

# The Hydrogen Alternative

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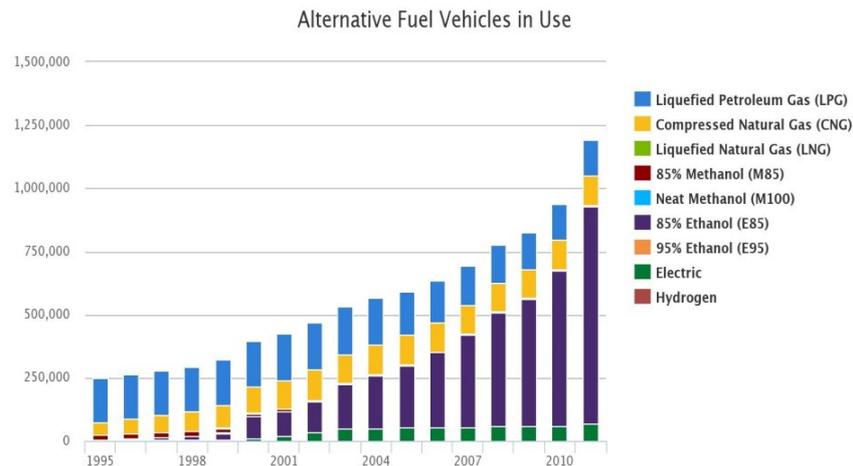
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## ABSTRACT

Hydrogen is the cleanest fuel known to man and the most prominent alternative to carbon-based fuels, although it is not available as a free gas on earth, it can be produced from various sources using the correct combination of pressure and temperature. The deep time that our planet has given life has allowed it to grow from a tiny seed of genetic possibility to a planet wide web of complexity we are part of today, where today heating, refrigeration, telecommunication and appliances have become vital in everyday life. Production of electricity using fossil fuels has been under the scanner for quite some time now because of their availability and effects on the environment hydrogen emerges out in this scenario as the future fuel and setting the stage towards the hydrogen economy. The clean nature of hydrogen and the efficiency of fuel cells taken together offer an appealing alternative to fossil fuels. This paper reviews the existing infrastructure of hydrogen production and storage, while simultaneously explores the reason why it will be an inevitability in the near future to meet our ever increasing energy needs.

## 1. INTRODUCTION

We tend to think of earth as unique because we have liquid water on the surface, one may think it's a rare commodity but if we include ice and vapor, water is incredibly abundant throughout the Universe which might not be so surprising because oxygen is the third most abundant element and hydrogen, the most abundant element in the Universe. The chorus of water molecules is formed by joining together hydrogen bonds. We live on a beautiful blue anomaly of a world. The only planet we know with its surface drenched in liquid water. One of the most attractive features of hydrogen as an energy source is that it can be produced from water. Also hydrogen is a very clean burning fuel with emissions lower than those produced by CNG or LPG. Thus, vehicles running on hydrogen can meet stringent emission norms.<sup>1</sup>



**Figure 1.** AFVs in use in the United States between 1995 and 2011<sup>2</sup>

This chart above shows the number of alternative fuel vehicles (AFVs) in use in the United States between 1995 and 2011. The number of AFVs in use has been increasing steadily during the past 15 years, largely due to federal policies that encourage and incentivize the manufacture, sale, and use of vehicles that use non-petroleum fuels.

## 2. ENERGY AND ENVIRONMENT IN DEVELOPING COUNTRIES

Over the last two decades in developing countries like India, there has been a tremendous increase in the number of automobiles. While transport sector plays a pivotal role in the economic development in any country, it brings an unavoidable specter of environmental deterioration along with it. Combustion of fossil fuels in mobile sources for transportation hassled to widespread release of pollutants such as CO, HC, NOX, SPM, and many other harmful compounds in the environment, and the resulting air quality deterioration and health effects especially in urbanized areas. In this regard, hydrogen can act as a salvation and play an important role in emission mitigation.

## 3. THE HISTORY OF HYDROGEN

The idea of hydrogen being a future fuel and a long range solution to problems associated with fossil fuels can be found in Jules Verne's "The Mysterious Island", a science fiction novel written in the 1870s. Hydrogen was first isolated by Henry Cavendish in 1766. The earliest attempt to develop a hydrogen engine was reported in 1820 by Reverend W. Cecil. Cecil presented his work before the Cambridge Philosophical Society in a paper entitled "On the application of hydrogen gas to produce moving power in machinery." The engine itself is operated on vacuum principle, where the power was produced using atmospheric pressure to drive a piston against a vacuum.<sup>3</sup> The partial vacuum was created by burning a hydrogen-air mixture, allowing it to expand, and then cooling it. Although the engine reportedly ran satisfactorily, vacuum engines, in general, never became practical.<sup>4</sup> Extensive work in the development of hydrogen as a fuel for surface transportation came through the works of German engineer, Rudolf Erren, who worked in Germany and in England. He prompted the use of hydrogen as a fuel for a variety of transportation purposes including submarines, trucks, buses, railcars and torpedoes. Unfortunately his records were lost during World War II. Since then several researchers have tried to use hydrogen as an automotive fuel with partial success due to unresolved technical problems of on-board generation and storage.<sup>5</sup>

## 4. HYDROGEN PROPERTIES

The combustion reaction for hydrogen is

$$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Energy}$$

Given below are some important properties of hydrogen which are important to consider in going for large scale production of hydrogen.

**Table 1:** Important Hydrogen properties<sup>6</sup>

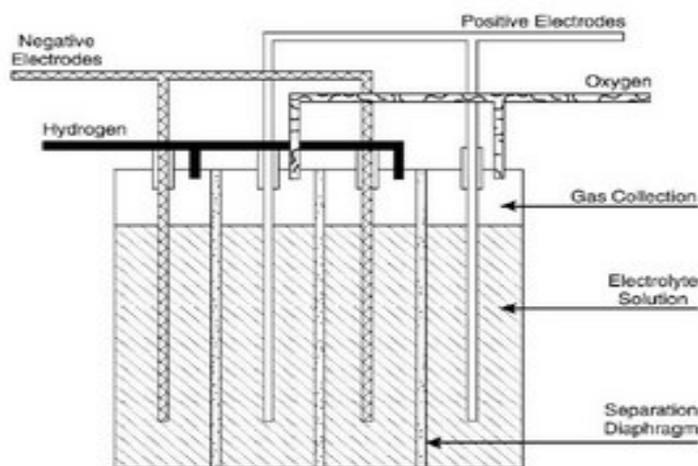
Molecular weight	2.02
Density	0.0013 kg/liter
Specific gravity	0.07
Freezing point	-275°C
Specific heat	14.2 kJ/kgK
Calorific value	120 MJ/kg
Diffusivity in air	0.064 cm
Research Octane number	130

## 5. PRODUCTION METHODS FOR HYDROGEN

Currently, refineries are the largest producers of hydrogen using steam reforming methods. However owing to the vast specter of applications from metallurgical processing to fuel for rocket engines, considerable debate is going on in the industry as to which methods of hydrogen production is economically viable.

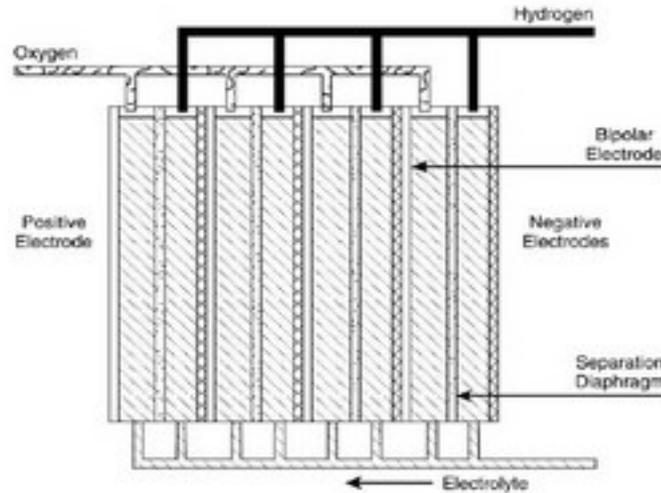
### 5.1 ELECTROLYSIS OF WATER

Electrolysis is the simplest method of hydrogen production. This method does not rely on fossil energy. Hydrogen produced by this method is pure in nature.<sup>7</sup> Process involves splitting the water molecule into hydrogen and oxygen atoms by passing a direct current through it. Water is made conductive by adding hydroxyl ions to it. As water itself is a poor conductor of electricity, an electrolyte, commonly aqueous KOH is used.<sup>8</sup>



**Figure 2.** Unipolar (tank) Electrolyzer design<sup>9</sup>

Tank type or (filter) press type electrolysis systems can be used. A diaphragm (usually woven asbestos) prevents electronic contact between the electrodes and passage of gas or gas bubbles. Figure 2 and 3 represents how these systems look like.



**Figure 3.** Bi-polar Filter Press Electrolyzer design<sup>9</sup>

Ideally, a decomposition voltage of 1.23 V per cell should be sufficient at normal temperature and pressure; however, due to various reasons a voltage of about 2 V per cell is applied in practice. The energy required is 3.9-4.6 kWh per m<sup>3</sup> of hydrogen produced. About 60-70% of this energy is actually utilized in electrolysis. Therefore, the efficiency of electrolysis process is about 60-70%, which can be improved up to 80% by using catalysts such as porous platinum or nickel.<sup>10</sup>

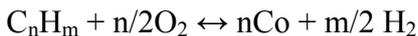
**Table 2:** Reactions at the Terminals

Reaction at Anode	Reaction at Cathode
$\text{OH}^- \leftrightarrow \text{OH} + \text{e}^-$ $2\text{OH} \leftrightarrow \text{H}_2\text{O} + \text{O}$ $\text{O} + \text{O} \leftrightarrow \text{O}_2 \uparrow$	Using KOH as an electrolyte:  $\text{K}^+ + \text{e}^- \leftrightarrow \text{K}$ $\text{K} + \text{H}_2\text{O} \leftrightarrow \text{K}^+ + \text{H} + \text{OH}^-$ $\text{H} + \text{H} \leftrightarrow \text{H}_2 \uparrow$

## 5.2 PARTIAL OXIDATION OF HEAVY OIL

Heavy oils are rich in hydrocarbons; these are oxidized to CO and H<sub>2</sub>. Process CO is removed to obtain pure hydrogen.

The oxidation reaction is given as:

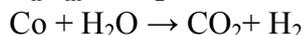


Reaction is exothermic and proceeds in the temperature range of 1150- 1315°C. Catalysts are needed to accelerate the rate of reaction. The synthesized gas exits at high pressures (6MPa or 880 psig), reducing or possibly eliminating the need for compression. Feedstock for this process ranges from methane to coal. Catalytic processes which occur at temperatures of about 590°C use feedstock ranging from methane to naphtha.<sup>11</sup> Non-catalytic process uses feedstock such as methane, heavy oil and coal. Reactor cost for this process is less than that of a steam reformer; however the overall cost for steam reforming process is low. This method of hydrogen production is expensive as it is capital.

### 5.3 CATALYTIC STEAM REFORMING

Steam reforming of methane is the most energy efficient, commercialized technology currently available and most cost effective when applied to large, constant loads. The method accounts for 95% of the hydrogen production in USA.<sup>12</sup>

The basic process involves the conversion of a hydrocarbon and steam to hydrogen and carbon oxides.

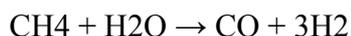


Where  $n=1$  and  $m=4$  if the feedstock is methane, and  $n=1$  and  $m=2.2$  if the feedstock is naphtha.

The process includes four steps:

1. Feedstock Purification (Removal of Sulfur)
2. Steam reforming process to form a mixture of hydrogen and carbon oxides.
3. Shift conversion of carbon monoxide to carbon dioxide.
4. Purification (removal of CO, CO<sub>2</sub>, and other hydrocarbons)

For methane, involves the catalytic reaction of methane with steam at temperature in the range of 1400 to 1500°F (760 to 816°C)



This reaction is endothermic and is carried out by passing the gas through catalyst-filled tubes in a furnace. The catalyst is usually in the form of hollow cylindrical rings ranging up to 3/4 in. (1.9 cm) in diameter. It consists of 25 to 40% nickel oxide deposited on a low-silica refractory base.<sup>13</sup>

**Table 3: Hydrogen Production Data**<sup>14</sup>

Process	Wt % on feed	SCF/bbl	Wt % on crude
Continuous regeneration reformer	3.5	1600	0.35-0.60
Semiregenerative reformer	1.4-2.0	600-900	0.15-0.30
Residue gasification	20-25	12,000-16,000	1-5
Catalytic cracking	0.05-0.10	30-60	0.01-0.04
Thermal cracking	0.03	20	0.01
Ethylene cracker	0.5-1.2	—	—
Steam (methane) reformer	30	12,000	—

Commercial fuels such as natural gas, LPG, biogas, coal gas, landfill gas and gasified coal can be used for large scale generation of power.<sup>15</sup>

### 5.4 GASIFICATION OF COAL

Coal used in coal gasification can be divided into three broad categories: anthracite, bituminous and lignite. There are two types of coal gasification process depending upon the way it is carried out:

1. At atmospheric pressure, Koppers-Totzek process.
2. At high pressure, Texaco process.

**Table 4:** Comparison of Coal gasification processes

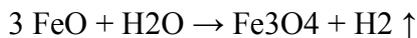
Koppers-Totzek process	Texaco process
<ol style="list-style-type: none"> <li>1. Operates at near ambient pressure.</li> <li>2. Gas must be compressed after the waste heat recovery process and treatment with water to remove ash.</li> <li>3. Hydrogen compression requires more energy and reduces efficiency of the process.</li> </ol>	<ol style="list-style-type: none"> <li>1. Operates at a pressure near 5.5 MPa.</li> <li>2. High pressure avoids the necessity for compression.</li> <li>3. As compression is avoided, process results in a more cost effective one.</li> </ol>

In this process, coal is fed to a gasification plant. Oxygen from the air separation unit enters the plant along with process steam. Process results in the production of raw gas and some ash. Ash is removed and the raw gas passes through a desulfurization unit to eliminate sulfur. The clean gas obtained is synthesis gas or syngas. Syngas is then subjected to shift conversion process to remove impurities such as CO and CH<sub>4</sub> and finally in the methanation process CO<sub>2</sub> is removed to obtain pure hydrogen.<sup>16</sup>

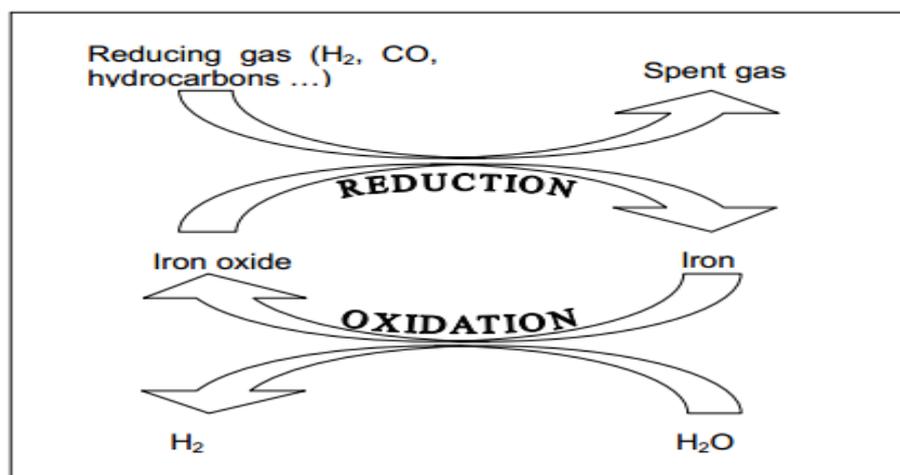
### 5.5 STEAM IRON PROCESS

Process involves steam reforming by reaction with hot iron.

The product of the process is rich H<sub>2</sub> gas and iron oxide. The steam undergoes decomposition during the process to produce H<sub>2</sub>.



The hydrogen produced contains impurities like CO and N<sub>2</sub> and can be removed by the methanation reaction. The cost of this process is dependent on the capital investment and the price of coal.<sup>17</sup>



**Figure 4.** Principle of Steam Iron Process<sup>18</sup>

When the “Steam-Iron” process is operated in the discontinuous manner, it can be considered as a method of hydrogen storage. The theoretical maximum amount of hydrogen capable to be stored and transported as the reduced oxide is 4.8 wt%, according to the mass ratio of H<sub>2</sub> to Fe in the hydrogen release reaction ( $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$ ).

This corresponds to 537 L of hydrogen gas (STP) that can be stored per kg of iron, and it is comparable to the hydrogen storage density of conventional metal hydrides. While reactor design and modeling are matters that have been analyzed by several research groups,<sup>19-22</sup> these topics still require more attention and investigation in order to increase the feasibility of hydrogen production by the “Steam-Iron” process in comparison with other technologies.

## 5.6 NUCLEAR FISSION

Hydrogen can be produced by nuclear fission by splitting the helium molecule using radioactive particles.<sup>23</sup> Splitting one nucleus of helium yields two hydrogen atoms. Reaction rate has to be controlled to avoid a chain reaction.

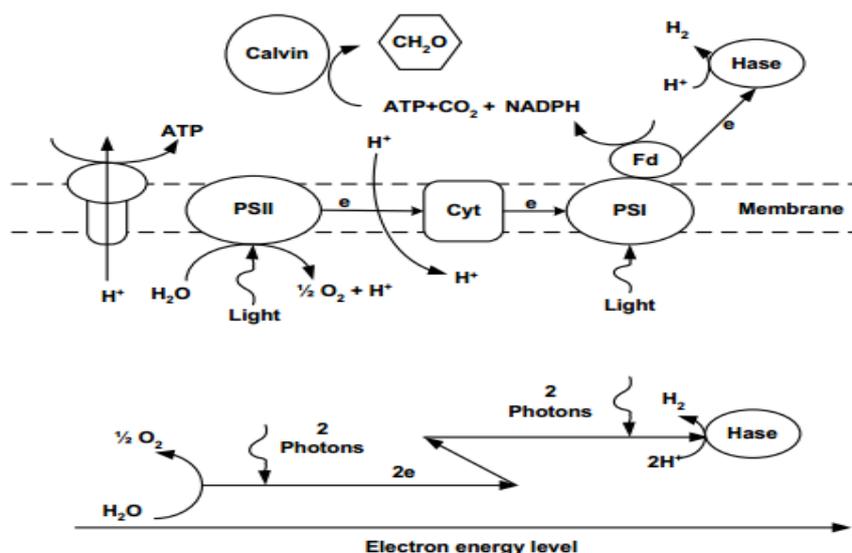
## 5.7 BIOLOGICAL METHODS (BIO-HYDROGEN)

A biological system is used to produce hydrogen from light. Photo-biological organisms currently under study include cyanobacteria, photosynthetic bacteria and eukaryotic (green) algae.<sup>24</sup>

Photoautotrophic microorganisms, either prokaryotic cyanobacteria or eukaryotic green microalgae, possess chlorophyll a and other pigments to capture sunlight energy and use photosynthetic systems (PSII and PSI) to carry out plant-like oxygenic photosynthesis.<sup>25-26</sup>

The pigments in PSII (P680) absorb the photons with a wavelength shorter than 680 nm, generating a strong oxidant capable of splitting water into protons ( $H^+$ ), electrons ( $e^-$ ) and  $O_2$  as shown in Fig. 5.

The electrons or reducing equivalents are transferred through a series of electron carriers and cytochrome complex to PSI. The pigments in PSI (P700) absorb the photons with a wavelength under 700 nm, which further raises the energy level of the electrons to reduce the oxidized ferredoxin (Fd) and/or nicotinamide adenine dinucleotide phosphate (NADP<sup>+</sup>) into their reduced forms. The proton gradient formed across the cellular (or thylakoid) membrane drives adenosine triphosphate (ATP) production via ATP synthase.  $CO_2$  is reduced with ATP and NADPH via a reductive pentose phosphate pathway or Calvin cycle for cell growth. The excess reduced carbon is stored inside the cells as carbohydrates ( $CH_2O$ ) and/or lipids.<sup>28-31</sup>



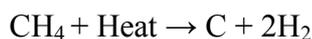
**Figure 5.** Schematic mechanisms of photosynthesis and bio-photolysis of photoautotrophic microbes<sup>27</sup>

Under special conditions, the reducing equivalents (ferredoxin) can also be used by hydrogenase or nitrogenase to reduce protons for evolution of molecular hydrogen ( $2H^+ + 2Fd^- \leftrightarrow H_2 + 2Fd$ ).<sup>32</sup>

Gaffron and Rubin first reported that *Scenedesmus*, a green microalga, evolved molecular hydrogen under light conditions after being kept in anaerobic and dark conditions.<sup>33</sup> The responsible enzyme for hydrogen evolution is a reversible hydrogenase because it catalyzes the reaction in both directions.<sup>34</sup>

## 5.8 THERMAL CRACKING OF NATURAL GAS

The thermal decomposition of natural gas was carried out earlier to obtain carbon black.<sup>35</sup> The decomposition has high energy requirement and most of it comes from the produced hydrogen.



Process is carried out in a furnace at near atmospheric pressure; a methane air flame at 1400°C is used to heat the furnace. Carbon particles produced from methane decomposition are collected in filter bags. Catalysts are used to achieve faster decomposition. This is a very economic method of producing hydrogen as prices of natural gas are lower as compared to other fuels.<sup>36</sup>

## 6. MISINTERPRETED ACCIDENT

Hydrogen did not cause the Hindenburg to blow up.

A study of the accident implicates the paint used on the skin of the airship, which contained the same component as rocket fuel. An electrical discharge ignited its skin, and a fire raced over the surface of the airship. The hydrogen burned quickly, upward and away from the people onboard the ship.<sup>37</sup>

## 7. STORAGE AND SAFETY

### 7.1 A LIQUID IN CRYOGENIC CONTAINERS

Liquid hydrogen storage has been the subject of considerable development in Japan, Germany and the United States. The conditions necessary to store liquid hydrogen are fairly severe:

Temperature: 20 K

Pressure:  $2 \times 10^5$  Pa

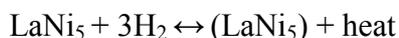
To maintain these conditions, liquid hydrogen is stored in a double walled, super-insulating vessel. Hydrogen can be drawn from either the liquid or gas phase of these vessels and delivered to the engine.<sup>38</sup> These vessels help to minimize the transfer of heat from the outside world, thus reducing boil-off hydrogen.

### 7.2 METAL HYDRIDES

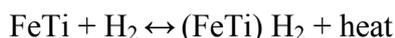
Metal hydride storage systems are based on the idea that gaseous hydrogen readily absorbs in metals, forming weak chemical bonds. Since they are in granular or powder form, they have large surface area and storage capacity. To release the hydrogen the hydride is heated to a certain temperature.

The reaction with three most promising hydrides of alloys is given below:

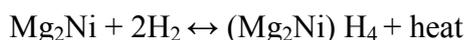
#### Lanthanum-Nickel



#### Iron-Titanium



## Magnesium Nickel



### 7.3 COMPRESSED HYDROGEN GAS

A high pressure vessel is used to store gaseous hydrogen. These vessels are typically aluminum cylinders wrapped with fiberglass. Other design being tested includes cylinders wrapped with Kevlar or graphite, plastic liners wrapped with graphite and high strength aluminum cylinders.<sup>39</sup>

Pressurized hydrogen systems at 20 MPa weigh nearly three times more than what a comparable liquid hydrogen system does, and they occupy more than twice the volume. This volume can be reduced by increasing the pressure of the compressed gas, potentially up to as high as 55 MPa.

### 7.4 ACTIVATED CARBON STORAGE

Hydrogen can, in principle be reversibly adsorbed on carbon structures (e.g. carbon nanotubes). Amount of adsorption can be increased as the temperature is lowered, but cryogenic temperatures are not needed.

Due to the molecular structure of the carbon in the nanotubes, hydrogen easily bonds with the carbon and subtle changes in temperature or pressure will cause the hydrogen to be released.<sup>40</sup>

However, the design of practical systems requires a better understanding of the fundamental adsorption/desorption process and development of high volume manufacturing process or the material.

**Table 5:** Safety systems for Hydrogen

Systems	Description
Leak Detection Systems	Installing hydrogen detectors at refueling areas
Fire Suppression System	Use of dry chemical powders to extinguish hydrogen flames
Electrical Protection System	All electrical equipment to be securely grounded to eliminate electrostatic sparks in the event of a leak
Purging Systems	System to be purged with inert gases like nitrogen to prevent air from forming combustible mixtures with hydrogen
Pressure Relief Devices	Venting of excess gas when pressure in vessel exceeds design value
Detonation and Shrapnel Protection	Considering geometry of the vessel, decreasing pipe length and increase the diameter

## 8. HYDROGEN & FUEL CELLS

Fuel cells are one of the key enabling technologies for future hydrogen economy. Fuel cells are viewed by many as the energy source of the 21st century. Fuel cell technologies are an attractive alternative to oil dependency.

**Table 6:** Applications of Fuel Cells

Stationary	Supplemental generators Distributed power sources
Transportation	Fuel Cell Vehicle Hybrid Vehicles Future: trains, airplanes, boats
Consumer Electronics	Laptops, cell phones, video recorders

Given in figure 6 is the overall chemistry for fuel cells.

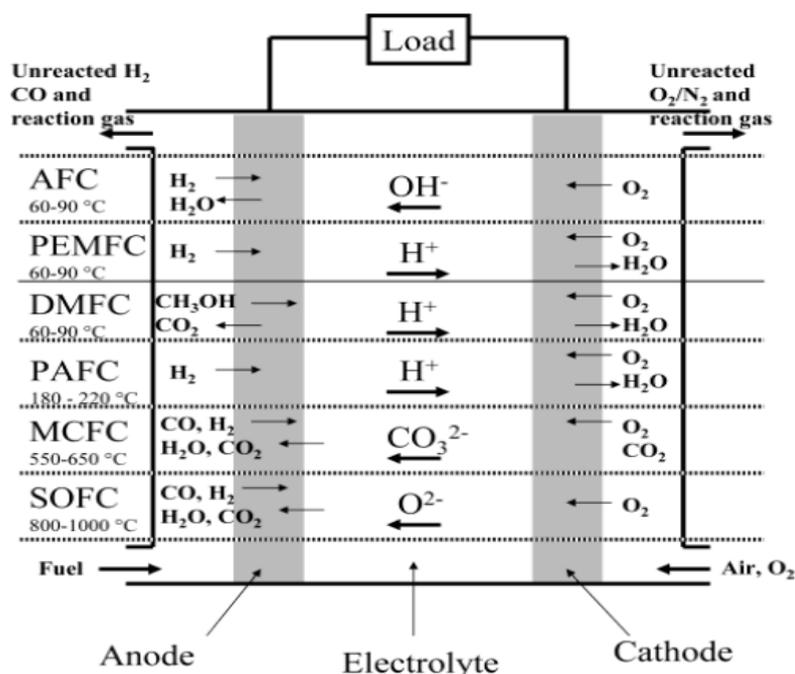


Fig 6: Summary of reactions in fuel cells<sup>41</sup>

## 9. CONCLUSION

The earth has been an interesting mixture of stability and upheaval, it had an environment that's never completely conspired to wipe out life but it constantly had thrown its challenges. The journey of discovery has already delivered more than just facts because it has given us a powerful perspective on the intricacy and beauty of our technologies. And it is clear that without alternative fuels like hydrogen, mankind will not have sustained eco-mobility in the future. Hydrogen is a powerful tool to tackle emission problems and mitigating dependence on crude oil. From IC engines to fuel cells, it provides an excellent platform. Countries like USA, Japan, Sweden and Germany have realized the importance of hydrogen as a fuel and have since led the world in promoting its use.

## ACKNOWLEDGEMENTS

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