5.8 HYDROGEN PRODUCTION AND STORAGE:

Hydrogen is the simplest element. An atom of hydrogen consists of only one proton and one electron. It is also the most plentiful element in the universe. Despite its simplicity and abundance, hydrogen does not occur naturally as a gas on the Earth – it is always combined with other elements. Water, for example, is a combination of hydrogen and oxygen (H2O).

Hydrogen holds the potential to provide clean, reliable and affordable energy supply that can enhance economy, environment and security. It is flexible and can be used by all sectors of economy. It is non-toxic and recyclable. Due to these qualities it is considered to be an ideal energy carrier in the foreseeable future. An energy carrier moves and delivers energy in a usable form to consumers.

Hydrogen can be produced by using a variety of energy sources, such as solar, nuclear and fossil fuels and can be converted to useful energy forms efficiently and without detrimental environmental effects. When burned as fuel or converted to electricity it joins with oxygen to produce energy with water as the only emission. When air is used for combustion instead of oxygen, some NO x is also produced, which can be reduced by lowering the combustion temperature.

Despite all these benefits, realization of hydrogen economy faces multiple challenges. Unlike gasoline and natural gas, hydrogen has no existing, large scale supporting infrastructure. Building of such an infrastructure will require major investment. Although hydrogen production, storage and delivery techniques are currently in commercial use by the chemical and refining industries, existing hydrogen storage and conversion technologies are too costly for widespread use in energy applications. The individual segments of hydrogen energy system; production, delivery, storage conversion and end use applications are closely interrelated and interdependent as shown in figure below. Design and application of a hydrogen economy must carefully consider each of these segments as well as the whole system.

Hydrogen can be produced in centralized facilities and distributed to an energy conversion site via pipeline or stored and shipped via rail or road. It can also be produced

at decentralized locations onsite where it will be stored and/or fed directly into conversion device for stationary, mobile or portable applications.

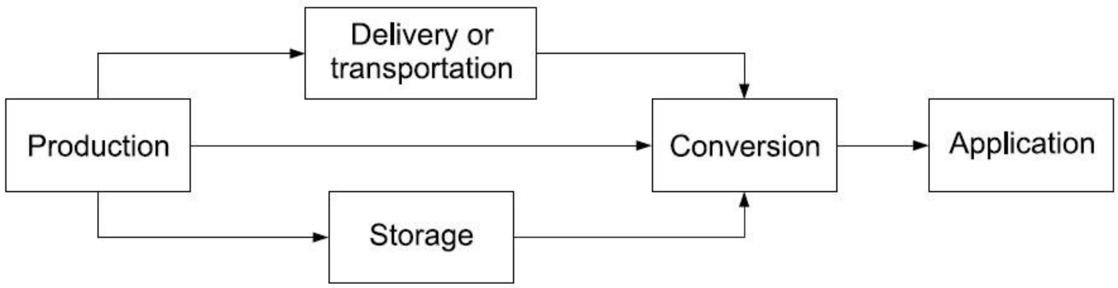

Fig 5.8.1 Hydrogen energy system

[Source: "Renewable Energy Sources and Emerging Technologies" by D.P.Kothari, K.C Singal, Rakesh Ranjan, Page: 395]

5.8.1 PRODUCTION:

Hydrogen is the third most abundant element on the earth, it does not exist in Free State, except for small quantities in the upper atmosphere. It is, therefore, not a primary energy source. However, large amounts of combined hydrogen are present in compounds such as water, fossil fuels and biomass. It can therefore, be produced through two routes:

(a) Fossil fuels, such as natural gas, coal, methanol, gasoline etc., and biomass are decomposed by thermo-chemical (steam reforming or partial oxidation) methods to obtain hydrogen. The CO produced in the process is eliminated by water gas shift reaction. This route of hydrogen production causes CO emission. The energy content of the produced hydrogen is less than the energy content of the original fuel, some of it being lost as excessive heat during production.

(b) Hydrogen can also be produced by splitting water into hydrogen and oxygen by using energy from nuclear or renewable sources such as solar, wind, geothermal, etc., through electrical or thermal means (i.e. electrolysis and thermolysis respectively). Water splitting is also possible through biophotolysis process using solar radiation.

Splitting of water is thus possible at the expense of renewable energy to produce secondary fuel H 2 . On use, H 2 and O2 recombine to produce water again and energy is released. This route is therefore a clean and sustainable route of energy supply.

1. Thermo-chemical Methods

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 per cent of the hydrogen production in USA.

2. Electrolysis of Water

Electrolysis is the simplest method of hydrogen production. Currently, this method is not as efficient or cost effective as thermo-chemical method using fossil fuels or biomass. But it would allow for more distributed hydrogen generation and open the possibilities for use of electricity generated from renewable and nuclear resources for hydrogen production.

An electrolysis cell essentially consists of two electrodes, commonly flat metal or carbon plates, immersed in an aqueous conducting solution called electrolyte, as shown in figure below. A direct current decomposes water into H_2 and O_2, which are released at cathode (–ve electrode) and anode (+ve electrode) respectively. As water itself is poor conductor of electricity, an electrolyte, commonly aqueous KOH is used.

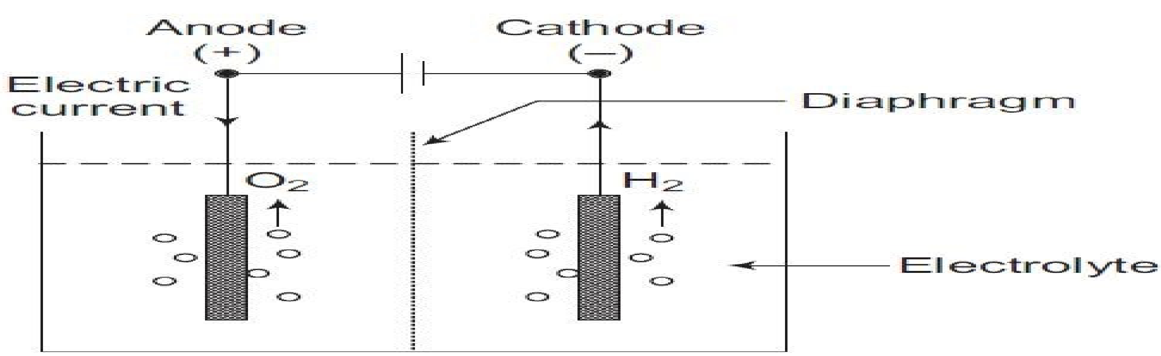

Fig 5.8.2 Electrolytic cell

[Source: "Renewable Energy Sources and Emerging Technologies" by D.P.Kothari, K.C Singal, Rakesh Ranjan, Page: 396]

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^3 of hydrogen produced. About 60–70 per cent of this energy is actually utilized in electrolysis.

Therefore, the efficiency of electrolysis process is about 60–70 per cent, which can be improved up to 80 per cent by using catalyst such as porous platinum or nickel. A diaphragm (usually woven asbestos) prevents electronic contact between the electrodes

and passage of gas or gas bubbles. Electrolysis method is most suitable when primary energy is available as electrical energy, e.g. solar photovoltaic energy. It is also suitable where cheap electricity is available from other sources such as wind, geothermal, etc.

3. Thermolysis of Water

- When primary energy is available in the form of heat (e.g. solar thermal), it is more logical to produce hydrogen by splitting water directly from heat energy using thermolysis. This would be more efficient than conversion of heat, first to electricity (using heat engine – generator) and then producing hydrogen through electrolysis.
- The efficiency of thermal plant is usually in range 32–38 per cent and that of electrolysis is 80 per cent. The overall efficiency through thermal-electrical- hydrogen route would thus be only 25–30 per cent.

4. Biophotolysis

In this method the ability of the plants (especially algae) to split water during photosynthesis process is utilized. An artificial system is devised, which could produce hydrogen and oxygen from water in sunlight using isolated photosynthetic membrane and other catalysts. Since this process is essentially a decomposition of water using photons in the presence of biological catalysts, the reaction is called photolysis of water.

There are three distinct functional components coupled together in the system as shown in figure below:

(i) Photosynthetic membrane, which absorbs light, split water to generate oxygen, electrons and protons

(ii) an electron mediator, which is reducible by photo-synthetically generated electrons

(iii) a proton activator that will accept electrons from the reduced mediator and catalyze the reaction:

$$2 H + + 2 e – H 2$$

A system with chloroplast (small bodies containing the chlorophyll in green plants) as a photosynthetic membrane to split hydrogen and oxygen, ferredoxin as e – mediator and hydrogenase (an enzyme) or finely dispersed platinum as proton activator, has been successfully tested.

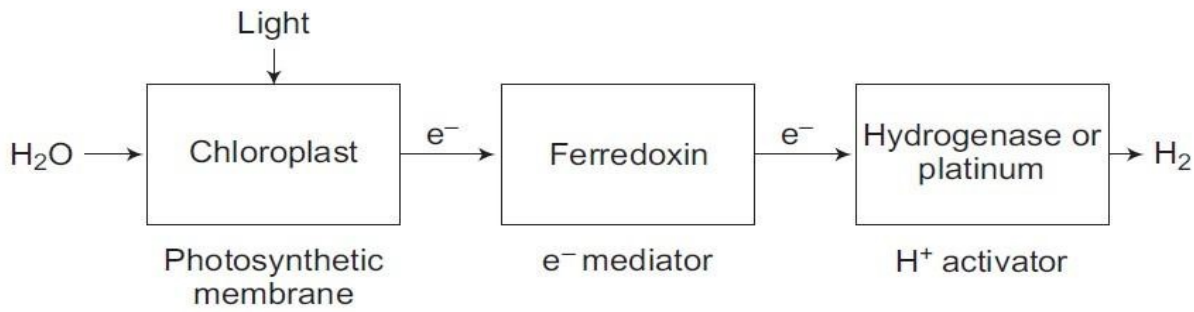

Fig 5.8.3 Functional Components of biophotolysis

[Source: "Renewable Energy Sources and Emerging Technologies" by D.P.Kothari, K.C Singal, Rakesh Ranjan, Page: 398]

5.8.2. STORAGE

- ➔ Hydrogen can be stored as a discrete gas or liquid or in a chemical compound. For a given amount of energy, hydrogen weighs about one third of the fossil fuels, but it is bulkier. In gaseous form it occupies 3.6 times the volume occupied by natural gas and in liquid form it occupies 3.8 times the volume occupied by gasoline.
- ➔ However, in practice the volume penalty is 20 to 50 per cent less, since hydrogen can be convertedto other forms of energy at the user end more efficiently than fossil fuels.
- ➔ Large amounts of hydrogen for subsequent distribution would probably be stored in the underground facilities similar to those used for natural gas, e.g. depleted oil and gas reserves and aquifers. On low or moderate scale, hydrogen is frequently stored in strong steel tank or cylinder.
- ➔ The storage of compressed hydrogen gas in tanks is the most mature technology though the very density of hydrogen translates to inefficient use of space. The inefficiency can be mitigated with high compression such as 350–700 atm. However, further improvement in cost, weight and volume efficient storage is required in order to make it more acceptable by the end user.
- ➔ Hydrogen can also be stored as compact storage in liquid form at low temperature. It takes up low storage volume but requires cryogenic containers, as boiling point of hydrogen is 20 K. Furthermore, the liquefaction of hydrogen is energy intensive process and results in large evaporative losses. About one third of the energycontent of hydrogen is lost in the process.

- Hydrogen can be stored at high densities in reversible metal hydrides. When required, it can be released by heating the hydride and original metal (or alloy) is recovered for further recycling. The chemical equations are:

Charging

H_2+ Metal hydride + heat (hydrogen is stored and heat is released)

Discharging

Hydride + heat H_2 + Metal (heat is stored and hydrogen is released)

- The pressure of gas released by heating depends mainly on temperature. At fixed temperature,the pressure remains essentially constant until the hydrogen content is almost exhausted. Metal hydrides offer the advantage of lower pressure storage, comfortable shape and reasonable volumetric store efficiency but have weight penalties and thermal management issues.
- It is also very safe. In case of accidental breakdown of storage, the gas remains in hydride and does not escape.

To be suitable as a storage medium, metal hydride should have following desirable properties:

(i) The metal (or alloy) should be inexpensive.

(ii) The hydride should contain a large amount of hydrogen per unit volumeand per unit mass.

(iii) Formation of hydride from metal by reaction with hydrogen should be easyand the hydride should be stable at room temperature.

(iv)The gas should be released from hydride at significant pressure and moderately high temperature (preferably below 100 °C).

The reactions with three more promising hydrides of alloys are given below:

(i) Lanthanum-Nickel: $La\,Ni_5 + 3\,H_2 \underset{\text{Dischareg}}{\overset{\text{Charge}}{\rightleftharpoons}} (La\,Ni_5)\,H_6 + \text{heat}$

(ii) Iron-Titanium: $Fe\,Ti + H_2 \underset{\text{Dischareg}}{\overset{\text{Charge}}{\rightleftharpoons}} (Fe\,Ti)\,H_2 + \text{heat}$

(iii) Magnesium-Nickel: $Mg_2\,Ni + 2\,H_2 \underset{\text{Dischareg}}{\overset{\text{Charge}}{\rightleftharpoons}} (Mg_2\,Ni)\,H_4 + \text{heat}$

- These hydrides contain somewhat more hydrogen then an equal volume. In theory (La Ni 5) H 6 Contains 1.35 per cent of hydrogen by weight, (Fe Ti) H 2contains 1.9 percent and

$(Mg_2Ni)H_4$ contains 3.6 per cent. Due to heavy weight, hydride storage is not suitable for mobile storage such as vehicles.

➔ Some complex-based reversible hydrides such as aluminates have recently demonstrated improved weight performances over metal hydrides along with modest temperatures for hydrogen recovery