atomic sodium reveals that the D-line actually consists of two lines called the D$_1$ and D$_2$ lines at 589.6 nm and 589.0 nm, respectively. This fine structure results from a spin-orbit interaction of the valence electron in the 3p electronic state. The spin-orbit interaction couples the spin angular momentum and orbital angular momentum of a 3p electron to form two states that are respectively notated as 3p($^2P^{0}_{1/2}$) and 3p($^2P^{0}_{3/2}$) in the LS coupling scheme. The 3s state of the electron gives rise to a single state which is notated as 3s($^2S_{1/2}$) in the LS coupling scheme. The D$_1$-line results from an electronic transition between 3s($^2S_{1/2}$) lower state and 3p($^2P^{0}_{1/2}$) upper state. The D$_2$-line results from an electronic transition between 3s($^2S_{1/2}$) lower state and 3p($^2P^{0}_{3/2}$) upper state. Even closer examination of the visible spectrum of atomic sodium would reveal that the D-line actually consists of a lot more than two lines. These lines are associated with hyperfine structure of the 3p upper states and 3s lower states. Many different transitions involving visible light near 589.5 nm may occur between the different upper and lower hyperfine levels. The invisible hydrogen flame turning yellow due to emission of sodium D line, is one convenient and viable way of circumventing the risk involved with the invisible hydrogen flame. However, there are certain disadvantages associated with this which warrants development of an alternate way for making hydrogen color visible. Another research group from Combustion Lab, Department of Aerospace Engineering, Indian Institute of Technology, Kanpur, India has demonstrated the experimental study of bluff-body stabilized LPG–H2jet diffusion flame with preheated reactant. They have shown the emission index of NO$_x$(EINO$_x$) be enhanced with increase in lip thickness and reactant temperature which may be caused due to both enhanced residence time and thermal effect, respectively.
GAP ANALYSIS
14.0 GAP ANALYSIS

14.1 GAS HYDROGEN STORAGE

The development of ultralight but strong composite materials in recent years has contributed to the development of lightweight high pressure storage containers for hydrogen. These are categorized under Class 4 and can take working pressures of 750 bar specified to make them applicable to mobile applications. However, currently, such cylinders are to be imported. Within the country, there are industries which are active on fabrication of components using high performance composite materials. However, their entrance into the high pressure H2 cylinder market would depend on the demand for such cylinders. For its in-house space related applications, ISRO is said to have developed wire-wound composite high pressure cylinders. This technology may be taken up for commercialization.

Cryogenic pressure vessels can store gaseous H2 at high densities without evaporation losses at reasonable cost. They are more compact and operate at lower pressures than conventional gas cylinders. However, these require high performance insulations. Maintenance of low temperatures in mobile devices is also an issue to be looked into. There is a need for considering this technology for use with automobiles.

14.2 LIQUID HYDROGEN STORAGE

The technology for handling LH2 is well established in space applications. However, the cryogenic temperatures (20 K) associated with LH2 presents serious technical and safety related challenges for automobile applications. Moreover, liquefaction is an energy intensive process. This may be a possible technology for large scale hydrogen transport, especially on barges using sea routes.
14.3 SOLID STATE HYDROGEN STORAGE

Safety due to reasonable pressures and temperatures is the main advantage of sorption based solid state storage. Significant developments have been made on the synthesis and development of storage materials. However, the major concern is still with the poor gravimetric capacities.

Capability to manufacture large quantities of both conventional (metal hydrides) and novel (complex hydrides, MoFs, etc) storage materials need to be developed.

While the knowledge base for the mechanical and thermal design of storage devices exists in the country, fabrication facilities for such large capacity devices need to be established.

14.4 Institutions involved in different stages of development of the products / processes and their infrastructure existing at present and details of new infrastructure to be created

In the area of hydrogen storage R&D, emphasis has been on the solid state materials led by Banaras Hindu University, Varanasi; Indian Institute of Technology Madras, Chennai; Rajasthan University, Jaipur; International Advanced Centre for Powder Metallurgy & New Materials (ARCI), Hyderabad; Non-Ferrous Technology Development Centre (NFTDC), Hyderabad; etc.

Thermal and mechanical engineering design of solid state hydrogen storage devices is extensively done by Indian Institute of Technology Madras, Indian Institute of Technology Guwahati; Indian Institute of Science Bangalore; Indian Institute of Technology Indore.
At the National Environmental Engineering Research Institute - Nagpur, R&D activities related to hydrogen storage in liquid organic hydrides are being carried out.

R&D on gas storage, especially on the development of composite cylinders is rather scarce except at the Central Mechanical Engineering Research Institute, Durgapur.

Indian Space Research Organization (ISRO) has extensive expertise in handling both gaseous and liquid hydrogen for its space programs. This wealth of knowledge needs to be tapped to extend hydrogen applications to automobiles and power generation in the country.

The MNRE funded Centre of Excellence in Hydrogen Energy at BHU has established facilities to synthesize and characterize storage materials of reasonable quantities. However, most of the other academic and research organisations have facilities for production and characterization of solid state storage materials only in small quantities. Therefore, suitable industrials units are required to be identified for production of materials in large quantities with a view to commercialise the materials developed by R&D institutions in the country. Such commercials units may also take up the job of production of canisters / devices of different storage capacities and operating conditions.

There is an urgent need for establishing facilities for the design, development and indigenous manufacturing of Type-III and Type-IV composite cylinders, which are presently being imported.

The Centre of Excellence for Hydrogen Energy at BHU specializes on the development, synthesis and characterisation of hydrogen storage materials. This can be further strengthened to develop new materials. There is also a need for setting up an exclusive Centre for the Technical Development of Storage Devices
and Systems. This should also include the estimation of Engineering and Thermo-Physical properties needed for the design of storage devices, accelerated life cycle testing, standardization of devices, etc.

14.5 To provide recommendations for promoting use of surplus hydrogen for supplying back-up power to telecom towers and for captive power generation

Presently, surplus hydrogen from Chlor-Alkali units is supplied in Type-I metal cylinders to the interested users. There is a need of developing more efficient methods of storing and transporting the surplus hydrogen from such units to the point of use. The alternatives could be tube trailers, use of high pressure composite cylinders, use of liquid organic hydrides and other innovative methods that will ensure higher gravimetric and volumetric hydrogen storage.
ACTION PLAN, TIME SCHEDULE OF ACTIVITIES & FINANCIAL PROJECTION
15.0 ACTION PLAN, TIME SCHEDULE OF ACTIVITIES & FINANCIAL PROJECTION

Suggested Action Plans are given in detail in this Section. These should be phased suitably (say in Three Phases) to complete by the year 2022. The activities are divided into Two levels as follows:

15.1 Action Plans for Immediate Action

15.1.1 High Pressure Gaseous Storage (HPG Hydrogen Storage)

(i) To carry out work of using hydrogen through (a) CNG cylinders (200 atm) and then (b) imported high pressure (250 to 400 atm) hydrogen cylinders for road transport in large scale starting from demonstration fleets. About 50 hydrogen fueled vehicles in each category may be prepared for demonstration to public. Based on successful demonstration of these vehicles, 500 to 1000 hydrogen fueled vehicles be prepared for large scale demonstration in next 5 to 8 years duration.

(ii) To take steps to foster consortium collaboration between HINDALCO, Indore and NPL, New Delhi to produce Aluminum cylinders reinforced with carbon fibre tapes and other high strength wrappings. BHEL, Hyderabad / IOCL, Nasik may also be roped in to join this effort. 50 cylinders (350 to 400 atm) may be prepared and tested online.

15.1.2 Solid State Storage: Metal, Intermetallic and Complex Hydrides

15.1.2.1 Vehicular (off board) Application

(a) Initiation of Large Scale Production of optimized, well known and already deployed hydride Mischmetal based (Indian has one of the
largest Mischmetal deposits in the world) optimized hydride e.g. Mm-Ni-Fe on pilot plant level (100 kg to 1 Ton Level).

(b) Vehicular Transport pilot level production of mischmetal based Hydride for on board applications: Small vehicles: Like three wheelers 50 in numbers (total required hydride quantities 2000 Kg); 10 nos. small cars (required hydride quantity 500 Kg).

15.1.2.2 Stationary (off board) Application

For the demonstration of 1000 Nos. Power Gen-Sets and production of hydride quantity in the range of 1 to 10 Tons, the Institutions such as BHU, IITD, CEL, MIDHANI, Mahindra Bajaj, TVS, Internationals Cars and Motors Ltd., and other auto companies may be engaged in the process of development with following assignments:

(i) Intensified R&D on material tailoring to obtain required parameters (gravimetric and volumetric efficiencies of 5 to 6 wt% and 60 Kg/m$^3$ hydrogen) for metal hydrides particularly catalyzed MgH$_2$ [Suggested Institution: BHU, Varanasi; NFTDC, Hyderabad; NEERI, Nagpur and other Institution engaged in this area].

(ii) R&D on other intermetallic hydride e.g. Zr Fe$_2$, Mg$_2$Ni type (3 to 6 wt%).

(iii) Upgradation of R&D efforts for evaluation of reproducible high efficiencies 5 to 6 wt% hydrogen in complex hydrides with particular emphasis on catalyzed MgH$_2$, NaAlH$_4$, LiAlH$_4$, NaAlH$_4$- MgH$_2$, Li-Mg-N-H systems.

(iv) Enhanced R&D efforts on Hydrogen Storage in nano-porous carbon storage capacity ~1 to 3 wt% at ambient conditions and 5 to 8 wt% at Liquid N$_2$ temperature.

15.1.2.3. Intensive Thermal Storage using Metal Hydrides
Recognizing the fact that the enthalpy of chemi-sorption in certain metal hydrides can lead to the high intensive and high efficiency thermal energy storage, it is recommended that Thermal Storage Devices of different capacities (500 kWth to 5 MWth) at different temperature levels (80 C to 300 C) may be developed. For achieving this, the materials (mainly Magnesium based) mentioned in the earlier mentioned Action Plans will be useful. Works related to this technology development is underway at IISc Bangalore.

15.1.3 Liquid Organic Hydride

In Indian context surplus hydrogen production at refineries and byproduct hydrogen from Chlor-Alkali industries may be targeted for storage in liquid organic hydride and its transportation to the delivery points, where hydrogen is recovered for the use in vehicles (fuel stations) or stationary power generation systems. Hydrogen storage in LOH and transportation at near ambient conditions is a potential method of hydrogen storage and delivery to long distance. Following action plan may be considered;

- Intensive research on liquid organic hydrides and other liquid hydrocarbons with high hydrogen storage capacity (both gravimetric and volumetric) may be taken up by setting a Center of Excellence on Liquid Hydrides with financial support from the Government.
- Under proposed Center of Excellence, a few more laboratories and industries working in the field of chemical process development may be networked with lead Institute like NEERI for rapid development of pilot plants. Petroleum industry may be networked to support the pilot runs
- R&D projects on further development of selective and stable catalysts may be funded
- International collaborative projects in mission mode with industry participation from both sides may be supported
- A demonstration project may be taken-up to study feasibility of the hydrogen storage through Liquid Organic Hydrides by setting up the
facilities near a refinery and providing hydrogen to telecom towers in the range of 50 to 100 kms. The project should demonstrate uninterrupted operation at least for one year.

15.2 Advanced Action Plans

15.2.1 Vehicular and Stationary Hydrogen Storage

15.2.1.1 High Pressure Gaseous Storage (HPG Hydrogen Storage)

(i) To carry out work of using hydrogen through high pressure (250 to 400 atm) hydrogen cylinders for road transport in large scale starting from demonstration fleets. Based on successful demonstration of 50 hydrogen vehicles in Phase-I, 500 to 1000 hydrogen fueled vehicles be prepared for large scale demonstration.

(ii) To get feedback from use of HPG (~350 to 400 atm) Hydrogen cylinders in (i) Road Transport (Buses and Trucks) and (ii) Power Generation: Gen Sets and Fuel Cells (>10kW), analyze these for future directions.

(iii) Based on these directions, production of indigenous high pressure hydrogen cylinders (~350 to 400 atms) based on Hindalco, NPL & BHEL technology; HPG Hydrogen cylinders to be manufactured (10,000 numbers and higher) by Bharat Pumps and Compressors and other similar companies. Attempts are to be made to shift to 100% indigenous production (350 to 400 atms) during 2022-2027.

(iv) To extend use of HPG (350-400 atms) Hydrogen cylinders (1,000 numbers to be produced from companies abroad and 10,000 numbers to be manufactured in India), for (a) HPG cylinders to be used in Hydrogen fueled small vehicles like 3 wheelers and large vehicles buses, vans cars and (b) HPG cylinders in stationary systems like Power Generating system (>10kW) 1000 Gen Sets and 500 in Fuel Cells.
(v) HPG Hydrogen cylinders Based on solid hydrides about 50% of present Gen Sets (10kW and higher) may be replaced in the crowded areas (e.g. Chandni Chowk at Delhi) (Chowk area at Varanasi) and similar other areas in the country.

(vi) Efforts to use the number of HPG fueled vehicles and Gen Sets to reach at least 30% of the total such devices in specific cities.

15.2.2 Solid State Storage: Metal, Intermetallic and Complex Hydrides

(i) Initiation of manufacturing of mischmetal based hydrides (1 Ton level) [Suggested Institution: CEL, MIDHANI and other Institution]

(ii) Vehicular Transport large scale manufacture and deployment of mischmetal based hydrides for, on board (a) 100 to 500 three wheelers, and 150 number small cars for transport. Stationary use: 1000 number of Gen-Sets 5 kW to 15 kW and 500 numbers of 5 kW to 15 kW Fuel Cells.

(iii) Selection of other (non-mischmetal based) viable intermetallic hydride coming out of R&D in I Phase; Initiation of pilot plant level (1 to 10 Tons) production of these hydrides [suggested Institution: BHU, ARC (Hyderabad), Jaipur University and other Institution].

(iv) Intensive R&D on Mg/MgH₂ hydrides
- Efforts of production of large quantities (100kgs to 1 ton)
- to decrease desorption, absorption temperature to about 200°C and lower, through the use of effective catalysts.
- To enhance the desorption / absorption kinetics.
- To improve recyclability from 100 to 1000 cycles through Mg agglomeration checking systems.
- To develop MgH₂ based vehicular transport like

(v) Intensified R&D to optimize gravimetric and volumetric efficiencies of complex hydrides (catalyzed NaAlH₄, Mg (AlH₄)₂, LiAlH₄ types) coming out of R&D in I phase; Evaluation of reversibility and cyclability on these [BHU, NFTDC (Hyderabad) and other Institutions].
(vi) Efforts on adopting PEM fuel cell instead of IC Engines for 25% of the above said vehicles.

(vii) Efforts to enhance hydrogen storage in nano/porous carbon and to use it in small vehicles.

15.2.3 Equipment using MH Thermal Energy Storage

Utilizing the technologies perfected in the earlier Action Plans for the development MH based of thermal storage devices, it is proposed to ‘integrate’ them with solar dish collectors for Concentrated Solar Power (CSP) up to the power capacity of 1 MWel for distributed power generation for remote non-grid areas. Also, MH thermal storage integrated ‘Steam Generators’ of different capacities may be demonstrated. IISc Bangalore is working on such developmental projects.

15.2.4 Hydrogen Cooker

Hydrogen cooker may replace LPG as cooking medium and it may take-up on priority, which will save huge quantity of the imported fossil fuel oil & financial support to make it affordable by the common people and emit no pollution.

An action plan has been suggested to further develop such hydrogen fueled home cookers. These may be fabricated in 1000 to 10,000 nos., distributed to the households, where they can be monitored. After successful demonstration, It may be followed by 25% to 50% replacement of LPG through public-private partnership.
### ACTIVITIES ON HYDROGEN STORAGE & OTHER APPLICATIONS

**MMP:** Mission Mode Projects; **RD&DP:** Research & Development Projects;

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Category of Projects</th>
<th>Time Frame (Year)</th>
<th>Financial Outlay (Rs. in Crores)</th>
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<tbody>
<tr>
<td>1</td>
<td>Mission Mode Projects</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Development and On-Field Deployment of High Pressure Gas Cylinders</td>
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<tr>
<td></td>
<td>Phase I</td>
<td>Type III</td>
<td>(Up to 250 bar)</td>
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<td></td>
<td>Phase II</td>
<td>Type III &amp; IV</td>
<td>(Up to 350 bar)</td>
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<tr>
<td></td>
<td>Phase III</td>
<td>Type IV</td>
<td>(Up to 700 bar)</td>
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<tr>
<td>1</td>
<td>Mission Mode Projects</td>
<td>Development of Solid-State Storage Devices &amp; Cartridges for Small Vehicles &amp; Stationery Power Packs (PPs)</td>
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<tr>
<td></td>
<td>Phase I</td>
<td>(2-wheelers &amp; PPs up to 20 kW)</td>
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<td></td>
<td>Phase II</td>
<td>(3-wheelers &amp; other apps to 50 kW)</td>
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<td></td>
<td>Phase III</td>
<td>(Large Capacity up to 250 kW)</td>
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<td>1</td>
<td>Mission Mode Projects</td>
<td>Manufacture of Solid-State Storage Materials In Large Scale</td>
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<tr>
<td></td>
<td>Phase I</td>
<td>(Pilot Plants for Mishmetal / Mg based hydrides)</td>
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<td></td>
<td>Phase II</td>
<td>(Large Scale manufacture)</td>
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<td></td>
<td>Phase III</td>
<td>(Advanced &amp; Complex hydrides)</td>
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<td>1</td>
<td>Mission Mode Projects</td>
<td>Development and Field Demonstration of Home Cookers with LPG mix &amp; with Complete Hydrogen</td>
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<td></td>
<td>Phase I</td>
<td>(Cookers with up to 75% LPG)</td>
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<td></td>
<td>Phase II</td>
<td>(Cookers with up to 25% LPG)</td>
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<td></td>
<td>Phase III</td>
<td>(Cookers with 100% Hydrogen)</td>
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<td>2</td>
<td>Development &amp; Demonstration Projects</td>
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<td></td>
<td><strong>Development and Field Demonstration of High Intensity Thermal Energy Storage Systems</strong></td>
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<tr>
<td></td>
<td><strong>Phase I</strong> (Capacity up to 250 kWth Temp. up to 200 Deg C)</td>
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<td></td>
<td><strong>Phase II</strong> (Large Capacity up to 1 MWth)</td>
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<td></td>
<td><strong>Phase III</strong> (Integrated Systems with CSP)</td>
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<td></td>
<td><strong>SUBTOTAL</strong> 100</td>
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**B/FRP: Basic / Fundamental Research Projects**

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<tr>
<th>3.</th>
<th>Basic / Fundamental Research Projects</th>
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<tr>
<td></td>
<td><strong>Synthesis &amp; Characterization of New / Novel Storage Materials and Devices</strong></td>
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<td></td>
<td><strong>Phase I</strong> Complex Hydrides, Carbons, MOF, etc)</td>
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<td></td>
<td><strong>Phase II</strong> (Scale up of Quantities)</td>
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<td></td>
<td><strong>Phase III</strong> (Fabrication of Devices)</td>
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<td></td>
<td><strong>SUBTOTAL</strong> 50 (10%)</td>
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**Grand Total** 550
CONCLUSIONS AND RECOMMENDATIONS
16.0 CONCLUSIONS AND RECOMMENDATIONS

16.1 Conclusions

16.1.1 Hydrogen in gaseous state is being utilized in various stationary or mobile devices / systems for generation of motive power or electricity. Currently, it is transported in compressed form (up to 200 bar pressure) in cylinders made of steel / aluminium from the site of its availability / production to the site of utility. The volumetric energy density of hydrogen is very low (i.e. \(\sim 12 \text{ MJ/m}^3\)) in comparison to natural gas, methanol, and propane. In view of this drawback, composite high pressure vessels of Type III have been developed. These vessels have a maximum service life of 15 - 20 years with refilling cycles 1000 nos./year. The cylinders have thin walled aluminium (AA6061) liner covered with carbon fibres. Over and above this layer epoxy resin matrix is wrapped. These cylinders are to be tested periodically (say once in 5 years). The Type IV cylinders with service life of 20 years and in various capacities have also been developed, and are 70% lighter than steel cylinders. Major manufacturers are M/s Quantum Technologies, M/s Luxfer Gas Cylinders and M/s Dynetek Industries Limited. Large number of cylinders from these manufacturers are in use for on-board applications in automobiles across the globe. Currently, carbon composite with aluminum liner type-III cylinder are not manufactured in the country. The metal liner with Kevlar fiber wound type cylinders are widely used in the country. Use of carbon composite wrapped metal liners have also been initiated. Use of type IV cylinders in the country is yet to start.

16.1.2 Hydrogen can be stored in liquid form in cryogenic conditions. So far, its application has been confined to space applications. Presently, this form of storage is not viable for widespread commercial applications. Liquid organic hydrides are potential candidates for hydrogen storage and delivery. The concept has been demonstrated successfully at laboratory level. Pilot level studies
demonstrate the efficacy of the system and possibilities of up-scaling. Considerable work has also been carried out at National level leading to generation of IPR for country. Further work is being conducted and expected to be supported by government/industry may lead to development of a technology for safe hydrogen storage and delivery at near ambient conditions for long distance transportation.

In order for the hydrogen program to be successful in India, development of required testing facilities, standards codes and regulations for cylinders, components, vehicles and fuel need to be developed in line with international regulations.

16.1.3 The alternative for gaseous hydrogen is the use of solid materials for on-board storage of hydrogen. But these have inherent limitations. Metal hydrides are reversible under ambient conditions, but are too heavy. Simple chemical hydrides are reversible at very high pressure and temperature. Complex chemical hydrides have high hydrogen density, but suffer from poor reversibility. Sorbent materials offer good reversibility at very low temperatures. Solid state storage in the form of hydrides is the most efficient as well as safest mode of hydrogen storage. It may be used in small sized automobiles and other systems/devices operating with hydrogen as fuel such as three wheelers, cars, fuel cell based gen-sets of smaller capacities of the range 5 kW to 15 kW. On-board hydrogen storage for transportation applications focuses primarily on low-pressure and materials-based technologies to allow a driving range of more than 500 km for hydrogen-fueled light-duty vehicles as per Department of Energy (DoE), USA. The DoE has set a short term goal against on-board hydrogen storage i.e. 5.5 wt% and 40 g/l by the year 2015. MgH₂, catalyzed with leached ball milled Al-Cu-Fe quasi crystalline alloy showed better hydriding kinetics at 200°C & 150°C by absorbing 5.5 wt% in 1 minute and 5 wt% at 100°C in 30 minutes under 20 bar pressure. Kinetics of this hydride was degraded slightly
over 51 sorption cycles. Further experiments are going on to observe the reversibility of this hydride up to 500 and 1000 cycles.

16.1.4 The use of hydrogen in gaseous form may be risky, because of low (0.2 mJ as against 0.24 for gasoline) self-ignition energy, if it is not properly handled. Japanese and other agencies estimated that bursting of high pressure gas (HPG) hydrogen cylinder will cover an area of about 6 meters diameter, in which human beings cannot survive. Therefore, HPG hydrogen cylinders can only be used safely in either for stationary storage or for large vehicles e.g. buses, trucks etc. For small vehicular utilities e.g. two, three wheelers, small cars and small power plants: Gen Sets, <10kW hydride storage modes are safe to practice.

16.1.5 Nano-materials can also be considered as part of solid state. These materials have high surface/volume ratio for hydrogen storage. various nanomaterials like nanotubes, nanofibres, nanohorns, nanospheres and nanoparticles have been examined for the hydrogen storage, which are yet to satisfy the required characteristics like storage capacity of around 6 weight percent, favourable and tuning thermodynamics around 30-55 kJ/mol of hydrogen and temperature of operation around 373 K with about 1000s of cycles of operation. The techniques other than ball milling like vapour condensation or sputtering can produce homogeneous nano structured materials without much imperfections. These materials showed remarkable properties of nanostructure after hydrogenation-dehydrogenation cycles.

16.1.6 Activated carbons fabricated from biomass resources like coal, palm shell, coffee waste, and rice husks have been studied and showed high performance because of their high specific surface areas. These are capable of storing hydrogen of 1.3 wt% at room temperature. At 298K, the stored hydrogen content of the activated carbons increases as the equilibrium pressure of hydrogen increases. The presence of catalysts affects the kinetics of the process. Catalyst LaNi5 showed remarkably higher sorption of hydrogen, when
the nanocrystalline alloy is mixed with catalyst. The nanocomposites system like Mg$_2$NiH$_4$ and MgH$_2$, desorption temperature is considerably reduced. The issues, which are to be addressed to include optimization of size of the nano-particles and establishment of the extent of dispersion of nanocatalysts in nanomaterials. The application of nano-materials for hydrogen storage is still in R&D stage.

16.1.7 Use of hydrogen as a compression ignition (CI) engine fuel can go a long way to meet the challenge of the growing diesel fuel scarcity, reducing menace of diesel smoke and nitrogen oxides emissions. Hydrogen has good prospect, because of its wide flammability limits, low ignition energy, high calorific value and high flame velocity. It does not need any substantial modifications in the existing hardware of the conventional diesel engine to run in dual fuel mode. The introduction of hydrogen with diesel fuel in compression ignition (CI) engine increases the H/C ratio, decreases heterogeneity of a diesel fuel spray due to the high diffusivity of hydrogen making the mixture better premixed with air and more uniform and reduces combustion duration due to hydrogen’s high speed of flame propagation.

16.1.8 A commercial 4 kW diesel engine gen-set was modified to operate as a dual fuel engine with up to 60% full load energy substitution by hydrogen without undue loss of power output and efficiency. With neat hydrogen supplementation, the maximum achievable hydrogen energy substitution could be as high as 85%. Considerable engine derating and efficiency loss was observed.

16.1.9 The SI engines operate on natural gas, but they can be optimized to run on propane, gasoline, biogas, or LPG etc. In India deployment of SI engines for power generation is on the rise. The SI engines can be operated with hydrogen only and in dual fuel mode also. Studies have shown that the addition of hydrogen to methane in a SI Engine enhanced the performance particularly when operating on relatively low equivalence ratio mixtures. The optimum concentration of hydrogen in the fuel mixture for producing a power gain and
avoiding knock appears to be about 20-25% by volume over the range of conditions.

16.1.10 In India, pollution from cooking using LPG, coal, wood and other bioproducts is a serious issue. Use of hydrogen can be an alternate fuel to address this issue, since it has superior characteristics in comparison to LPG fuel in terms of ignitability, low ignition delay, and higher flame stability. Hydrogen burner is so designed that it prevents kindling of hydrogen in air (by maintaining hydrogen-air mixture less than \(~5\) vol\% hydrogen and catalyst surface at a temperature lower than the self-ignition temperature of hydrogen) and surface area of the catalytic burner was so designed and optimized (as \(\sim20\text{cm}^2\)) that heat generation rate did not exceed the dissipation rate of heat and temperature could be maintained between \(~200\) to \(~500^0\text{C}\), which may be controlled by the feed rate of hydrogen. Research groups in Japan, China, Germany, USA, have been focusing on burner geometry, catalytic combustion of fuel, uniform distribution of surface temperature, air equivalence ratio on nitric oxide emissions, premixing of air to fuel, flame speed of fuel etc. where fuel contained \(\text{H}_2\), or \(\text{H}_2/\text{CO}\) or methane / \(\text{H}_2\) or LPG/\(\text{H}_2\) mixture. The most important task is to adapt hydride material for \(\text{H}_2\) storage, which requires the heat of the surrounding air for dehydriding, but it should have adequate mass storage capacity in a safe way. In the country, a few R&D groups have demonstrated cookers. However, flammability / safety related issues for public consumption of hydrogen need to be addressed. An action plan has been suggested to further develop such hydrogen fueled home cookers.

16.1.11 High intensity, high temperature thermal energy storage using the chemisorption heat when hydrogen reacts with metal hydrides is very promising for integration with distributed solar thermal power systems. The conventional phase change materials and molten salts have several operational drawbacks and also are expensive. A variety of low cost metal hydrides (especially magnesium based) which are ideal for thermal energy storage are available in the country
and are ready for field use. Several pilot units have been demonstrated by a couple of research institutions. This will be very useful to the success of the overall renewable energy program.

16.2 Recommendations

16.2.1 Considering merits and de-merits of all the modes of hydrogen storage and specific applications other than transportation, following are recommended:

(i) Institution of cost analysis study for the use of solid state hydride storage of hydrogen with compressed gaseous hydrogen in composite cylinders for specific applications to be developed in the Mission Mode projects.

(ii) Project for acquisition of reformer technology and development of indigenous reformer technology by Thermax and BHEL jointly with possible association of IICT, Hyderabad and NCL, Pune.

(iii) Project for commercialization of Type III cylinders for buses and Type IV cylinders for small vehicles (like 4- & 3-wheelers) by Tata Motors in collaboration with ISRO. DRDO and BHEL may also be involved in this effort.

(iv) Project for the development of a hydrogen storage device / cartridge for specific purpose for fuel cell power pack jointly by BHU, IIT Guwahati, NFTDC, IIT Indore and IISc Bangalore.

(v) Metal hydride based high intensity high efficiency thermal energy storage system development of the type ongoing at IISc Bangalore should be widened in terms of capacities and applications such as CSP and stand-alone Steam Generators.

(vi) Organization of a Workshop with CII / FICCI for possible commercialization of the devices / systems developed by the academic / research institutions. MNRE may facilitate organization of the workshop.

(vii) Review of the activities of Hydrogen Energy Centre at BHU by a suitable Expert Committee and utilization of their recommendations to establish a
Centre of Excellence. Also, establish a few Satellite Centers for specific tasks such as development of high pressure cylinders, development of sensors and controls, thermal, thermo-physical and mechanical properties evaluation, etc.
17.0 BIBLIOGRAPHY

17.1 General


17.2 Hydrogen Storage in Gaseous State

1. Product brochures of the composite pressure vessels
2. NASA NSS 1740.16, Safety standard for Hydrogen and Hydrogen Systems
17.3 Solid State Storage

The information required for making this report has been collected from the sources given below:


M.A. Miller and N. Sridhar, Measurement and Prediction of Material Performance Subject to Hydrogen Exposure, Hydrogen Gas Embrittlement Workshop, ASTM T.G. 01.06.08, ASTM Meeting, Reno, NV, May 17, 2005

17.4 Hydrogen Storage in Nano-Materials


(x) B. Viswanathan, M. Sankaran, A. Ariharan and K. Lekhi, Heteroato substituted carbon -potential hydrogen storage materials, Advanced porous materials, 1, 114-121 (2013)

17.5 Power Generation through hydrogen fueled IC engine

(1) www.beeindia.in
energy_managers_auditors/documents/guide_books/3Ch9.pdf
(2) All India Study on Sectoral Demand of Diesel & Petrol, Report by Petroleum Planning and Analysis Cell 2013, Ministry of Petroleum and Natural Gas
(3) ww1.eere.energy.gov/hydrogenandfuelcells/pdfs/fct_h2_fuelcell_factsheet.pdf


17.6 MH based Thermal Energy Storage, Cooking, Heat Pumps, Refrigeration, Compression, etc.

2. Chen Dong, Qulan Zhou, Qinxin Zhao, Yaqing Zhang, Tongmo Xu, Shien Hui, Fuel 88 (2009) 1858–1863


33. Hopkins RR, Kim KJ. Hydrogen compression characteristics of a dual stage thermal compressor system utilizing LaNi$_5$ and Ca0.6Mm0.4Ni5 as the working metal hydrides. Int J Hydrogen Energy 2010;35(11):5693-702.


