International Journal of Sustainable and Green Energy
2022; 11(1): 29-34
http://www.sciencepublishinggroup.com/j/ijsge
doi: 10.11648/j.ijrse.20221101.14
ISSN: 2575-2189 (Print); ISSN: 2575-1549 (Online)

Review Article

Generation and Storage of Hydrogen Gas from Non-metal and Metal Hydrides Using Metal Complex Catalysts: A Review

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To cite this article:
Given Kalonga, Adrian Habanyama, Ned Silavwe, Rodrick Symon Katete. Generation and Storage of Hydrogen Gas from Non-metal and Metal Hydrides Using Metal Complex Catalysts: A Review. *International Journal of Sustainable and Green Energy*. Vol. 11, No. 1, 2022, pp. 29-34. doi: 10.11648/j.ijrse.20221101.14

Received: February 10, 2022; **Accepted**: March 1, 2022; **Published**: March 12, 2022

Abstract: Sustainable renewable and environmentally friendly sources of fuel are in high demand. Hydrogen fuel appears to be the best energy source that is sustainable, renewable and environmentally friendly. In order to change the fossil fuel driven world economy to climate friendly hydrogen fuel driven economy, there is an urgent need for large scale development of new infrastructures and technologies to generate and store hydrogen. Pollution free hydrogen gas is the energy of the future. The application of hydrogen fuel in mobile machineries requires that hydrogen is stored in compact and lightweight systems. The storage of hydrogen in solid state has many advantages compared to compressed gas or cryogenic liquid in volumetric terms. The difficult with solid state hydrogen storage is that metal hydrides tend to release hydrogen at or above 90°C. The most critical component to the development of a hydrogen driven economy is elucidation of materials with efficient hydrogenation/dehydrogenation kinetics at a reduced operational temperature. This is possible with improvements in development of alloys and catalysts. By using advanced computer modelling for possible hydrogen storage complex metals, it is possible to develop a special type of a hydride metal complex that allows absorption and desorption of hydrogen at a much lower temperature for mobile application. Such a metal complex can allow development of hydrogen fueled automobiles and cheap large-scale application of hydrogen in generation of electricity for sustainable development worldwide, quickly replacing nuclear energy and fossil fuels. This paper identifies current difficulties that need to be overcome for hydrogen driven economy to be realized and proposes practical solutions.

Keywords: Hydrides, Hydrogen Storage, Hydrogen Gas, Complex Metal Hydrides, Non-metal Hydrides

1. Introduction

It is generally agreed across the world that the global energy needs are expected to drastically change in the coming decades. Over reliance on the current unsustainable polluting sources of fuel to meet the high demands for energy poses clear danger to the future of our planet [1, 2]. Sustainable renewable and environmentally friendly sources of fuel are in high demand. There is an urgent need to improve and sustain global economies and at the same time save the human race from self-destruction from the consequences of climate change. Hydrogen fuel appears to be the best energy source that is both renewable and environmentally friendly [3]. In order to change the fossil fuel driven world economy to climate friendly hydrogen fuel driven economy, there is an urgent need for large scale development of new infrastructures and technologies to generate and store hydrogen.

Apart from advances in hydrogen production using methods that do not pollute the environment, the key to realization of hydrogen fuel economies is the design and construction of suitable hydrogen storage materials. The transport sector remains the highest consumer of fossil fuels across the global. Up to 95% of the transport sector relies on fossil fuels [4]. Thus, the transport sector is the major contributor to greenhouse gases and global warming. The advantages of hydrogen fuels are so many compared to fossil fuels. Fossil fuels are not only the major pollutants [5]; they are also exhaustible. On the other hand, hydrogen is inexhaustible, convenient, clean, environmentally friendly and much more it will be completely independent from foreign control or the state of affairs of other countries.

It is clear that once few obstacles of production and storage of hydrogen are overcome, hydrogen is going to power the automobiles, industries, homes, electricity production in the near future. The Polymer Electrolyte Membrane Fuel Cell (PEMFC) directly coverts the chemical energy of hydrogen directly into electrical energy [6, 7]. Thus, the current automobile engines will need to be replaced with PEMFC. The PEMFC engines do not covert chemical energy to mechanical energy through heat. So far, the biggest obstacles to the realization of pollution free hydrogen fuel economies are efficient production of hydrogen and storage. The current methods of storing hydrogen in a form of liquid or compressed gas requires a lot of space and it's not conducible to the mobile application [8]. The best way is to design methods of safely storing hydrogen in metal hydrides, chemical hydrides or complex hydrides or molecular hydrogen adsorbed on metal surfaces [9]. The key parameters in the selection and design of hydrogen storage materials are the hydrogen content they are able to store, how quickly they can adsorb hydrogen at a specific temperature and pressure and their dehydrogenation properties [10].

The main aim of this review is to highlight the recent progress in production and storage of hydrogen fuel. It will provide areas that need intensive research so that hydrogen economies can be realized globally. Investing in hydrogen driven economy will make most countries become fully energy independent. It is clear that countries around the world are in desperate need of environmentally sustainable renewable energy sources [11, 12]. Thus, this paper will have an impact in this critical energy area, answering such important questions on how to overcome overdependency on unstainable polluting energy sources. Out of all the continents in the world, the African continent is the only one that is lagging behind in hydrogen energy technology.

2. Non-metal Hydrides

Hydrogen forms compounds with many non-metals. The number of hydrogen atoms in these compounds depends on the valence electrons in the non-metals. Table 1 summarizes the number of hydrogen atoms needed to form the named compounds for five selected non-metals. The number of hydrogen atoms needed to form the stable compounds is equal to the number of electrons needed to complete the octate, but not more than the existing number of valence electrons in the non-metal.

Table 1. *Selected non-metals and their interaction with hydrogen to form stable hydrides.*

Non-metal	Atomic Number	Electronic Configuration	Hydrogen Atoms Needed	Stable Compound Formed	Compound Name
Fluorine	9	2, 7	1	HF	Hydrogen Fluoride
Oxygen	8	2, 6	2	H_2O	Water
Nitrogen	7	2, 5	3	NH_3	Ammonia
Carbon	6	2, 4	4	CH_4	Methane
Boron	5	2, 3	3	BH_3	Borane
Silicon	14	2, 8, 4	4	SiH4	Silane

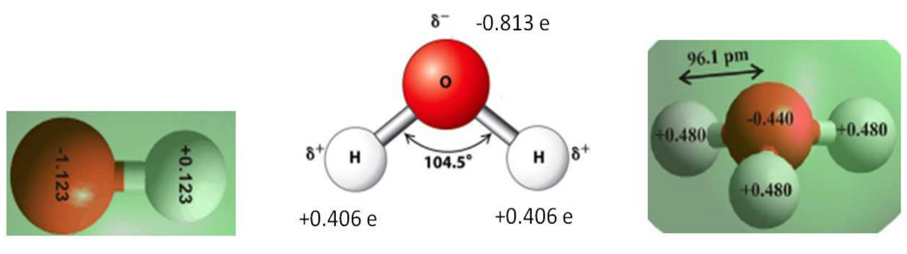
Common Hydrides of Oxygen

$$O + H \rightarrow HO^{\cdot} \text{ (Hydroxyl radical)}$$

$$HO^{\cdot} + H \rightarrow H_2O \text{ (Water)}$$

$$H_2O + H \rightarrow H_3O^{+} \text{ (Hydronium radical)}$$

$$H_2O + O \rightarrow H_2O_2 \text{ (Hydrogen Peroxide)}$$



(a) (b) (c)

Figure 1. *Chemical structures showing the three hydrides of oxygen with partial charges for (a) hydroxyl radical, (b) Water, and (c) Hydronium radical.*

Though water is a stable hydride of oxygen, the oxygen and hydrogen atoms on it have partial negative and positive charges, respectively. This is attributed to two factors; firstly, it is from the fact that oxygen is a much bigger atom compared to hydrogen hence valence electrons are not shared equally between the two as they spend more time on the oxygen side. As a result, oxygen gains a partial negative charge while hydrogen gains positive. Secondly, the hydrogen atoms form bond in a 2D triangular pyramid shape with oxygen. Similarly, in hydronium they form a 3D triangular pyramid. This makes the molecule to have a head and tail, with oxygen forming the head and the hydrogen atoms tails. This can be described as the general bonding affinity in almost all hydrides. Because of this, extra hydrogen atoms can be added to oxygen, in the case of water to form higher compounds of hydrogen. An addition of one hydrogen atom to water forms a hydronium radical, with individual atoms still having partial charges. The concentration of hydronium ions is commonly known as the measure of the pH of the aqueous solution. The more the concentration, the lower the pH, whilst the more the concentration of hydroxyl ions the higher the pH.

2.1. Dehydrogenation of the Non-metal Hydrides in the Presence of a Catalyst

The non-metal hydrides have shown the ability to decompose into hydrogen gas in the presence of suitable catalysts [13]. The catalysts take the forms of anode and cathode electrodes with the hydrogen gas evolving at the cathode while the non-metals evolve or precipitate at the anode.

The following shows the decomposition of each one of them and take note of the amount of hydrogen evolved. This is important as it guides efficiency in the production process. The decomposition is generally modelled under the electrolysis of water.

2.1.1. Water Decomposition

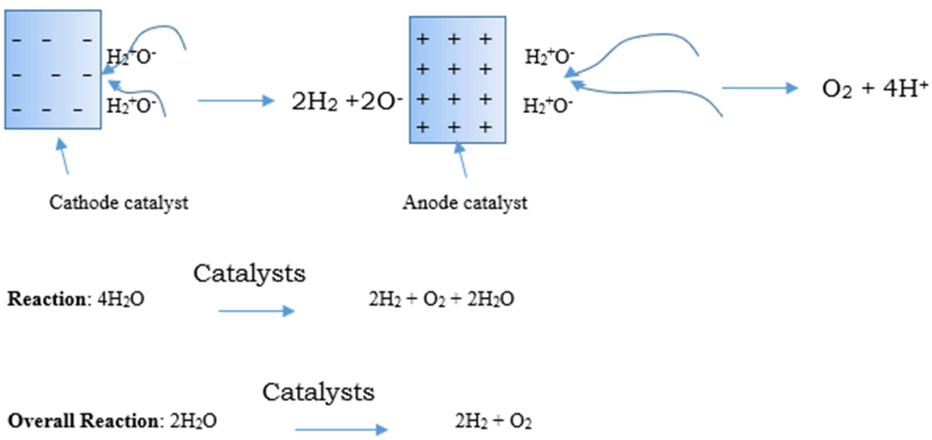


Figure 2. Water Decomposition.

2.1.2. Hydrogen Peroxide Decomposition

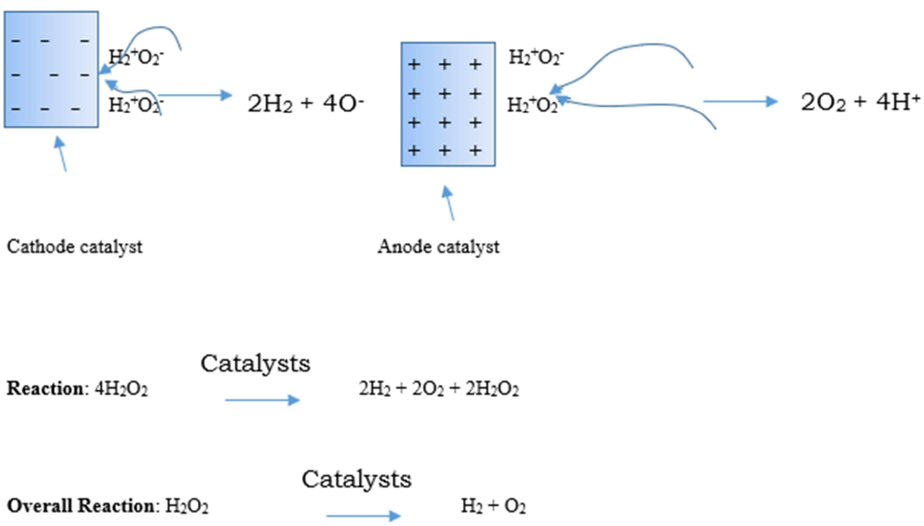


Figure 3. Hydrogen Peroxide Decomposition.

2.1.3. Hydronium Radical Decomposition

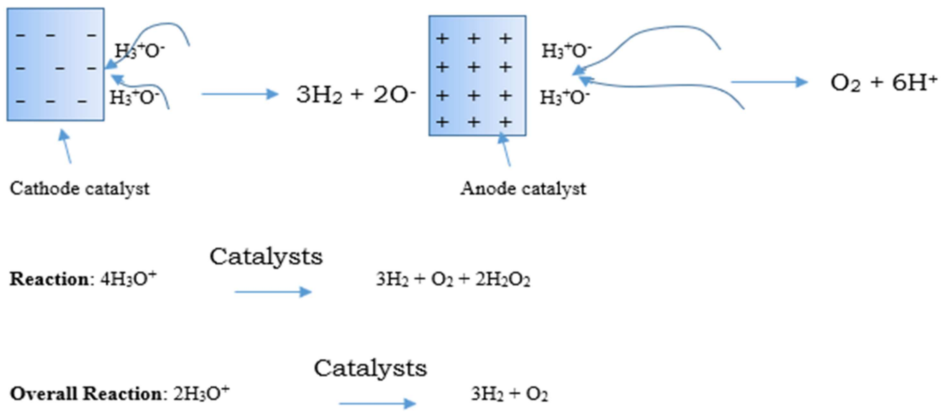


Figure 4. *Hydronium Radical Decomposition.*

From Figures 2 to 4, it is clear that the largest amount of hydrogen gas would be produced from hydronium compared to water or hydrogen peroxide given the same quantities as raw materials.

Table 2. *Highest H_2 Gas produced by the Species of the Selected Non-metal Hydrides.*

Non-Metal	Selected Species with Highest Molecules H_2 Gas	Number of H_2 Gas Molecules Produced
Carbon	CH_5^+	5
Nitrogen	NH_4^+	4
Boron	BH_4^+	4
Oxygen	H_3O^+	3
Fluorine	H_2F^+	2

2.2. Hydrogenation and Dehydrogenation of Transition Metal Alloys

The metal hydride storage tanks for hydrogen are given by the following equation

$$M(s)+H_2(g)\leftrightarrow MHx(s) \quad (1)$$

Where M is a metal and H is a hydrogen and MH is the metal hydride. This chemical equation takes into account the heterogeneous nature of the hydrogenation process. The reaction is influenced by the thermodynamics, kinetics and the properties of the metal hydride [14, 15].

The US Department of Energy (DOE) set the standards for the design of hydrogen storage system for automobile industry such as [14]:

1. Appropriate thermodynamics (favourable enthalpies of hydrogen absorption and desorption),
2. Fast kinetics (quick uptake and release),
3. High storage capacity (specific capacity to be determined by usage),
4. Effective heat transfer,
5. High gravimetric and volumetric densities
6. Long cycle lifetime for hydrogen absorption/desorption,
7. High mechanical strength and durability,
8. Safety under normal use and acceptable risk under abnormal conditions,
9. Cheap components and materials

Currently there is no metal hydride that has successfully manage to meet all the requirements from the US DEO. Many of them are still under investigation. Storage of hydrogen in metal alloys has so far proven to be superior to gas or liquid storage of hydrogen for automobile industries since it overcomes the volume issues [16-18]. In hydrogenation the harvested hydrogen is reacted with metal alloys to form the hydrides. Among the many transition metal hydrides that have attracted attention in the recent past are the alloys of lithium and magnesium. Some common lithium-transition metal novel complex hydrides include $LiAlH_4$, Li_5MoH_{11}, Li_5WH_{11}, Li_6NbH_{11} and Li_6TaH_{11} [19]. Hydrogenation is important as it acts as a means of hydrogen storage. Stored hydrogen can then be reserved and transported to where it is needed.

Table 3. *Some of the complex hydrides of lithium.*

Hydrogenation Reaction	ΔH_r (kj/mol)
$5LiH + Mo + 3H_2 \rightarrow Li_5MoH_{11}$	-105
$5LiH + W + 3H_2 \rightarrow Li_5WH_{11}$	-128
$6LiH + Nb_{0.65} + 2.175H_2 \rightarrow Li_5NdH_{11}$	-91
$6LiH + TaH_{0.65} + 2.175H_2 \rightarrow Li_5NdH_{11}$	-117

Most recently storage of hydrogen in magnesium and its alloys has attracted a lot of attention [20]. Magnesium hydrides are low cost and have high hydrogen capacity and good reversibility kinetics. Magnesium is the sixth most abundant metal on earth and its extraction and preparation is well documented [21].

The biggest bottleneck of using hydrogen as a source of fuel has been storage. The practical application of metal alloy hydrogen storage is hindered by the high desorption temperature coupled with poor hydrogen adsorption and desorption kinetics [21]. Currently research to improve hydrogen storage in metals is focusing on metal alloying, nanostructuring, nanoconfinement, and catalysts [21].

The new dawn of hydrogen energy is here. Hydrogen energy economy will require massive investment in infrastructure in all sectors that include energy production, storage, and distribution. Hydrogen energy economies are the only ones so far capable of rescuing planet earth for self-destruction of climate change due to the current unstainable and polluting sources of energy. The design of catalysis that use solar energy to hydrolyze water to hydrogen and oxygen is one of the major requirements for the realization of hydrogen driven economies so that the source of hydrogen is sustainable and renewable for future generations. In addition to this is safe storage of hydrogen. The development of hydrogen fuel cells is already under way in developed countries.

Hydrogen fuel cells produce electricity by combining hydrogen and oxygen atoms. This reaction produces electricity, water and small amount of heat. There are a growing number of hydrogen fuel cells in USA, producing almost 250 megawatts of electricity [22]. Furthermore, more hydrogen powered vehicles refueling stations are under construction in California [22]. Currently, the European Union is investing more than $10 billion in hydrogen technology alone. The overall reaction that happens in the fuel cell is give as;

Overall reaction: $2H_2$ (gas) + O_2 (gas) $\rightarrow 2H_2O$ + energy

Thus, the hydrogen fuel cell, through an electrochemical reaction, combine hydrogen gas with oxygen gas to produce electricity and water as a byproduct [23]. The hydrogen fuel cell is made up of two electrodes; one an anode and the other a cathode. The anode and cathode are separated by the electrolyte membrane. On the anode side of the fuel cell, hydrogen is split into protons and electron with the assistance of a catalyst. The oxygen, which enters the fuel cell through the cathode, reacts with positively charged protons which has diffused through the membrane to the cathode, with water as a byproduct. The electrons in the other hand, flow through an electric wire creating an electric current. Thus, as long as hydrogen is being supplied into the fuel cell, electricity will continuously be produced. Furthermore, stacking the fuel cells can produce enough electricity to power an entire city with zero pollution and noise.

3. Conclusion

Hydrogen is the most abundant element in the universe. It is also readily available in many inorganic and organic compounds on earth. Hydrogen driven economy will certainly transform the whole world and reverse adverse effects of fossil fuels on climate. The bottleneck to realizing this future is the storage of hydrogen. Hydrogen can be stored in the cryogenic form, gas or in solid metal hydrides. Metal hydrides have proven to be much more practical in automobile industries. The difficulty is to find a metal alloy that can store hydrogen with fast absorption and desorption kinetics at lower temperature. This can be achieved with improved catalysis. Intensive research in urgently needed in the development of catalysis that can improve application of hydrogen in automotive industry. Out of so many metal hydrides, magnesium hydride is the most promising hydride due to its readily availability, light weight, cheap and reversibility. Resent research in transition metals catalytic effect on magnesium hydrides has shown to improve its hydrogen storage capabilities [24]. A combination of carbon nanotubes and a reduced graphene oxide together with transition metal alloys can also improve the magnesium hydride hydrogen absorption and desorption kinetics [24, 25]. Thus, going forward, more research is needed to develop magnesium alloys and transition metal catalysts. The developing countries can benefit a lot from hydrogen driven economies.

Conflict of Interest

Authors declare no conflict of interest.

Acknowledgements

The authors would like to thank their colleagues at their respective universities for moral support during the preparation of the manuscripts.

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