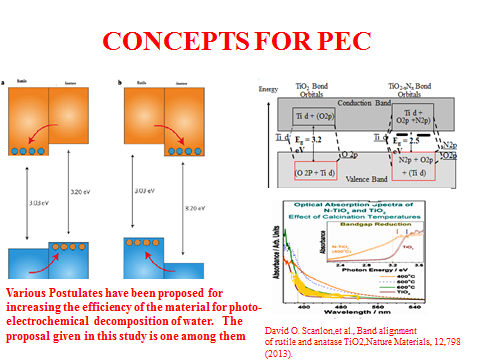
CHAPTER 9

HYDROGEN AS ENERGY CARRIER

* **Steam Reforming and partial oxidation**
* **Thermal**
* **Thermo-chemical (Fe-X2;S-I2)**
* **Electrolysis**
* **Electrochemical**
* **Photolysis**
* **Photochemical**
* **Photoelectrochemical(PEC PVC)**
* **Biological**
* **Bio-chemical, photobiological**



Hydrogen: Fuel of the Future Hydrogen is emerging as the favorite alternative to fossil fuels as an energy carrier. Auto manufacturing, for example, have come up with models that run on either hydrogen used as fuel in internal combustion engines (ICEs), or fuel cell cars that use gasoline in the ICE and, additionally, a fuel cell producing electricity-using hydrogen as fuel. Recently, a car running on just hydrogen completed a journey through continental Australia -- the grueling 4000 kilometer long journey proved that these cars are as tough as any other. The US government has embarked on an initiative to develop technology for the production, transportation and storage of hydrogen and using it as an alternative fuel as and when the need arises. But there are plenty of technological challenges that need to be addressed before hydrogen can become the day-to-day fuel. Fig.1. Relative emissions of carbon for various fuels and combustion engines Fig.1. compares the relative carbon emissions per kilometer resulting from the use of gasoline versus hydrogen in ICE alone as well as hybrid ICE + fuel cell vehicles. It is An Introduction to Energy Sources 229 apparent that the use of fuel cell powered vehicles using hydrogen generated from renewable energy sources brings down the emissions to almost zero. The advantages of hydrogen as a universal energy medium are: 1. The combustion of hydrogen results in the formation of steam and liquid water. In this respect, the use of hydrogen is completely safe from environmental standpoint. 2. It is non-toxic. 3. It is easily assimilated into the biosphere: its combustion products are recycled by plants in the form of carbohydrates. 4. It is possible to produce hydrogen from the most abundant chemical on earth: water. Hydrogen can be obtained electrolytically, photoelectrochemically, thermochemically, by direct thermal decomposition or biochemically from water. 5. Hydrogen can be used as a feedstock for the chemical industry, enabling the production of entire gamut of chemicals from hydrogen and conventional petrochemicals. 6. It is the most suitable fuel for use in fuel cells - direct conversion of chemical energy into electricity without the heat route with an enhanced efficiency. 7. Transmission of energy in the form of hydrogen is more economical than through high voltage AC lines for large distances. Methods of producing hydrogen Hydrogen is the most abundant element in the Universe. Hydrogen is the simplest of atoms, composed of one proton and one electron. But pure, diatomic hydrogen (H ) — the fuel of choice for fuel cells — does not exist naturally. Since hydrogen easily combines with other elements, one is most likely to find it chemically bound in water, biomass, or fossil fuels. 2 To get hydrogen into a useful form, it must be extracted from one of these sources. This process requires energy. Accordingly, the cleanliness and renewability of this energy is of critical importance. While a hydrogen – oxygen fuel cell operates without producing emissions, producing hydrogen can give rise to significant greenhouse gases and other harmful byproducts. Once obtained, hydrogen is a nearly ideal energy carrier. The various ways to obtain hydrogen are : Direct electrolysis 230 Hydrogen Production Water electrolysis involves passing an electric current through water to separate it into hydrogen (H2) and oxygen (O2). Hydrogen gas rises from the negative cathode and oxygen gas collects at the positive anode. The reactions involved in the electrolysis of water are: Reduction electrode (Cathode): 2 H2O + 2 e- 2 OH- + H2 Oxidation electrode (Anode): 2 OH- H2O + 1/2 O2 + 2 eComplete cell reaction: H2O H2 + 1/2 O2 The values of the cathode and anode half-cell potentials, are known to be 0.401 V and - 0.828 V respectively at 25°C at a pH of 14. If the activities of water and the gaseous species are considered unity, the cathode Hydrogen: Fuel of the Future Hydrogen is emerging as the favorite alternative to fossil fuels as an energy carrier. Auto manufacturing, for example, have come up with models that run on either hydrogen used as fuel in internal combustion engines (ICEs), or fuel cell cars that use gasoline in the ICE and, additionally, a fuel cell producing electricity-using hydrogen as fuel. Recently, a car running on just hydrogen completed a journey through continental Australia -- the grueling 4000 kilometer long journey proved that these cars are as tough as any other. 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Overvoltages are composed of activation or charge transfer overvoltage, concentration or diffusion or mass transfer overvoltage and resistance or ohmic over voltage. In general, an aqueous solution of caustic potash or soda is used as the electrolyte for water electrolysis. The nature of anode and cathode is decided based on their hydrogen and oxygen over voltages in the electrolytic medium in addition to their stability in the particular medium. The cathode and anode are separated by a diaphragm, which prevents the mixing of hydrogen and oxygen gases produced at the cathode and anode surfaces respectively. The diaphragm should be stable in the electrolyte and minimizes the diffusion of gas molecules without affecting the conductivity of the medium. Effect of temperature and pH on the decomposition potential An Introduction to Energy Sources 231 The amount of electricity required to produce one mole of hydrogen by splitting one mole of water is 2 Faradays, which is equal to 236.96 kJ of energy. Whereas, heat generated by combustion of one mole of hydrogen is 285.58 kJ at 25 0 C. The extra energy of 48.63 kJ must be absorbed from the surrounding of electrolytic cell if the water is electrolyzed with 1.229 V at 25 0 C. Applying electrical energy of 285.58 kJ, i.e. 1.481 V, to a water electrolyzer at 25 0 C would generate hydrogen and oxygen isothermally. The values 1.229 and 1.481 V are called as the reversible and thermo-neutral voltage. The variation of reversible and thermo-neutral voltage with temperature is shown in Fig. 2. 0 100 200 300 400 500 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 thermoneutral voltage Not possible to generate H reversible voltage 2 gas H2 gas generated with absorption of heat H2 gas generated with evolution of heat Electrolyser cell potential (V) Temperature(o C) Fig.2. Variation of cell potential as a function of temperature It can be seen from the Fig. 2, that when the temperature increases the reversible voltage decreases, whereas the thermo-neutral voltage slightly increases with temperature. It can also be seen from Fig. 2 that, in the region below the reversible voltage, hydrogen production is not possible. In the second region, the hydrogen is evolved with absorption of heat from the surrounding. In the third region, the hydrogen is evolved with liberation of heat, i.e. the extra energy as potential above the thermo-neutral potential is released as heat energy. In general, the commercial industrial electrolytic cells are operating between 60-80 0 C. The hydrogen and oxygen evolution potentials at various pH are shown in the Fig.3. It can been seen from the figure that the net potential needed for the hydrogen and oxygen evolution at any given pH between 0 to 14 is 1.229 V at 25 0 C. 232 Hydrogen Production Fig.3. Hydrogen and oxygen electrode potential against pH of the electrolyte Due to the corrosive action on the electrode material especially at the anodes, the acidic solutions are avoided for the water electrolysis. A typical water electrolysis cell is shown in Fig. 4. Fig.4.Typical water electrolysis cell Electrolysis produces extremely pure hydrogen, which is necessary for some types of fuel cells. But a significant amount of electricity is required to produce a usable amount of hydrogen from electrolysis. In ideal case, this would come from renewable sources like wind and photo-catalysis. But the hydrogen produced from electrolysis will in no way help reduce the pollution of atmosphere if the electricity needed for the reaction is obtained through fossil fuels.

Steam-Methane Reformation An Introduction to Energy Sources 233 Hydrogen can also be extracted or "reformed" from natural gas. A two-step process at temperatures reaching 1100°C in the presence of a catalyst makes four parts hydrogen from one part methane and two parts water. It is a relatively efficient and inexpensive process, and can be made still more efficient with harvest of the waste heat (commonly referred to as cogeneration). This latter feature makes steam-methane particularly attractive for local use. CH4 + H2O CO + 3 H2 Catalyst 930ºC CO + H2O CO2 + H2 Catalyst 350ºC While this process is well understood and can be implemented on a wide scale today, it produces moderate emissions of carbon dioxide. Other innovative carbon-sequestration techniques are in development. Unlike renewable electrolysis, steam-methane reformation depends on fluctuating price of natural gas. Nonetheless, steam-methane reformation is poised to be the near-term hydrogen production method of choice on the road towards completely renewable methods. Biomass Gasification Hydrogen can be extracted from hydrogen-rich biomass sources like wood chips and agricultural waste. When heated in a controlled atmosphere, biomass converts to synthesis gas, which primarily consists of carbon monoxide (CO), carbon dioxide (CO2), and hydrogen (H2). Gasification technology has been under intensive development over the last 2 decades. Largescale demonstration facilities have been tested and commercial units are in operation worldwide. Fortunately, hurdles in biomass gasification have been economic rather than technical. Until recently, biomass gasification has been employed to produce low-value products like electricity or heat, which rarely justify the capital and operating costs. But the increasing demand for hydrogen promises to make biomass gasification economically viable in the near future. Hydrogen from Coal Vast coal resources have often been viewed, as a potential source against future energy needs. Unfortunately, coal mining pollutes and spoils the landscape, and burning coal produces many harmful emissions. Yet coal does contain hydrogen, and techniques are being developed to sequester the remaining carbon. These processes generally involve coal gasification to produce hydrogen and electricity, followed by re-injection of CO2 or mineralization via carbonates. Biochemical Hydrogen production 234 Hydrogen Production Life requires metabolism, a complex web of redox chemistry. This requires energy, which can be obtained by breaking of bonds (the multi-step breakdown of glucose to generate ATP and CO2) or from electronic excitation. For example, plants, algae, cyanobacteria and photosynthetic bacteria can use light energy to raise electrons into higher energy states. In case of plants, algae and cyanobacteria, the source of excitable electrons is water. The excited electrons are stripped from water, which then splits into oxygen and protons. Hydrogen is produced in micro-organisms by enzymes capable of reducing free protons to molecular hydrogen. Examples of these enzymes include hydrogenases and the nitrogenases. The production of hydrogen by these enzymes is usually coupled to some other biochemical processes. The energy used by these enzymes is usually in multiple steps from an organism’s central energy inputs and is provided in the form of electron carriers such as ferredoxin or NADPH and energy yielding molecules like ATP. Obtaining useful amounts of hydrogen from microorganisms will require increasing the efficiency of hydrogenases and overcoming other obstacles. One problem is that some hydrogenases and nitrogenases are inhibited by oxygen. Oxygen is produced by photo-system II (PSII) during oxygenic photosynthesis. In the summer of 2001, researchers manipulated the photosynthetic process of spinach plants to produce hydrogen. But these biological means of hydrogen production are known only as laboratory experiments. Intense research persists to better understand ways to improve these hydrogen production methods. Quantum leaps in this field could be the equivalent of striking oil. Biological hydrogen production is the most challenging area of biotechnology with respect to environmental problems. The future of biological hydrogen production depends not only on research advances, i.e. improvement in efficiency through genetically engineered microorganisms and/or the development of bioreactors, but also on economic considerations (the cost of fossil fuels), social acceptance, and the development of hydrogen energy systems. Thermo-chemical decomposition of water: The decomposition of water into hydrogen and oxygen can be achieved when energy is supplied in the form of heat and work. The positive value of ΔG0 decreases with increase in temperature, but rather slowly because of the nearly constant enthalpy change, as a function of temperature and ΔG0 becomes zero around 4700K. This means that even the highest temperature available from a nuclear reactor, in the range of 1300K, is not sufficient to decompose water. Therefore, single-step thermal decomposition of water is difficult unless other methods like electrolysis are resorted to. Two step decomposition An Introduction to Energy Sources 235 of water wherein a metal oxide, metal hydride or hydrogen halide is involvinvolved according to the equations: H2O + M MO + H2 MO M + 0.5 O2 or H2O + M MH2 + 0.5 O2 MH2 M + H2 or H2O + X2 2 HX + 0.5 O2 2 HX H2 + X2 However, even these two-step routes require temperatures of the order of 1273 K or more. Water cannot be decomposed in one or two thermo-chemical steps when the available temperature is below 1273 K. However this can be done in a multiple-step process wherein each step is easy to accomplish with either a negative or a little positive ∆G for the reaction. For example if the desired reactions is H2O H2 + 0.5 O2 (1) it can be achieved in a sequence of steps as follows: 2 H2O(g) + I2(g) + SO2(g) 2 HI(g) + H2SO4(g) (2) H2SO4(g) H2O(g) + SO2(g) + 0.5 O2(g) (3) Ni(s) + 2 HI(g) NiI2(s) + H2(g) (4) NiI2(s) Ni(s) + I2(g) (5) In this sequence the first reaction has a large positive ∆G (87.6 kJ/reaction) while all other reactions have negative ∆G values. Replacing step (1) by the following step will give a negative ∆G value. 2 H2O(g) + I2(g) + SO2(g) 2 HI(aq) + H2SO4(aq) (6) Carrying out the reaction in the four steps (Equations 6,3,4 and 5) at 300, 510, 570 and 1070K respectively requires –74.3 kJ. Therefore any thermochemical cycle can be chosen by incorporating the following four reaction steps : water decomposition or hydrolysis, hydrogen generation, oxygen generation, and the regeneration of any intermediates formed. Some other therm-chemical cycles that are available for hydrogen generation are 236 Hydrogen Production • Mark 15 process (iron-halogen system) • Mark 13 process (sulfur dioxide-iodine system) Photochemical hydrogen production: A photochemical hydrogen production is similar to a thermochemical system, in that it also employs a system of chemical reactants, which carry out the splitting of water. However, the driving force is not thermal energy but light, generally solar light. In this sense, this system is similar to the photosynthetic system present in green plants. One can effectively utilize photochemical means to promote endergonic (energy requiring) reactions. The sensitized oxidation of water by Ce4+ using irradiation of 254nm light by the following reaction is known. Ce4+ + 0.5 H2O Ce3+ + 0.25 O2 + H+ ∆H = 3.8 kcal/mol Ce3+ can be used with light of lower wavelength to promote the hydrogen generation reaction: Ce3+ + H2O Ce4+ + 0.5 H2 + OHThe quantum efficiency of these processes is very low. Similarly Ru(bpy)3 2+ and related complexes have relatively low excited-state lifetimes and can serve as electron donors or electron acceptors. A typical reaction is: [AR2] 2+(ClO4)2 2- \*[AR2] 2+(ClO4)2 2- \*[AR2] 2+(ClO4)2 2- + H2O H2 + 0.5 O2 + [AR2] 2+(ClO4)2 2- where R = C18H35 and A = Ruthenium bipyridyl complex Fig.5. Ruthenium bipyridyl complex hγ excited state An Introduction to Energy Sources 237 Photoelectrochemical hydrogen production: In its simplest form, a photoelectrochemical (PEC) hydrogen production cell consists of a semiconductor electrode and a metal counter electrode immersed in an aqueous electrolyte. When light is incident on the semiconductor electrode, it absorbs part of the light and generates electricity. This electricity is then used for the electrolysis of water. Fujishima and Honda first demonstrated the electrolysis of water using solar energy in a PEC cell about 30 years ago. A schematic of their cell is shown in the Fig. 6. Fig.6. Schematic showing the structure of a PEC cell As seen from the diagram, the cell consists of a semiconductor (TiO2) photo-anode, which is irradiated with the UV-Visible radiation. The counter electrode is a metal. Following processes take place in the cell when light is incident on the semiconductor electrode: 1. Photo generation of charge carriers (electron and hole pairs) Semiconductor 2 e- + 2 h+ 2. Charge separation and migration of the holes to the interface between the semiconductor and the electrolyte and of electrons to the counter electrode through the external circuit. Now, holes are simply vacancies created in the valence band due to promotion of electrons from the valence band to the conduction band. However, in the study of electronic behavior of materials, "holes" are considered to be independent entities, with their own mass. hν 238 Hydrogen Production 3. The holes move to the interface and react with water producing oxygen: 2 h+ + H2O 0.5 O2(gas) + 2 H+ (aq) 4. The electrons travel in the external circuit and arrive at the interface between the counter electrode (cathode) and electrolyte. There, they reduce the H+ ions to H2: 2 e- + 2 H+ (aq) H2(gas) The complete reaction is absorption of photon and splitting of water into hydrogen and oxygen.The representation of the same process in band energy terms is shown in Fig. 7. The cell depicted in Fig.7 is a single photoelectrode type cell, with the anode being the active photoelectrode. The lower band is the valence band of the n-type semiconductor, while the upper band is the conduction band. The energy difference between the top of valence band and the bottom of conduction band is termed as the band gap of semiconductor, Eg. Some other configurations of the PEC cell are also possible: 1. The semiconducting material may be a p-type material. In this case, it will act as photo cathode, and reduction of H+ ions to H2 will take place at this electrode. The counter electrode may be a metal in this case. 2. Both electrodes, the cathode and anode, are photoactive semiconducting materials. In this case, the n-type electrode will act, as anode and favors oxidation of water to oxygen and H+ will take place at this electrode. The p-type electrode will act as cathode, where H+ ions will be reduced to H2. An Introduction to Energy Sources 239 Fig.7. Operating principles of a photoelectrochemical cell Photocatalytic hydrogen production: Essentially the photocatalysed reactions have generated considerable interest after the photocatalytic splitting of water on TiO2 electrodes was first demonstrated by Fujishima and Honda in 1972. Subsequently, various kinds of photocatalysts have been employed for hydrogen production and remediation of pollutants from water. Dispersed heterogeneous semiconductor surface provides a fixed environment that influences the chemical reactivity. Simultaneous oxidation and reduction reaction occurs on the surface of the catalyst on photoexcitation. The other advantages are, easy separation of catalyst after the reaction by centrifugation, availability of large surface area, low cost and stability. In heterogeneous photocatalytic systems, absorption of the light is an essential requirement for successful photocatalysis. In addition, it should be stable at the reaction conditions employed and it should be chemically inert. Among the available materials like metals, semiconductors and insulators, the semiconductors have been used because 240 Hydrogen Production the band gap of semiconductor is optimum, band edge positions are suitable for oxidation/reduction of water and one can possibly use sunlight as energy source to excite the electron from the valence band. In addition to the favorable band gap and band positions, semiconductors are inexpensive, non-toxic, easily recoverable and capable of retaining the catalytic activity. Also, loading of metal on the semiconductor surface and coupling of two semiconductors can increase the efficiency of the semiconductor photocatalysed reaction. Even though the light absorption is essential, other parameters like band gap, surface area, crystal phase, morphology, rate of interfacial charge transfer, carrier density and stability are also essential for the observed photocatalytic activity. Photocatalysis involves the initial absorption of photons by a semicondductor to excite electrons from valence band to conduction band. This results in the formation of electron-hole pair within semiconductor. Excitation and redox processes taking place in semiconductor photocatalyst are shown in Fig. 8. Fig.8. Excitation and redox reactions in semiconductor For efficient photocatalytic reaction the electron-hole pair recombination must be suppressed. Either trapping the photogenerated electron or hole or both can lead to this. The electron in the conduction band moves to the surface and reduction reaction takes place either with adsorbed molecule or surface groups. Self-recombination with the hole in the valence band depresses the activity of the semiconductor. An Introduction to Energy Sources 241 The reduction and oxidation strength of the photoexcited electron and hole can be measured from the energy of the lower edge of the conduction band and upper edge of the valence band. Depending on the relative positions of the top of valence band, bottom of conduction band and the redox potentials of the species, the oxidation and reduction processes are promoted. Fig. 9. Energy levels of various semiconductors In general, the selection of semiconductor for a particular reaction is based on the position of the valence and conduction band edges and redox potential of the adsorbed species of interest, stability towards photocorrosion and the value of bandgap. Bandgaps and energy levels of various semiconductors are shown in Fig. 9. To reduce water, the potential of the bottom of conduction band must be more negative than the hydrogen reduction potential; for oxidation reaction, the top of valence band should be more positive than the oxidation potential of water; Energies of various semiconductors are shown in the Fig.9. with respect to normal hydrogen electrode (NHE). Since the energy of valence and conduction levels of TiO2 is optimum to oxidize most of the organic species, and its high oxidation ability of photogenerated holes (E = 2.9V vs NHE at pH = 0) makes it as the best choice for photo-catalyst. In addition TiO2 is inert, resistant to photocorrosion, thus making it as a good photo-catalyst. Among three structural modifications of TiO2 (brookite, rutile and anatase), anatase is the form that is active. Even though there are other semiconductors to fulfill these criteria; some of them 242 Hydrogen Production suffer from “photocorrosion” under the experimental conditions employed. Fig. 10 shows the typical photocatalytic water splitting setup. Fig.10. Photocatalytic water splitting setup The major problem associated with photocatalytic splitting of water is the higher bandgap of the available semiconductor materials like TiO2. Because of the higher bandgap, these materials require UV light irradiation for carrying out the reaction whereas sunlight contains only 5% of UV radiation. The remaining part of the solar spectrum is composed mainly of visible and IR radiation. Research now focuses on reducing the bandgap of the available materials by various methods and finding new photoactive materials with lower bandgap. Summary Even though there are various methods available, the processes like direct electrolysis, steam methane reformation, biomass gasification, and hydrogen from coal and thermochemical decomposition they require other forms of energy like heat and/or electricity which can be obtained from fossil fuels or other expensive methods like nuclear energy. Also some of the methods lead to evolution of green house gases like carbon dioxide. Methods like photochemical hydrogen production have very less quantum efficiency. An Introduction to Energy Sources 243 Only the processes like photoelectrochemical, photocatalytic and biochemical hydrogen production have the potential to replace fossil fuels. For that an effective semiconductor photocatalyst, which has the desired bandgap, which absorbs light in the visible region, needs to be developed. The biochemical methods are highly sensitive to the environment and needs to be optimized for working under normal atmospheric conditions. Currentresearch has shown more progress in this field and hopefully we will see some methods in future, which will produce hydrogen with completely renewable sources without any emission of polluting gases. References 1. R. Narayanan, B. 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