**HYDROGEN ENERGY STORAGE: RESEARCH AND INNOVATIONS TOWARDS GREEN TECHNOLOGY**

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# **Abstract**

There is a need to use sustainable sources of energy to produce power and at the same time does not emit greenhouse gases. Hydrogen has served this purpose well because the energy by mass produced by hydrogen is three times that of those produced by hydrocarbon liquid fuels. This makes hydrogen-based technology important for future energy requirements and its storage is of an utmost important for the successful commercialization of hydrogen-based energy applications. Storage techniques must be efficient to aid in transport as well, thus choosing the best is important. There are many conventional and advanced promising methods used for hydrogen storage, but each have their own limitations. In this chapter the methods used to store hydrogen are discussed highlighting the most sustainable method to store hydrogen and methods that are required in the future. Along with that the importance of a zero-emission hydrogen production which has shown immense promise for the future called green hydrogen is also discussed.

**Keywords:** Hydrogen energy, green hydrogen, Hydrogen storage, Hydrogen production, Sustainable energy

# **Introduction**

The sources of renewable energy are present all throughout the environment from the sun, wind, water, waste, and heat from the Earth, and it does not release greenhouse gases or pollutants into the atmosphere. With the immense increase in population and hence the energy demand, sustainable energy sources are on the rise. One important source is hydrogen, which is an excellent choice as an energy source because it is the most abundant element on Earth. It is used in industry, power generation, driving vehicles, households, and agriculture. Due to its zero emission of CO2, high energy density, versatility, storage capacity, hydrogen will be the fuel for future. This chapter presents hydrogen as an energy carrier, hydrogen production and its applications various methods for hydrogen storage are discussed, including high-pressure and cryogenic-liquid storage, absorption storage in high-surface-area adsorbents, chemical storage in metal hydrides and complex hydrides methods (Eberle et al.,2009). Green hydrogen is an emerging solution to produce hydrogen without the emission of other gases, their advances and technologies used in the storage system will move towards green and sustainable environment.

# **Hydrogen Production Methods**

In molecules where it exists, hydrogen must be separated from other elements to form hydrogen. Hydrogen is primarily produced from two types of sources: fossil fuels and renewable energy sources. It can be produced by various methods including thermochemical process, electrolytic and biological processes. Recently, several processes including pyrolysis and hydrocarbon reforming have been used to produce hydrogen from fossil fuels. In the presence of a catalyst, the steam combines with other methane vapours, such as natural gas or biogas, to form hydrogen and carbon dioxide (CESA-Lipman-H2-Prod-Storage-050311, n.d.). Water and various biological materials can be used to produce hydrogen.

## A. Hydrocarbon Reforming

In a steam reforming reaction, steam and hydrocarbons combine at high temperatures and to convert those gas into hydrogen and carbon oxides. A nickel-based catalyst is often used. After reforming, the gas mixture passes through a heat recovery step before being injected into water. In a gas shifter reactor, more H2 is produced when CO combines with steam. After the mixture is purified to 100% high purity once CO2 is removed by the pressure swing absorption.

## B. Gasification of Hydrocarbons and Biomass

Hydrogen can also produce through pyrolysis-based hydrocarbon gasification processes in the absence of oxygen, with similar estimated delivered costs at larger scale. Partial oxidation is a gas that can yield hydrogen from a variety of hydrocarbon fuels, including coal, heavy residual oils, and other low-value refinery products. At temperatures between 1200 and 1350℃, the hydrocarbon fuel undergoes this reaction with oxygen to form carbon monoxide and hydrogen. Through gasification, syngas can be produced from renewable feedstocks such as lignocellulosic biomass. The Water Gas Shifter process converts the resulting gas into hydrogen.

## C. Hydrogen from Biomass

The process which involved in the Hydrogen production from biomass is thermo-chemical and biochemical. Thermo-chemical method, it can be either gasification or pyrolysis (heating biomass in the absence of oxygen) to produce hydrogen and carbon monoxide, and in Enzyme-based biochemical digester processes are limited to wet, sugar-based feedstocks.(Holladay et al., 2009)

## D. Electrolysis of water

These Hydrogen producing technologies using alternative routes without the intermediate product syngas. Electrolysis of water is a mature hydrogen production technology that uses renewable energy obtained from wind, solar, geothermal, and nuclear energy, and it is stated to be a clean technology. Water is the most abundant resource for hydrogen production, and it can be split into hydrogen and oxygen if enough energy is provided without harmful emissions using electricity and an electrolyser device. The overall electrolysis reaction equation is shown in Eq (1) (Balat 2008). The two most common types of electrolyzers are alkaline (potassium hydroxide electrolyte) and PEM (Polymer membrane electrolyte). These methods are considered as the green hydrogen production process.

e- + H2O ½ O2 + H2  -----(1)

Electrolysis of water using any electrical source such as utility grid power, solar power, wind energy, hydropower or even nuclear energy can produce hydrogen (CESA-Lipman-H2-Prod-Storage-050311, n.d.). with many new applications of hydrogen, there is still an increasing demand for the hydrogen production technology. Nowadays, around 70.106t/y of hydrogen in its pure form is produced globally, of which the majority is obtained from fossil sources (76% from natural gas via steam methane reforming and 22% from coal via gasification) while only around 2% using electrolysis of water, which remains a great challenge in sustainability. These fossil-based production methods contribute to high amounts of greenhouse gas (GHG) including CO2 emissions, have various other negative impacts on the environment and are associated with the colour grey.(Hren et al., 2023) . Although hydrogen is a colourless gas, it is commonly referred to by a color to denote how clean it is: black, grey, and brown being least clean, blue sometimes referred low carbon and green as “Green hydrogen” which reduce emissions to net zero by 2050 shown in Table 1. (Alasadi, Tareq; 2022)(Ajanovic et al., 2022).

**Table 1**

**Hydrogen production techniques and CO2 emissions.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Technology for H2 production** | **Hydrogen colour** | **Source** | **Products** | **CO2 emissions** |
| Gasification | Brown hydrogen | Brown coal (Lignite), | H2 + CO2 | High |
| Gasification | Black hydrogen | BlackCoal (Bituminous), refinery oil | H2 + CO2 | High |
| Reforming | Grey hydrogen | Natural gas, biomass | H2 + CO2 | Medium |
| Reforming + Carbon capture | Blue hydrogen | Natural gas | H2 + CO2 | Low |
| Electrolysis | Green Hydrogen | Water | H2 + O2 | Minimal |

# **Hydrogen Storage technologies**

Storage of Hydrogen is necessary to several links of chain from the production to usage. Some of the basic hydrogen storage methods are high pressure gaseous H2, Cryogenic liquid, adsorbed on carbon nanotubes, absorbed to form hydrides, absorbed to form complex, Hydrides. Developments in nanoscale electrocatalysts, solid oxide and proton exchange membrane fuel cells, lithium-ion batteries, and photovoltaic techniques comprise the area of energy storage and conversion.(Li et al., 2018). High pressure gaseous hydrogen storage is currently the most common and mature method, achieving high pressure of up to 77Mpa using standard piston -type mechanical compressors(Nikolaidis & Poullikkas, 2017). There are two technologies were used to store hydrogen which is Physical based, and Material based storage system.

## **A. Physical based storage system**

Physical hydrogen storage methods are based primarily on compression of hydrogen as a gas requires high-pressure tanks and as a liquid hydrogen requires cryogenic temperatures. Effective compression and storage of liquid hydrogen is possible under cryogenic and high-pressure conditions (-252.8 °C and 5000- 10000 psi) for temperature and pressure.(Schoenung, 2011)

### a. Compressed Hydrogen Storage

It is a method in which hydrogen stored in high-pressure gas cylinders must be compressed to operating pressure of around 200 bar, while hydrogen vehicle tanks operate at 344-690 bar. Compressed hydrogen storage is a highly efficient storage methodology because the energy density increases volumetrically with the pressure of hydrogen gas. Currently, compressed hydrogen can be stored in four types of pressure vessels: a metallic pressure for industrial applications. The high-pressure vessels can then be transported via tube trailers, (Eberle et al., 2009). The disadvantages of the pressure vessels are linear blistering due to saturation and decompression along with high manufacturing cost, low storage capacity, limitation in dimensions and maximum pressure used in the tanks (Hren et al., 2023)

### b. Liquified Hydrogen Storage

Liquefied storage is a conventional hydrogen storage technique and works by liquefying hydrogen at high pressure and at -253 °C. There must be proper insulation in the vessel with an external protective jacket and inner pressure vessel for better efficiency. Reducing thermal conductivity between the inner vessels is important for efficiency thus the vessel is wrapped with layers of aluminium film or coated with perlite. This form of hydrogen is used when medium to large scale storage and transport (rail, road, intercontinental) is required. This method is still under development(Hren et al., 2023)

## **B. Material based storage system**

The last few decades have used metals and alloys as a storage method because the metal matrix can be expanded and hydrogen atoms can be absorbed and filled.(Eberle et al., 2009). Physical and chemical absorption can be used to store hydrogen. Hydrogen molecules are split into atoms and combined with the chemical structure of the material in the process of chemical sorption. Among all, metal hydrides (eg: LiAIH4) are the most famous group of materials that can be used for chemical sorption. This method also has its own disadvantages like cost, weight, and operating temperature, enhancing the charge-discharge rate controlling the formation of unwanted gases during desorption.

### a. Metal hydrides

There is a technique that doesn’t require high temperatures for storage of hydrogen, and it involves the use of metal hydrides which only need moderate temperature and pressures. It consists of metal ions that form lattice structure. Hydrogen adsorbs at a metal centre, dissociates to form atomic hydrogen, and is finally inserted into the metal lattice. The total process is exothermic. The metals Li, Be, Na, B and AI have been considered for hydrogen storage. Mg has been a major metal hydride used for storage but others like Ti or La are also used. (Preuster et al., n.d.)

### b. Complex hydrides

Apart from simple metal hydrides complex hydrides are also used. These are produced from a reaction involving boron, nitrogen, or aluminium hydrides with alkali metal hydrides. Typical examples include LiBH4, NaAIH4, and LiNH2. Many transition metals with their alloys are react with the hydrogen to generate hydrides. Materials that have shown possibility for solid-state hydrogen storage materials include metal hydrides (eg: MgH2, TiH2, and AIH3). MgH2 offers favourable properties such as high hydrogen capacity (up to 7.6wt%)(Preuster et al., n.d.). Other alternative chemical sorption such as N-ethyl carbazole, methanol, dibenzyl toluene and others can be used wherein hydrogen is bonded chemically with hydrogen-lean molecules and is released through a catalytic dehydrogenation. The advantage of this method is that they are not toxic and corrosive. Coming to their limitations, these have low storage capacity.

# **Challenges and Limitations of Hydrogen Storage**

Due to its low volumetric density, hydrogen is difficult to store for the future applications. It is the simplest of all elements and at the same time it is lighter than helium, so is easily lost into the atmosphere. This is the major challenge when it comes to efficient storage. Liquid hydrogen has a very low boiling point (-253 °C) which poses another challenge. As a gas too it is not an easy task because it requires the use of high-pressure tanks (350-700 bar/ 5000-10000 psi). Hence there is a need to develop safe, reliable, and cost-effective hydrogen storage and transport is of the utmost importance. As far as transportation is concerned, it is difficult to store and transport high density hydrogen storage. Conventional methods result in releasing of Greenhouse gas (GHG). Similarly, these technologies do not produce hydrogen on the same scale, presenting one of the main limitations. The important limitations of hydrogen storage methods are shown in Table 2.

**Table 2**

**Hydrogen storage process and its limitations.**

|  |  |  |
| --- | --- | --- |
| **Hydrogen Storage processes** | **Limitations** | **References** |
| Compressed hydrogen storage | Not suitable for large scale energy storage as expensive high-pressure tanks required. | (Eberle et al., 2009) |
| Liquified hydrogen storage & cryo compressed | Difficult to store & handle.  Requires expensive equipment | (Hren et al., 2023) |
| Material based hydrogen storage | Limited hydrogen capacity and  Expensive devices are required | (Molaeimanesh &  Torabi, 2023) |
| Chemical Hydrogen storage | Expensive & challenging to scale up | (Molaeimanesh &  Torabi, 2023) |

# **Energy storage Systems for future**

Green hydrogen produced from this process can be stored and converted back to electricity when required. Green hydrogen carries great potential for energy storage because it can be burned when required without carbon dioxide emissions or used directly in fuel cells. Recently hydrogen storage systems and batteries are the most advantageous option for storing the energy, because batteries require lower maintenance, easy to operate, acquire higher energy capacity and these are the better gravimetric and volumetric densities. (Molaeimanesh & Torabi, 2023). The Hydrogen storage batteries typically store hydrogen as a hydride compound inside a solid metal alloy. When heated, these batteries release the hydrogen that has been stored, which can then be utilised to produce power in a fuel cell.

## A. Conventional Battery Technology

Conventional batteries such as Lithium-ion, nickel-cadmium and lead-acid batteries are used extensively in several commercial applications. The mechanism in all conventional batteries is that a redox reaction occurs in which one of the electrodes release electrons that are used for supplying load in the external circuit and then carried to the other electrode. Rechargeable Li-ion batteries are the most effective typical battery technology with a relatively long service life.

## B. Molten salt batteries

Molten salt batteries require salt ions and exhibit higher efficiency as there is no charge loss. An example is a sodium-sulphur battery that depends on sodium ion. This method is useful for applications where the temperature ranges from 270 to 350℃.

## C. Redox flow batteries

The reactants are attenuated in the electrolyte solution and stored in external tanks in the redox flow batteries. Their advantage over conventional batteries is that they are not affected by the depth of discharge. Examples of currently used redox-flow batteries include Zinc bromide, vanadium, and iron-chromium batteries used for energy storage applications (Andujar A M; 2022).

## D. Hydrogen fuel cells

Hydrogen fuel cells use hydrogen as a fuel. This is an electrochemical process wherein hydrogen combines with oxygen to produce electrical energy and water. Green hydrogen is produced from the reverse process of electrolysis, and the by-product being oxygen from. This method can use a range of renewable energy resources (wind, wave, solar) to produce hydrogen power as a uniquely clean hydrogen source that can produce heat and whose only by-products are water. Hydrogen fuel cells are renewable, clean, and flexible energy source to support zero carbon energy strategies, more powerful and energy efficient.(Pellow et al., 2015)

## E. Regenerative Hydrogen fuel cells

RHFC’s are extensively suited for large-scale energy storage. Hydrogen can also be used as a flexible energy storage medium which can be used in stationary fuel cells, internal combustion engines, or fuel vehicles. RHFC contains alkaline water electrolyser and a PEM fuel cell and analyse the impact of different technology and design variables on the system’s lifetime energy balance. With comparing in a lithium-ion battery storage system, which has the highest ESOI ratio among the battery technologies currently used for grid-scale storage (Pellow et al., 2015).

# **Green Hydrogen**

Carbon footprints have increased at so many levels and reducing carbon amount in the world is one of the major goals that countries around the world have a set for 2050 to reduce global warming and neutralize the effects of climate change. One of the ways to achieve these goals at least in hydrogen storage is green hydrogen. The present as well as future hydrogen market wants a no emission production of hydrogen i.e., green hydrogen. At the same time there is an intention to replace the gas-emitting technologies in the energy system. This might facilitate in reduction of fossil fuel consumption and carbon footprint. (Zwickl-Bernhard & Auer, 2022). Green hydrogen is becoming a promising fuel alternative for future sustainable development and energy transition due to fact that it can be produced from water and renewable energy sources through electrolysis process, and there is no GHG emissions as well as it addresses the issues of climate changes.

# **A fuel for future**

It is significant to improve new methods of hydrogen production for the expected emerging hydrogen economy. Hydrogen is one of the trend research topics, and it is a promising energy carrier in future energy system. Soon Hydrogen will be the significant fuel. High efficiency, Fair performance of hydrogen as an energy storage medium, Relevance toward sustainable development, energy transition and green economy- building, potential mitigation of greenhouse emissions, Higher energy density of hydrogen storage than fossil fuels. Green hydrogen is 100% sustainable, easily storable, and versatile. There is no emission of GHG either during the combustion or production of green energy and at the same time it is easy to store for the later purposes. And predicted by the world Hydrogen council, if the hydrogen production costs reduce by 50% in 2023, undoubtedly it will be looking for the fuel for future. To minimize the environmental impact of hydrogen production we should reduce the CO2 emission, and renewable energy sources should be used. (Hren et al., 2023). Hydrogen vehicles: Due to its zero-pollutant discharge abilities, hydrogen vehicles are being promoted as the preferable future transportation platform. The transportation areas which hydrogen fuel cell vehicle technology can be applied is numerous. Lightweight vehicles, large shipping containers, heavy passenger vehicles, trains, and autonomous cars can all be replaced by this technology. New Zealand and Paris showed interest in adopting the idea of hydrogen fuel for big trucks to adhere to the zero greenhouse gas emission targets.

# **Trends in Hydrogen storage**

For the direct production of hydrogen from renewable electrolysis, Metal hydride storage technology is ideal for that. Through the fuel cell it has been converted in the form of gas, heat or electricity. With the demand for hydrogen being expected to increase by about 8-folds in 2050 over (Rasol M G et al; 2022). However, the high cost of manufacturing and the high need for storage remain challenges to the growth of hydrogen energy. The development of new materials for hydrogen storage has emerged as a key challenge in hydrogen storage research, and in photoelectrochemical (PEC) water splitting, hydrogen is produced from water using sunlight and specialised semiconductors called photoelectrochemical materials, which directly split water molecules into hydrogen and oxygen using light energy.(Liu et al., n.d.)

# **Conclusion**

Hydrogen storage remains a critical challenge for widespread deployment of hydrogen as a clean and sustainable energy carrier. Although various hydrogen storage techniques have been developed, each one has advantages and limitations of its own. The efficacy, adaptability, and cost-effectiveness of hydrogen storage methods must be increased to address the difficulties associated with hydrogen storage. Some of the methods like metal hydrides, electrolysis and photocatalytic process of hydrogen production are one of the promising methods for the production and storage hydrogen energy. However, photocatalytic water splitting's solar-to-hydrogen (STH) efficiency has remained incredibly low. Here, we present a method for achieving a high STH efficiency by combining focused solar light, pure water, and an indium gallium nitride photocatalyst. For the widespread use of hydrogen as an energy carrier, efficient storage options are essential. Innovations in the methods of chemical hydrogen storage devices, high-pressure gas storage, liquid hydrogen storage, and solid-state hydrogen storage materials like metal hydrides, the research seeks to the cost effectiveness, safety and saving potential of hydrogen energy for a sustainable future.

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