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HYDROGEN PRODUCTION BY PHOTOPROCESSES

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ABSTRACT

The concept of producing hydrogen fuel from sunlight is inherently appealing and has captured the imagination of many scientists, innovators, and decision makers. In fact, there are numerous routes to produce hydrogen from solar energy through photoprocesses. Generally, they can be grouped into four processes: electric conversion, thermal conversion, indirect conversion, and direct photon conversion.

Electric conversion is the process whereby hydrogen is produced by the electrolysis of water from electricity. The electricity may be produced from solar photovoltaic cells or from other solar-driven electronic processes such as thermoelectric or thermionic reactions. In thermal conversion, high-temperature heat produced by solar concentration drives thermochemical cycles, direct thermal reactions, or hybrid thermochemical-electrochemical reactions to split water. Hydrogen also may be produced by thermal conversion using a heat engine to produce electricity for electrolysis. Indirect conversion uses solar energy stored as ocean thermal gradients, wave power, wind, or hydro power that produce mechanical power, which is converted to electricity for electrolysis. Hydrogen probably cannot be produced for less than \$20-\$40/MBtu by the thermal processes. In principle, electrolysis is a viable option for hydrogen production, but depends almost entirely on the availability of inexpensive electricity. Costs of 1¢-2¢/kWh are needed to produce hydrogen at ~\$7/MBtu, the cost of hydrogen from steam reforming of methane.

An attractive but longer term option is photon conversion. This involves direct conversion of water, for example, into hydrogen (and oxygen) using sunlight as the driving force. Photon conversion may be carried out through photobiological, photochemical, or photoelectrochemical processes. Photobiological systems are photosynthetic organisms that use sunlight to convert water or carbon compounds into hydrogen. The organisms are of three types: the green algae, cyanobacteria, and photosynthetic bacteria. Algae and cyanobacteria function like plants, have two photosystems, and can split water to hydrogen, although efficiencies are also low. The photosynthetic bacteria have only one photosystem and cannot split water, but they produce hydrogen by acting on carbon substrates such as organic wastes, and much higher conversion efficiencies are possible. Photochemical systems contain synthesized molecules in a homogeneous solution. The molecules are typically porphyrin-quinones that are designed to mimic photosynthesis. Such photochemical systems suffer losses from back reactions and at present have low conversion efficiencies. In photoelectrochemistry, semiconductors immersed in aqueous solution absorb photons, which produce electron-hole pairs that drive redox reactions to split water and produce hydrogen. The semiconductor may be a slurry of fine particles so that the photosensitive system is a volumetric reactor rather than a surface collector. With research advances to achieve conversion efficiencies of 10%-20%, hydrogen may be produced by photon conversion for \$3-\$8/MBtu.

INTRODUCTION

Hydrogen can be used both as a renewable fuel and as a medium for storage and transmission of energy. There are a number of key considerations when developing hydrogen as an energy medium or fuel, but the overriding issue is the relatively high cost of production. The principal source of hydrogen is currently from the steam reforming of methane¹ from natural gas at a cost of approximately \$7/MBtu. The major uses of hydrogen today are for chemical synthesis and refinery operations. The energy represented by this hydrogen is more than one quad.

Numerous routes are possible for hydrogen production, but they can be categorized as those based on fossil fuel feedstocks such as natural gas and coal, nuclear generated electricity, or those that are solar photoprocesses. As with any use of fossil fuel, the production of hydrogen contributes CO₂ to the environment. An attractive long-term approach to hydrogen production is based on photoprocesses through the use of solar energy to produce renewable hydrogen. There are many potential routes to produce hydrogen by solar photoprocesses that can generally be grouped into four areas: electric conversion, thermal conversion, indirect conversion, and photon conversion.

SOLAR CONVERSION PROCESSES

Figure 1 shows the alternatives for hydrogen production from solar-driven processes; most of them are based on the splitting of water.^{2,3}

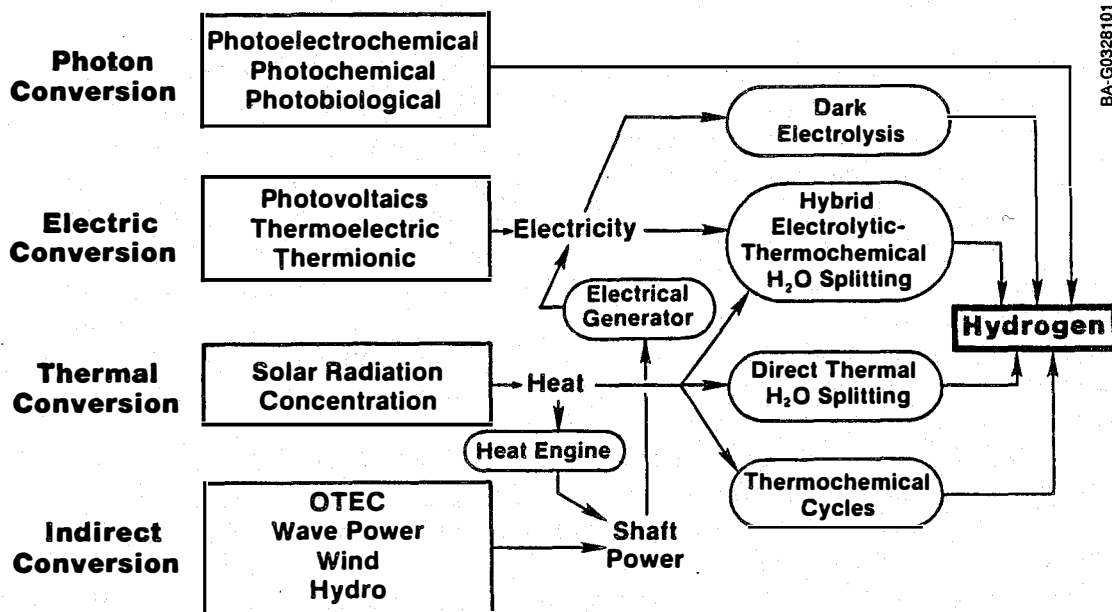
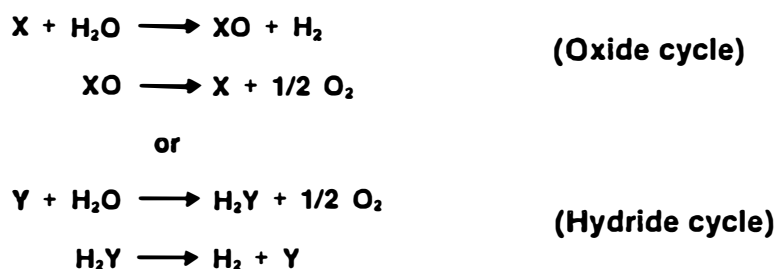


Figure 1. Solar-Driven Hydrogen Production

Electric conversion is the process whereby hydrogen is produced by dark electrolysis of water from electricity. The electricity may be produced by solar photovoltaic cells or from other solar-driven electronic processes such as thermoelectric or thermionic reactions. Electrolysis is a viable option for hydrogen production, but the cost of the hydrogen depends almost entirely on the cost of electricity. Inexpensive electricity, between 1¢ and 2¢/kWh, is required to produce hydrogen competitive with the current cost of hydrogen from reforming of methane.

In thermal conversion, solar radiation is concentrated to produce high-temperature heat for several thermal process options. One approach is to use the heat collected by a central receiver heliostat field in a heat engine thermodynamic electric power generation cycle for electrolysis. The same consideration for inexpensive electricity as relates to electric conversion processes applies here as well. Other options for thermal conversion are based on the fact that by concentrating sufficient heat into water it is thermodynamically possible to dissociate it to hydrogen and oxygen. Thermochemical cycles have been the most extensively researched of the thermal cycles. Figure 2 shows both an oxide and a hydride cycle scheme with specific examples for each cycle. The GA Technologies sulfur-iodine process has been developed more extensively than any other process. Current projected costs for this process indicate that hydrogen probably cannot be produced for less than \$30/MBtu.



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The greater the number of steps, the lower the temperatures

Examples:

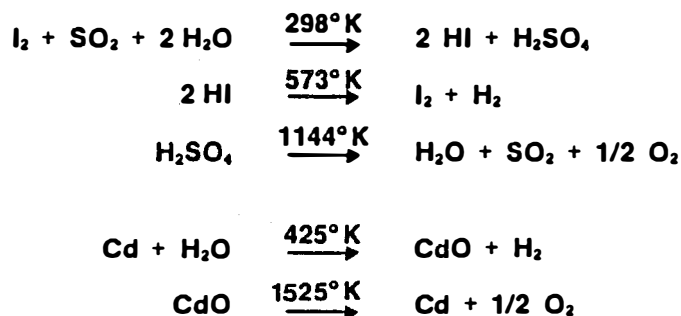
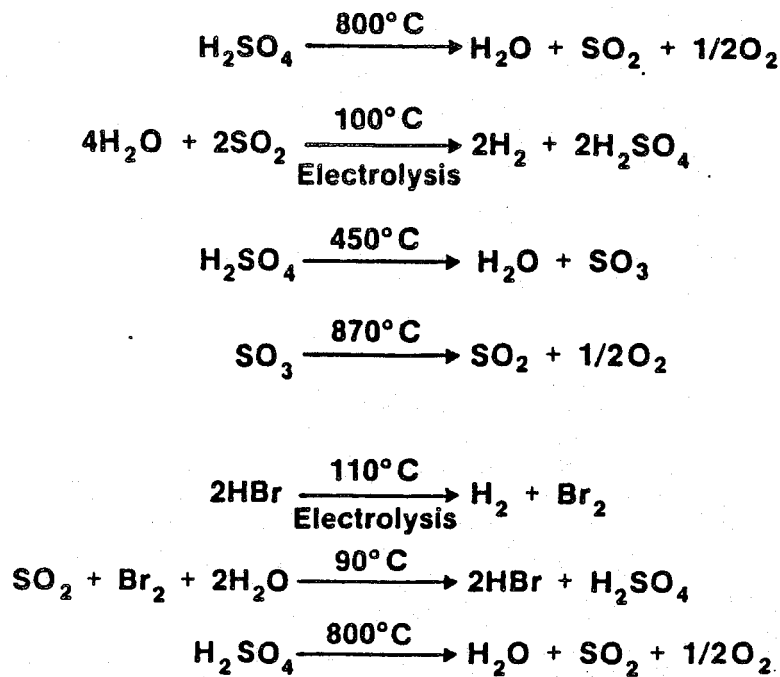


Figure 2. Thermochemical Cycles

Another cyclic process is the hybrid electrochemical-thermochemical water splitting concept. Figure 3 gives the two main processes developed of this type. The first is the Westinghouse sulfuric acid cycle and the second is the Ispra (Italy) hydrogen-bromide cycle. These cycles have the problem of materials compatibility with sulfuric acid at high temperatures. No definitive cost data are available, but it is expected hydrogen costs would be from \$20 to \$40/MBtu. Direct thermal water splitting is theoretically possible by applying high temperatures directly to water. However, to achieve acceptable conversion efficiencies requires temperatures greater than 2500 K (see Figure 4). Because of the high temperatures, materials are a problem, and such a system would likely require the use of advanced ceramics. No cost data are available for this concept.

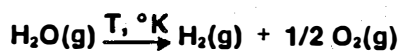
Indirect conversion uses solar energy stored as ocean thermal gradients, wave power, wind, and hydro power. These technologies are being developed to convert the stored solar energy into mechanical power and then to electricity. Hydrogen would be produced by electrolysis. The cost of the electricity produced by these technologies determines whether hydrogen production is economical.

The cost of electricity from the various solar-driven processes ranges from a low of 3¢/kWh to well over 30¢/kWh. Hydrogen costs from electrolysis would therefore be between \$14/MBtu and \$140/MBtu. The technology goals for all of these processes are between 3¢ and 8¢/kWh with wind and hydro power offering the best near-term promise at 3¢-4¢/kWh. This means that hydrogen could be produced for \$14-\$19/MBtu, which is twice as expensive as necessary to compete with methane-reformed hydrogen today.



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Figure 3. Hybrid Thermochemical/Electrochemical Cycles



$$K_{EG} = \frac{(P_{\text{H}_2}) (P_{\text{O}_2})^{1/2}}{P_{\text{H}_2\text{O}}}$$

$$\Delta G_{298}^\circ = 56.8 \text{ Kcal/mole}$$

$$\Delta H_{298}^\circ = 68.4 \text{ Kcal/mole}$$

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<u>Temp.</u>	<u>K_{EG}</u>
300°K	9.0 × 10 ⁻¹¹
2000°K	3.0 × 10 ⁻⁴
3000°K	4.5 × 10 ⁻² (~ 13% conversion)
3400°K	— (~ 20% conversion)

Figure 4. Direct Thermal Water Splitting

In photon conversion, solar photons are captured and serve as the driving force with no intermediate steps to produce hydrogen by one of several processes. Theoretical solar conversion efficiencies are very high; therefore, these processes offer significant potential.⁴ Photon conversion may be carried out through photobiological, photochemical, or photoelectrochemical processes and is the major topic of this paper.

PHOTOBIOLOGICAL HYDROGEN PRODUCTION

Photobiological conversion is the most fundamental of the photon conversion processes to produce hydrogen. This process is associated with photosynthesis carried out by a number of organisms. Figure 5 shows the photobiological hydrogen-producing options and the participation of three different types of organisms: the green algae and cyanobacteria splitting water and photosynthetic bacteria converting organic substrates.^{5,6} Natural photosynthesis is a process whereby organisms extract energy from sunlight. This energy is collected and used in a complex process and directed to growth of cell mass. Enzymes, including hydrogenase and nitrogenase, are produced by green algae and by cyanobacteria; under certain conditions these enzymes catalyze the production of hydrogen from water. Current photobiological research is largely devoted to understanding the mechanism of photosynthesis so that whole cell systems can be manipulated through genetic engineering, for example, and improved systems can be developed. Photochemical hydrogen production, described in the next section, seeks not only to mimic photosynthesis, but actually improve on it by tailoring the steps involved.

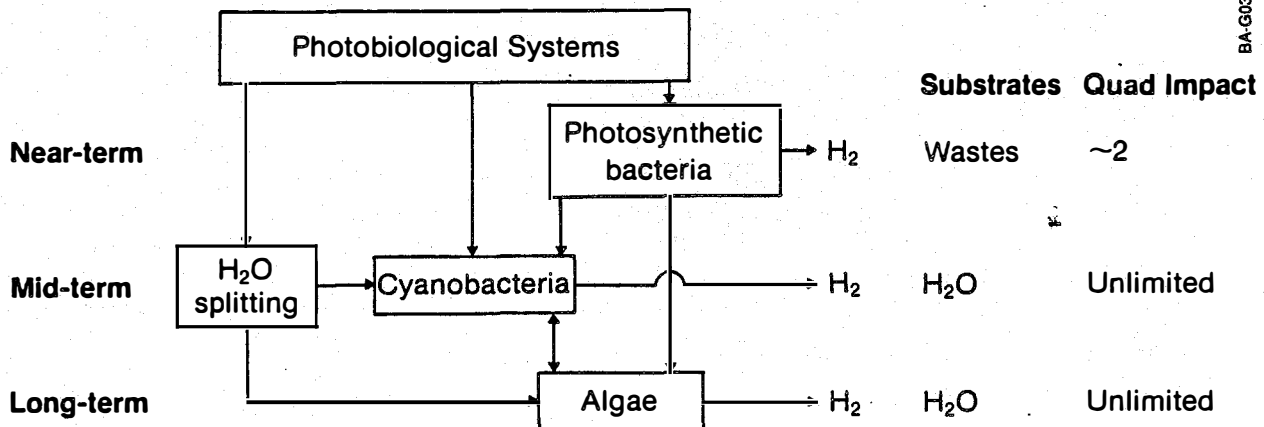


Figure 5. Photobiological H₂-Production Options

Within a cell, photosynthesis occurs in the thylakoid membrane within the chloroplast. The steps in photosynthesis are as follows and are depicted in Figure 6:

1. Photons are collected by antenna pigments comprised of chlorophyll and other compounds.
2. Charge is separated in a specialized chlorophyll complex called a reaction center (P680 or P700).
3. Electrons are extracted from water by photosystem II (PS II) producing hydrogen ions and molecular oxygen.
4. Charge is then transported as the electron is shuttled through molecular intermediates from photosystem II to photosystem I (PS I).
5. The electron passes through photosystem I where it is given a second pulse of photon energy.
6. The electron reduces NADP⁺, and chemical energy is stored.
7. Enzyme-mediated biochemical reactions convert H⁺ to hydrogen (not shown in Figure 6).

Green algae and cyanobacteria use this process to produce hydrogen, and efficiencies of less than 1% have been achieved in the laboratory.

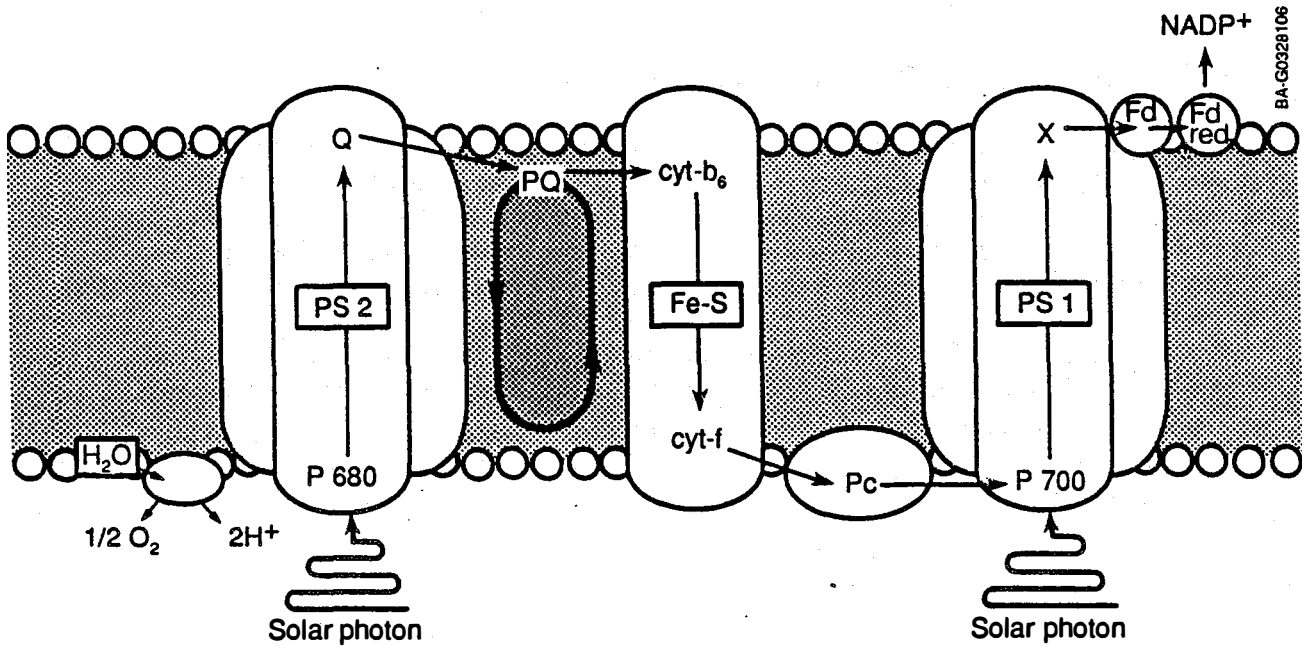


Figure 6. Steps in Photosynthesis

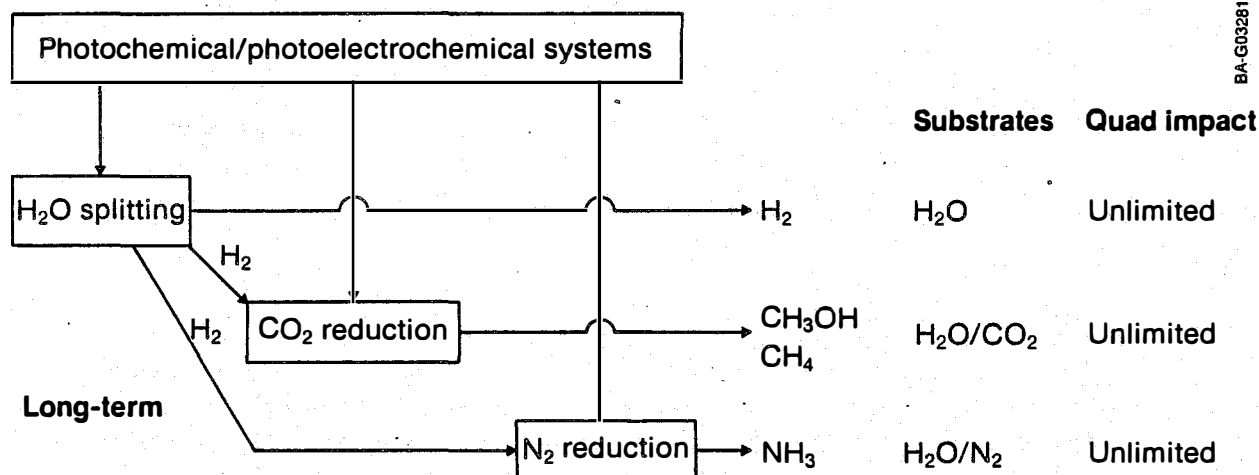
The other area of photobiological conversion results from the use of photosynthetic bacteria that consume waste organic substrates and produce hydrogen. Photosynthetic bacteria have only one photosystem and cannot split water, but derive a portion of their energy from the organic substrate. The efficiency of light conversion by this process is approximately 5%. Conversion with photosynthetic bacteria has the best near-term potential for economic hydrogen production because both sunlight and the organic substrate contribute energy to the process, but the amount of hydrogen that could be produced is limited by available organic substrate materials.

The technical feasibility of photobiological hydrogen production depends on overcoming numerous problems. Oxygen that is produced in some of the processes inhibits both the hydrogenase and the nitrogenase enzymes. Some progress has been made in selecting green algae for oxygen tolerance, and bioengineering techniques offer a number of whole-cell and cell-free options to minimize oxygen sensitivity. Another problem is that in cell-free systems, the biological components lose activity rapidly at all temperatures above freezing. Solutions to this phenomenon may lie in improvements in component stability through biotechnology techniques such as chemical modification of the thylakoid membranes, immobilization of chloroplasts in gel, or entrapment of chloroplasts into a porous matrix of specially treated glass beads.

Finally, the currently observed overall efficiency for conversion (1%-5%) remains lower than necessary for economic hydrogen production. While current efficiencies are approximately 1%, it is anticipated that in both whole-cell and cell-free systems, efficiencies of greater than 10% are possible. Greater efficiencies in cell-free systems depend largely on successful stabilizing and coupling of the biological components. Although liquid systems are currently envisioned, solid matrices such as artificial membranes or colloidal particles may offer important alternatives.

PHOTOCHEMICAL HYDROGEN PRODUCTION

The photochemical hydrogen production process mimics the natural photosynthesis process; therefore, designs are sought to evaluate the seven basic steps of photosynthesis discussed in the previous section. Figure 7 shows the enormous potential for the photochemical production of hydrogen and other fuels and chemicals. The approach taken for photochemical systems has been to synthesize photoactive molecules that serve as synthetic reaction centers. These molecules absorb light and carry out charge separation that results in an electron on one side of the molecule and a hole on the other side. The challenge is how to stabilize the charge-separated state long enough to drive the chemical reaction to produce hydrogen.



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Figure 7. Photochemical and Photoelectrochemical H₂-Production Options

The approach taken in photochemical system development⁷ has been to design synthetic donor-acceptor molecules such as the porphyrin-quinone molecule shown in Figure 8. The large porphyrin ring at the left traps light energy, which causes an electron to leave the porphyrin ring and move across the molecular bridge to the quinone ring at the other end of the molecule. Such a system suffers from spontaneous and rapid back reaction before the free electron can be used to drive chemical reactions such as hydrogen production. Hence, the major challenge in photochemical systems is the synthesis and use of an appropriate molecule. Another important consideration is the environment chosen for the molecules, but it depends on the molecule chosen for application.

Although current efficiencies are around 0.1%, such systems are inherently very attractive with effectively designed molecules. A photochemical system could be synthesized from chemical constituents, and a solar collection reactor concept would allow for a volumetric reactor rather than simply a surface collector because of the homogeneous nature of the system.

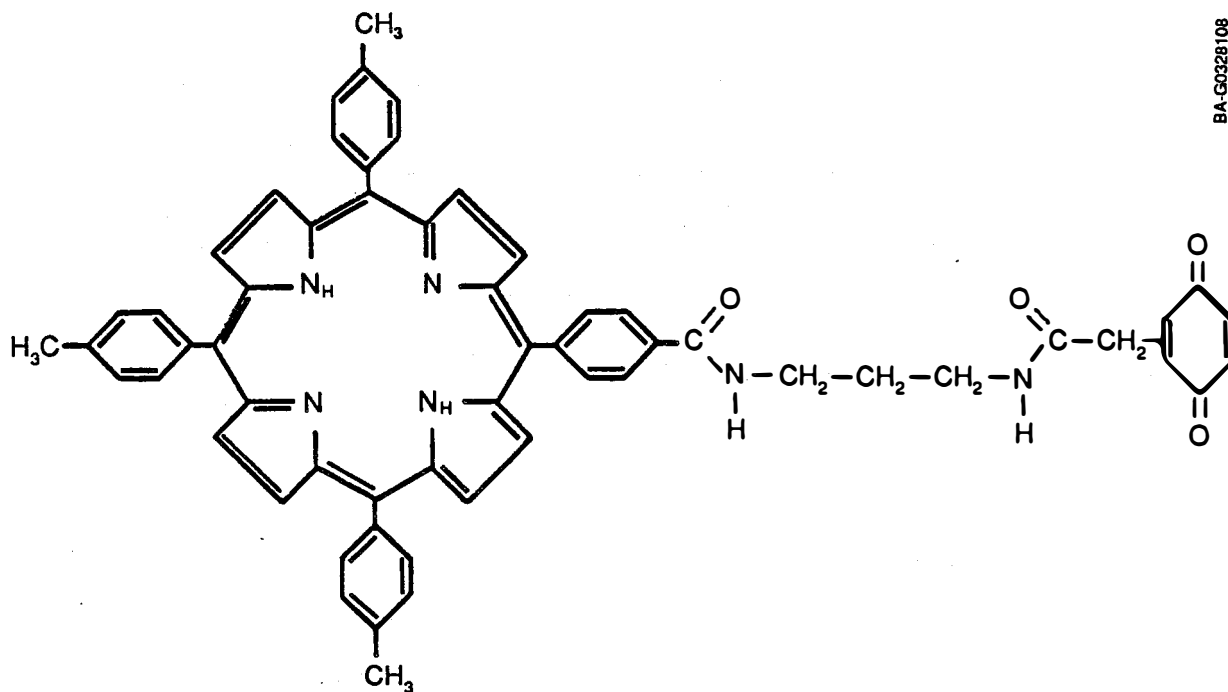


Figure 8. Porphyrin-Quinone Photoactive Molecule

PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

In photoelectrochemical hydrogen production processes, solar photons are absorbed in semiconductors immersed in aqueous solutions and produce electron-hole pairs. These pairs separate at the semiconductor-liquid junction and drive chemical reactions at the surface to produce hydrogen. Because these semiconductors have been well studied for photovoltaic and other semiconductor applications, considerable progress has been made in improving conversion efficiencies and in the basic understanding of such systems.^{8,9}

The photoelectrochemical cell for hydrogen production (Figure 9)¹⁰ is best considered in the framework of a semiconductor-metal Schottky junction or a p-n junction that is split with an electrolyte interposed between the two halves. The chemistry is done in the electrolyte, and hydrogen is produced in the solution. The efficiency of the semiconductor-metal junction is severely limited, but if both the p- and n-type semiconductors are irradiated, the efficiency of the p-n junction increases substantially. The efficiency for hydrogen production by a photoelectrochemical cell should always exceed that of a photovoltaic cell using the electricity to do electrolysis because of the efficiency losses in the two-step process.

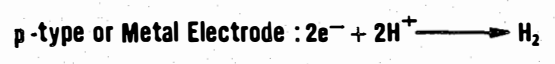
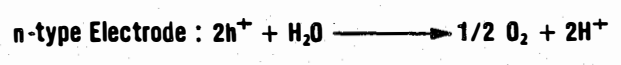
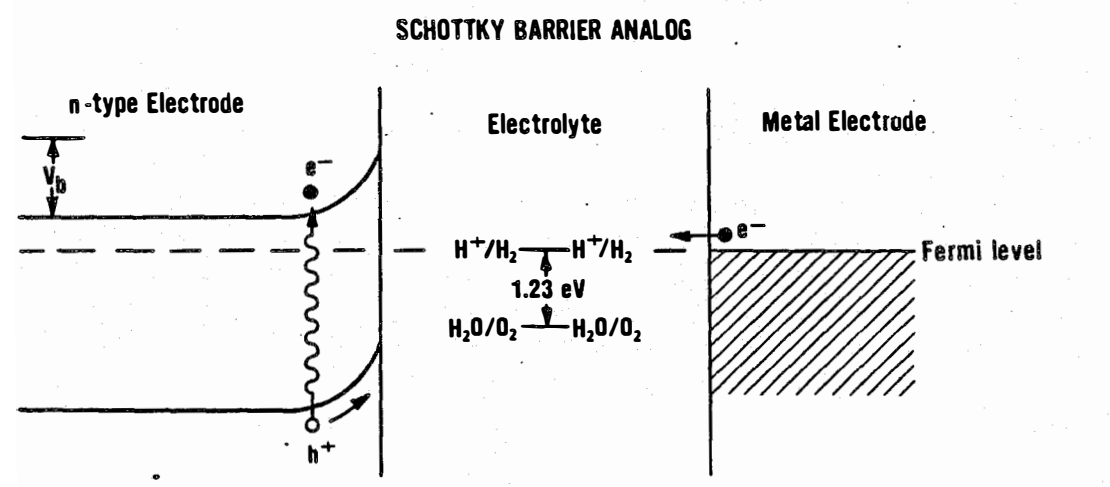
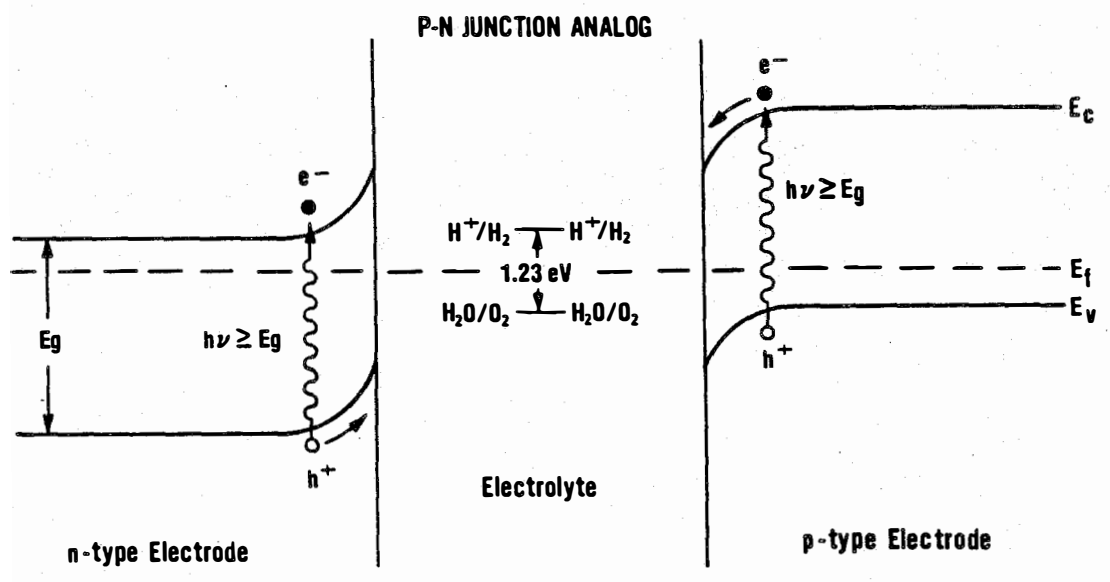
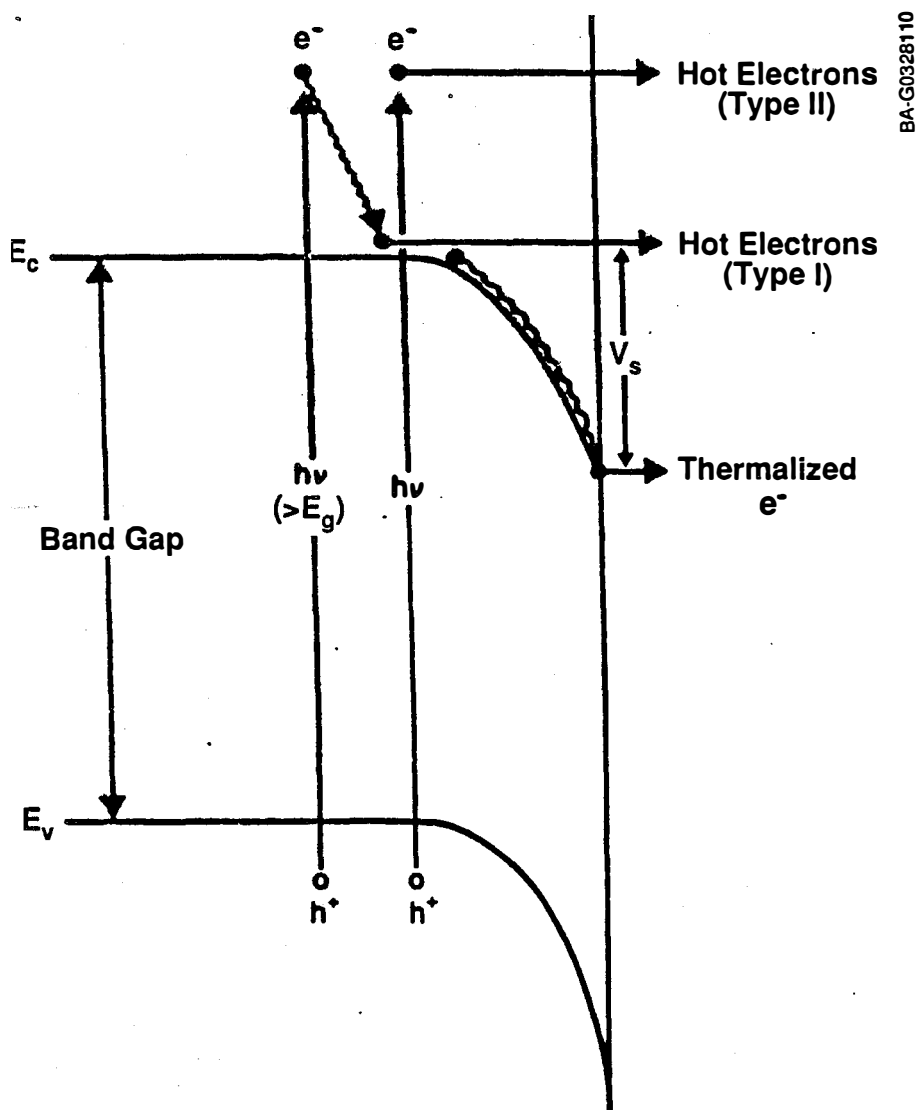


Figure 9. Photoelectrolysis Cells

The major challenges in producing economic hydrogen from photoelectrochemical cells is to reduce photocorrosion of the semiconductor in the electrolyte and increase the photon conversion efficiency and reduce the cost of fabrication of the devices. Photocorrosion is being addressed in a number of ways including seeking conducting polymers as protective coatings for the semiconductor material. Different material combinations are being developed and tested to find more stable performance.

Current photon conversion efficiencies have reached 13% for photoelectrochemical production of hydrogen with an external voltage applied. A practical system cannot require an external voltage as it reduces the net energy balance severely. The theoretical limit is 32% for normal systems, so there remains substantial opportunity for improvement. Further, if hot electrons are used successfully, theoretical efficiencies are as high as 67%.¹¹ Figure 10 shows the concept of hot electron injection into the



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Figure 10. Hot Electron Effects

electrolyte.¹² Here a device is prepared that allows for acceleration of the electron across the depletion region before the electron is thermalized and thus dumping more energy into the electrolyte for chemistry. Current work is focused on developing superlattice devices (multilayer systems) that are multiband absorbers and produce hot electrons in alternating layers. Schemes are being developed to extract the hot electrons out of the devices. There are sufficiently novel approaches in this arena that it is reasonable to expect substantial improvements in efficiency in the future.

Reducing the cost of fabricating the device is a problem shared with photovoltaic researchers. New fabrication approaches and thin layer devices are being tested for performance. A novel way to tackle the problem is to develop very small particle or colloidal (100Å - 1µm) semiconductors that are dispersed in solution. Figure 11 illustrates the principle whereby hydrogen is being produced. The reactor concept would be substantially simpler than for planar semiconductors and allows for a volumetric reactor rather than a surface, a feature that should ultimately improve efficiency. Current efficiencies for these systems are less than 1%, but work is relatively recent in this area.

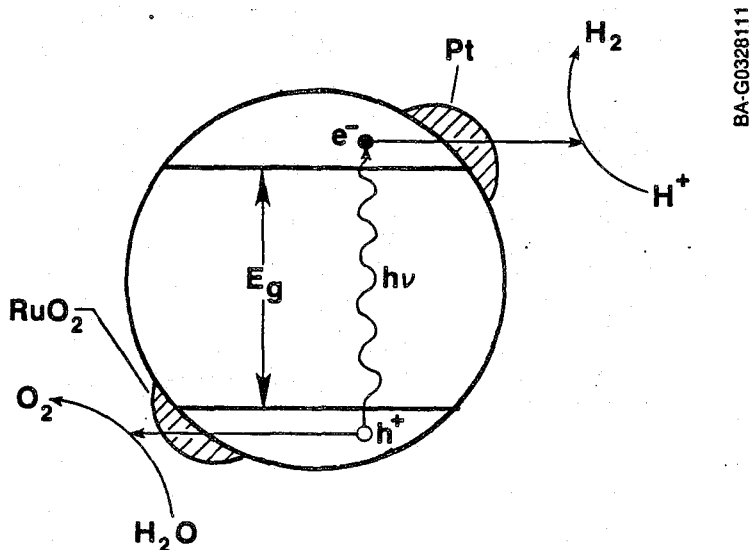


Figure 11. Photochemistry with Particles or Colloids

SUMMARY

The four major alternatives for solar conversion processes can be summarized into three major areas: heat-driven processes, electrolysis, and direct photon conversion. The heat driven processes rely on a thermochemical cycle or direct thermal water splitting, but require temperatures in the range of 800-2500 K. Significant materials compatibility problems exist for these processes, and costs are not expected to go below \$20-\$40/MBtu. Electrolysis is an inherently attractive approach as it is well understood

and is a relatively simple process. The cost of hydrogen from electrolysis depends almost entirely on the cost of electricity. A number of renewable technologies are under development with the goal of producing competitively priced electricity. To compete with hydrogen produced from steam reforming of methane, electricity costs of 1¢-2¢/kWh are required. With price escalations in the future, it may be sufficient to produce electricity for approximately 4¢/kWh.

The direct photon conversion processes offer significant potential for producing inexpensive hydrogen, although they require years of development. Photobiological processes form the basis for all the direct photon conversion processes as they all emulate the natural process of photosynthesis. Most research is still focused on understanding photosynthesis. Current conversion efficiencies are approximately 1%, although efficiencies greater than 10% are envisioned either for genetically modified whole-cell systems or constructed cell-free systems. Photochemical systems are based on molecules that are synthesized to function as artificial photosynthesis systems. They are in the early stages of development and current efficiencies are less than 0.1%. Photoelectrochemical systems are the most advanced, partly because of the synergism with the rapid development of semiconductors for a variety of applications including photovoltaics. Efficiencies as high as 13% have been achieved for photoelectrochemical systems. Theoretical efficiencies as high as 67% are possible by extracting hot electrons out of superlattice devices. The use of small photoelectrochemical particles could significantly simplify device fabrication and reactor design concepts for hydrogen production.

Overall, direct photon conversion processes show promise for economic hydrogen production. Dramatic progress is being made in the laboratory, and we can look forward to continued success.

ACKNOWLEDGEMENT

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