

ON THE SPLITTING OF WATER

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Abstract—Future energy needs and requirements in manufacturing processes (like fertilizers, synfuels, etc.) makes hydrogen an important chemical commodity. It is projected that hydrogen required for various processes may reach 1.8×10^9 MBTU by the year 2000. This increases the importance of producing hydrogen especially from a cheap raw material like water. A survey of the different approaches for splitting water (electrolysis, plasmolysis, magnetolysis, magmalysis, photolysis, photoelectrochemical methods, radiolysis, etc.) is made and discussed in detail in this review.

INTRODUCTION

The interest in methods of splitting water arises in view of the fact that hydrogen is a necessary substance in the merchant hydrogen market (ammonia, fertilizers, fats and oils, etc.) together with the fact that synfuels will be made by adding hydrogen to carbon-rich materials, e.g. coal.

Hydrogen at present is made by reacting steam with natural gas, naphtha, etc. In the longer term, it could be made by two methods which would also involve fossil fuels. The first of these involves the direct reaction of steam with coal [1]. Such a method has to be carried out in conjunction with the gas shift reaction which involves reaction of the CO produced with steam to form CO₂. Hydrogen produced by this method would be cheap (\$6-7 per MBTU, or GJ) [2]. A slightly cheaper method [3] would involve the reaction of iron with steam, giving hydrogen and Fe₃O₄; the latter is then reacted with carbon giving CO₂ and regenerating the iron [4].

These cheap methods have a major fault: they produce air pollutants. The first of these is SO₂, with acid rain (Fig. 1) [5]. Sufficient removal of sulfur from coal before coal is burnt or from stacks, turns out to be impractical because of the expense, together with difficulties in disposing of sulfur. In terms of longer consideration, the continued addition to the environment of CO₂ would cause a rise in the sea level of several meters by mid-century (Fig. 2) [6].

However, a greater reason for interest in hydrogen at this time is the fact that the raw materials from which it is now being produced will pass through a maximum [7], in respect to the rate of production during the coming two decades so that by some date during the 1990's, the rise in the cost of natural gas, and hence

hydrogen and ammonia, will not be contrived: but a result of scarcity.

For this latter reason alone, research on the production of hydrogen from water becomes urgent. There are other reasons, those connected with the desire to make atomic and solar energy viable. Thus, at present, atomic energy (with its difficulties) is oriented to the production of electricity, but in the case of most industrialized countries this is only about 20-25% in the total form of energy and for developing countries this is much less. Solar energy, correspondingly, appears at first not to be viable as an important general energy source because of diurnal variation. Thus, the coupling of hydrogen with atomic energy would make the latter safer—because reactors could then be placed many hundreds of miles away from population centers,* owing

GLOBAL HUMAN - CAUSED SULFUR DIOXIDE EMISSIONS

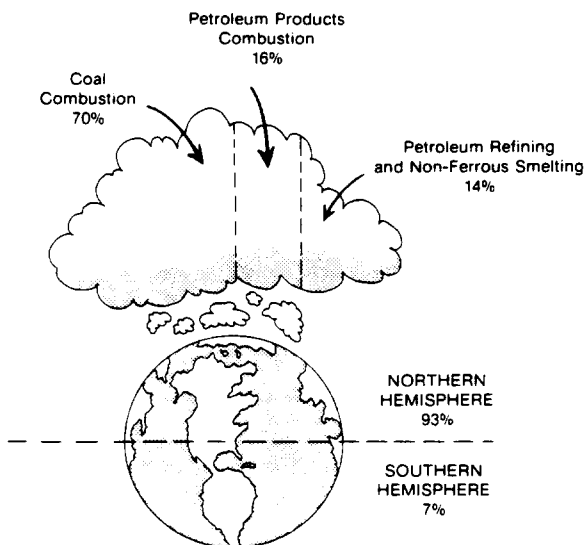


Fig. 1.

* While the dangers of the results of the Three Mile Island incident are made less dangerous by the use of remote carriers, there remains the problem of waste disposal. However, this would seem solvable at any place, if a sufficiently deep cavity in geothermal rock (4-5 miles deep) is reached. The advantage of hydrogen is that it avoids the low intensity radiation difficulties and thus reduces cancer risks to a negligible degree.

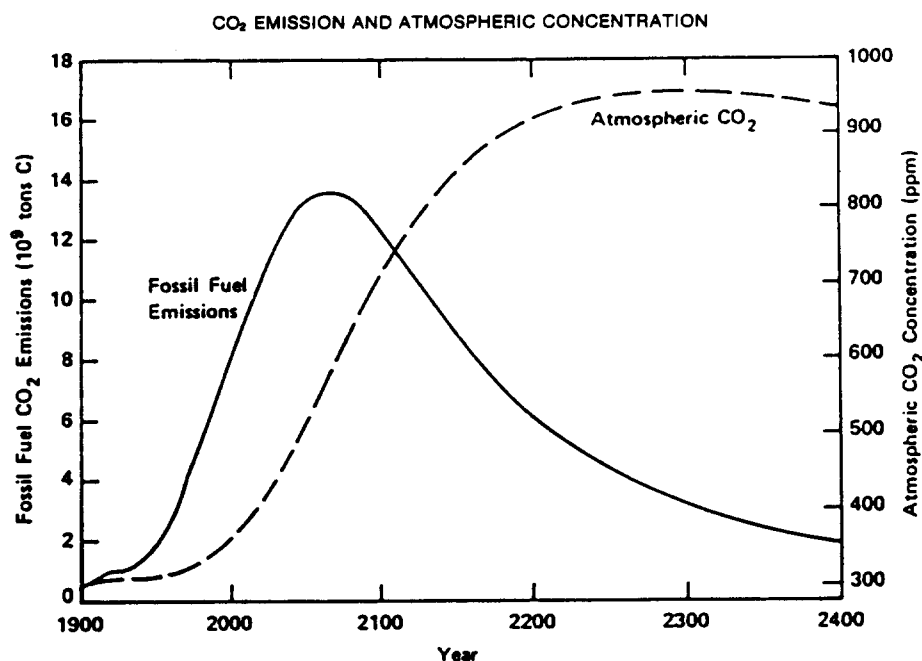


Fig. 2.

to the fact that transport of hydrogen through pipelines costs only $\sim 0.2 \text{ ¢ kWh}^{-1} (1000 \text{ km})^{-1}$; but, more importantly, it would enable atomic reactors to supply not only the electrical but the whole of the energy supply. Hydrogen from distant sites could give electricity via fuel cells; those sectors of the economy now supplied by natural gas, oil or coal could be supplied without pollution. Correspondingly, production of hydrogen from solar energy and transfer of this in pipes to city centers would mean that the solar source would be transformed from an impractical one because of diurnality to a practical source which could (given competitive overall economics* for photovoltaic or Ocean Thermal Energy Conversion associated with hydrogen production) provide all present needs.

Possible methods for producing hydrogen from water will hence be discussed in this review.

1. ELECTROLYSIS

Electrolysis has been known for the production of hydrogen since the early nineteenth century. It gives

hydrogen at 99.99% purity compared with the 98% hydrogen obtained from fossil sources. The equation which relates the dollar cost† of 1 MBTU or 1 GJ of hydrogen to the price of electricity and to the potential difference across the cell is given by [8]:

$$\text{Cost of 1 GJ (or 1 MBTU) in \$} = 2.29 Ec + 3. \quad (1)$$

The value of 2.29 involves the assumption of 100% Faradaic efficiency, E is the potential difference across the electrodes to produce a certain current density (usually in the range of $100\text{--}500 \text{ mA cm}^{-2}$) and c is the cost of electricity in cents per kWh of electricity. The factor of 3 comes from a calculation taking into account various factors, such as the interest rate on the initial capital borrowed, maintenance, operating costs, labor, depreciation of plant, local taxes, insurance, etc. The constant factor at the end of equation (1) varies from 2 for an interest rate of 10% to 3 for a 15% interest rate.

The value of c is not that applied to householders. If hydrogen is made on a very large scale by means of electrolysis, the value of c can be much less than that normally charged for several reasons.

(a) The transmission costs would be zero because the hydrogen electrolysis plant can be in the neighborhood of the electricity producing plant. This often means halving of the cost of the electricity;

* Including, of course, consideration of the economics of long-term damage caused by pollution.

† Other methods of calculation give a price, not a cost, and include a profit. They are often around 30–50% higher than the values given by this equation.

Table 1. Cost comparison of various processes for production of hydrogen

Process	Source	Cost of the source (\$ per MBTU)	Cost of the hydrogen produced (\$ per MBTU)
Steam reforming	Natural gas	8	~11
Coal gasification	Coal	1	7
Electrolysis of water	Electricity	6	13 (c-dependent)

(b) The power can be bought in great blocks† with long-term contracts and this again reduces the cost of the power by several tens of percent;

(c) The power can be utilized during the night, which allows for further lowering of the cost by some 30–40%. Taking these advantages together mean in practice that the *cost* of electricity can be less than half that of the ordinary consumer and may be as little as one quarter.§

Between about 1970 and 1984 research mainly on the use of appropriate electrocatalysts has reduced the value of E for a current density of about 500 mA cm^{-2} from around 2.2 V to around 1.6 V, the value of the latter being taken at 100°C . Somewhat lower values can be expected in the future: by the use of electrocatalysts which have low Tafel slopes, the ultimate value of E is probably around 1.47, which is also the thermoneutral voltage.||

It is reasonable to assume that commercial electrolyzers functioning at 1.6 V per cell could be manufactured by 1995, with appropriate research and operating at a current density of 500 mA cm^{-2} .

† For instance in Canada electric power is available at the present time in the region of 2¢ kWh^{-1} (e.g. Manitoba, Ontario, and Quebec). Thus if a water electrolysis plant is sited near a source of hydroelectric power in Canada, it would be possible to produce hydrogen at a price at which gasoline is sold in the United States. It is conceivable this hydrogen may be fed into natural gas pipelines which would take it from Canada to the United States and the mixture introduced into fuel cells. The natural gas is inert in fuel cells but hydrogen would be active. Cheap hydroelectric power could be available in this way, effectively in the form of electricity, at any point in the United States served by a gas pipeline.

In estimating the precise cost of this operation it would be necessary to take into account the fact that natural gas needs a pressure of more than 50 atm and would have to be recompressed, after consumption of the hydrogen in fuel cells, to the original pressure.

§ These statements do not mean that electricity at less than half the consumer cost is *available* for big plants using interruptible power and situated near plants. It means that such costs *could* be available if the utilities would see it in their business interests to sell electricity in this way.

|| The potential at which (neglecting the effects of IR drop) the cell neither heats nor cools upon operation.

The cost of hydroelectricity at the present time depends upon the location of the plant and its age. There are still contracts which are operative [9] in which the cost of electricity is 1.5¢ per kWh. The cost of electricity from a modern hydroelectric plant is in the region of 3¢ per kWh (at the plant), and less at night. Utilizing these figures in the above equation gives \$8.25 and \$17.00, respectively, for 1 GJ of hydrogen. Taking the mean of these figures, the cost of hydrogen by electrolysis is around 70% greater than that at which it could be obtained from coal. Table 1 gives a cost comparison of hydrogen produced by electrolysis and from fossil fuels.

Electrolysis must be considered as viable in some situations. On the one hand, it is convenient, giving hydrogen already separated from oxygen; gas produced in great purity; the production of oxygen and not only hydrogen; and the plants have simplicity and durability.

Further, although the straight electrolysis of water may not be advanced below about 1.5 V, there may be indirect ways of utilizing electrolysis which have yet to be fully investigated. Among these, for example, is the replacement of the anodic reaction of oxygen evolution by other reactions which can be induced to occur at lower potentials and which involve a cheap depolarizer [10–16]. It may be possible, for example, to obtain cheap iron sulfide as a waste product involved in the removal of sulfur from coal. In this case one may be able to invoke the reaction:



where the S^{2-} comes from a sulfide dissolved in the solution. In this instance, the potential for electrolysis would be greatly reduced and could be even in the 0.5 V region. Conversely, the reaction would yield sulfur on the electrode, but a low cost method may be found for utilizing this and recovering it in a useful way. Further, use of lignite and anthracite as a depolarizer has created a new field: coal slurry electrolysis for the production of hydrogen. The main principles of this process are given in Fig. 3. One advantage of this process is that there is no oxygen evolution but there will be some valuable organic by-products. Farooque and Coughlin [12, 13] have reported a higher yield of hydrogen by

WHY USE COAL SLURRIES TO OBTAIN CHEAP ELECTROLYTIC H₂?

1. Normal Electrolysis of Water:

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00V
$2\text{H}_2\text{O} \rightarrow 1/2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	1.23V
Practical Potential	~1.80V
2. Coal Electrolysis:

Organic compounds react instead of H₂O. No O₂ evolved.

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00V
$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{H}^+ + 2\text{e}^-$	0.52V
or	
$\text{C} + \text{xH}_2\text{O} \rightarrow \text{xH} + \text{yH}^+ + 2\text{e}^-$	~1.00V (Practical Potential)

Hence:

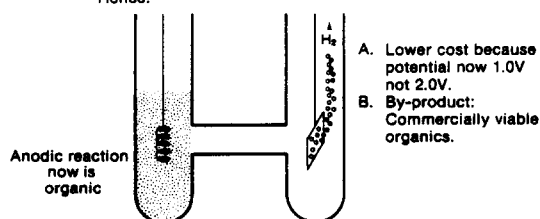


Fig. 3.

using unwashed coal. Okada *et al.* [10] have seen that the maximum feasible hydrogen production rate is reduced by the use of thoroughly washed coal, in which the Fe²⁺ content of the solution is small. They have concluded that the anodic depolarization route to hydrogen production would provide hydrogen at a lesser cost than that of normal electrolysis.

Having said this, it is necessary to bring attention to the fact that methods using electricity to produce H₂ from water have the following fundamental disadvantage: if the electricity is obtained with a heat engine, it involves the Carnot efficiency limitation. Thus, if the electricity is obtained from coal, then with a normal efficiency of electricity production of around 39%, about 61% of the energy is lost as heat, and this is not easily recoverable.

Thus, the energy cost of the electrolytic hydrogen (and oxygen) related to the original source of energy in the fossil fuel concerned, should be 1/0.39 or about 2.6 times greater than those methods which used a source of energy more directly. The low cost potentially available from hydroelectric sources of electricity (or those from wind) do not involve this difficulty.

Let us then leave electrolysis as a basic method which is available if electricity is sufficiently cheap (as possibly in the future from atomic or solar* production) and consider other methods.

2. PLASMOLYSIS

One of the possibilities of obtaining hydrogen from

* The cost of solar electricity by means of photovoltaic cells, looks hopeful. Thus, at the present time the predictions [17] for a 1990 date are 6–8¢ per kWh.

water has always been seen as a direct heating to extreme temperatures (3000°C) in which the water is substantially dissociated, in terms of thermodynamic equilibrium laws, to hydrogen and oxygen. The principal difficulty foreseen in such a method in the past has been the lack of durability of materials at high temperatures.

One method by which this difficulty may be avoided is to utilize electrically produced plasmas [18]. Electrical generation of the plasmas involves transformation of the energy from an electric field (microwave, radio frequency or d.c.) into kinetic energy of electrons which is further transformed into molecular excitations and to the kinetic energy of heavy particles. These discharge plasmas may be broadly divided into hot, arc or thermal discharges and cold, low temperature or glow discharges. The latter are termed nonisothermal low pressure plasmas since the electron temperatures lie far above those of the discharge gas whereas the thermal plasmas have electron temperatures close to that of the discharge gas [19]. Electron temperature can range from thousands to tens of thousands of degrees in both types of discharges. The differences in the energy content as a function of temperature are shown in Fig. 4. Thus, the low temperature discharge has sufficient energy to split water.

Plasma-assisted material processing and chemicals production has already been realized [20–22].

Chemical aspects of thermal discharges have been treated by assuming local thermodynamic equilibrium in the arc while chemical and transport kinetics control the quench of the high temperature species. There may

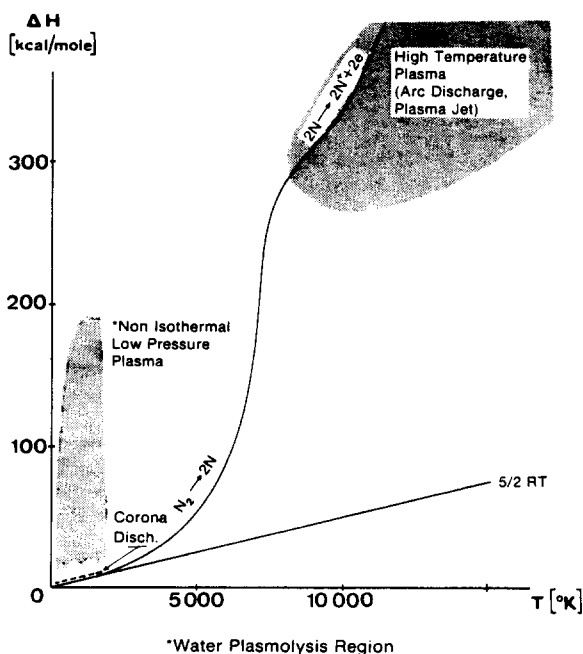
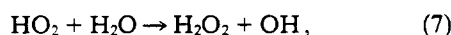
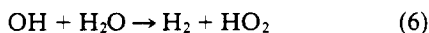
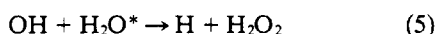
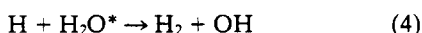
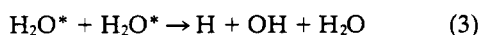


Fig. 4.

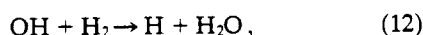
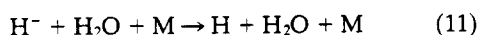
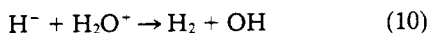
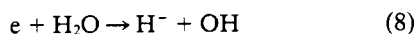
be potential for H₂ production by injection of H₂O into the developing large plasma torches but this area has been hitherto insufficiently researched. The chemistry of nonisothermal plasma has been more difficult to handle because of the lack of thermodynamic equilibrium but significant progress is being made [23–26]. In fact, a degree of control has been obtained over the volume chemistry in these latter plasmas since the energy distribution in the molecular and atomic species is predictable and can be manipulated by variable plasma conditions. However, reaction pathways must be experimentally determined and for the plasmolysis of water these are yet to be established. Research in hydrogen production from water by nonisothermal plasmas has been mainly done in the Soviet Union [27–30].

The main energetic species in the nonisothermal plasmas which can open water splitting pathways are the free electrons which gain energy from the electric fields at higher rates than do the ions. In addition, the electrons are thermally isolated from the atoms and molecules by their mass difference. They can thus accumulate sufficient kinetic energy to sustain gas ionization through inelastic collisions while the heavier gas particles remain at a low temperature. Since electron–molecule reactions are responsible for dissociation and ionization in the plasma, the electron–molecule reaction rate constants depend on the average electron energy, $\bar{\epsilon}$, and the electron energy distribution function. Their state can be described by a Maxwellian velocity distribution function which can be specified by an electron temperature, T_e . The degree of ionization, the number of free electrons divided by the gas density, n_e/N , is a descriptive parameter of particular concern in the plasma chemistry of water [30].

In water vapor decomposition in a nonequilibrium plasma, the main portion of the energy in the discharge is expended in vibrational excitation and dissociative attachment. According to Bochin *et al.* [27] the decomposition via vibrationally excited states goes according to the reaction sequence

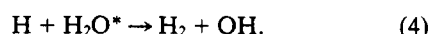
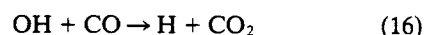
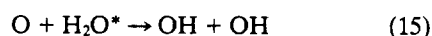
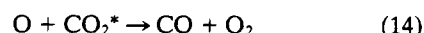
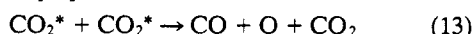


where the latter two reactions have poorer kinetics due to higher activation barriers. The dissociative attachment route is



where the latter reaction (12) decreases the yield of H₂.

Irrespective of the actual reaction sequence, the problem with this approach appears to be the requirement for a high ionization degree which is difficult to attain. However, CO₂ has been found to be a catalyst in the direct production of hydrogen from water by plasmas since it mitigates the need for high degrees of ionization and reduces the OH free radical concentration which is a main problem in the second reaction sequence given above. The following reaction sequence proposed by Bochin *et al.* [27] is



The efficiency has been projected [30] at possibly up to 50% for the H₂O plasmolysis without the CO₂ catalysts and at about 80% with the CO₂ catalyst. The latter is the more attractive of the two because of the lower degree of ionization required. A schematic diagram of the plasmolysis of water is shown in Fig. 5. Givotov *et al.* [30] have attempted to produce hydrogen by plasmolysis of water in one stage and in two stages with CO₂ reduction. Though they have not succeeded very well with the one-stage plasmolysis of water, from a preliminary study of the two stage process they have projected a figure of 4 kWh per cubic meter of hydrogen production. Experimental verification of this value is needed at the present stage.

Belousou *et al.* [29] have shown that plasma technology can be applied directly to CO₂, an abundantly available compound, to produce CO and O₂ which upon separation could be doubly useful because of the fact that it not only reacts with water to form hydrogen and CO₂ but also could form methanol and eventually other substances under different conditions. Thus, satisfactory and economic plasmolysis of CO₂ could be a way towards the foundation of an organic chemistry not based upon natural products.

The plasmolysis method seems at first an attractive one. However, it brings with it the following difficulty. It utilizes electric power, and were it to be done upon a large scale with the concept of obtaining hydrogen from water as a substance for the merchant hydrogen market, it would have to compete with electrolysis. Both use electricity, and therefore the competition would be a direct one. However, electrolysis can be at least 85% efficient and there are laboratory indications that it can be driven even towards 100% in its efficiency (electrolysis at 1.47 V would be electrolysis at 100% energy efficiency) so that the hypothetical 1.5 V assumed to be possible in a ten-year future would be a 98% efficiency of electrolysis and the already attained 1.6 V would correspond to a 92% efficiency. This difficulty may be decreased by the current rapid growth in plasma plants where water splitting might be directly

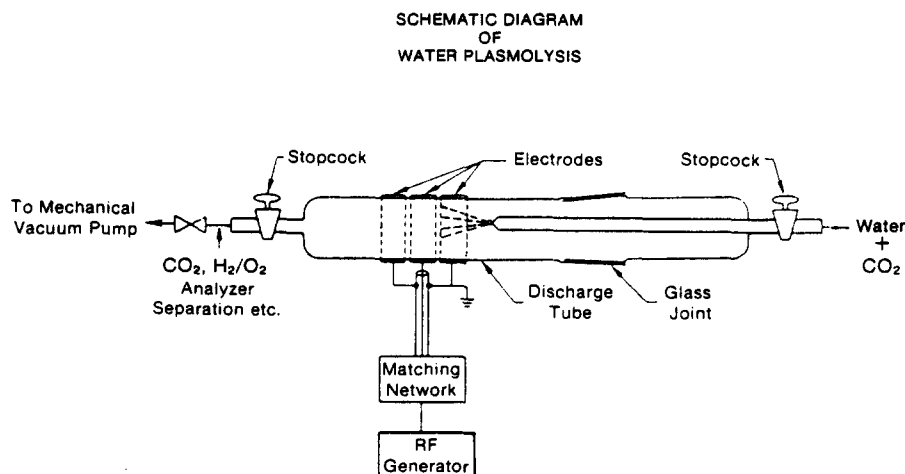


Fig. 5.

incorporated into the overall process or operate as an adjunct to the existing capital equipment.

An additional disadvantage is the need to separate the H₂ and O₂ from the product gas stream and each other. However, mass separation in a rotating plasma in crossed electric and magnetic fields may be a future development since it is currently under active investigation [31]; however, the prospects currently are undetermined for a clear discussion.

The conclusion to the consideration of plasmolysis is that it has potential if the large plasma reactors and technology continue to proliferate. However, the chances of an individual stand-alone plant for hydrogen production dedicated to H₂ from water appears tenuous at this time.

3. MAGNETOLYSIS

In normal electrolysis, the potential of the cell stack is around 2 V or less if the electrolysis plant is working in parallel and 2 V multiplied by the number of cells in the stack if it is working in series. The conventional way of producing the low potential required for this purpose by generation of electricity in thermal hydroelectric power-stations at high voltages (500–1000 kV) and then transmitting as a.c. over power lines. This is then stepped down by transformers and rectified to obtain the requisite small d.c. potentials. It has been shown [32] that the various transformations (mentioned above), each of which is 95% efficient, leads to a loss in energy of about 15%. In addition to this, the equipment needed for these operations (to step down and rectify the high-voltage a.c. to low-voltage d.c.) is expensive and hence adds to the cost of hydrogen production.

To eliminate these steps of conversion and rectification which increase the cost of hydrogen production by electrolysis, Bockris and Gutmann [31] suggested in 1981 that the electrolysis should be carried out by gen-

erating the necessary potential difference by magnetic induction inside the electrolyzer. This is an application of the classical concept of a homopolar generator conceived by Faraday [33].

The idea of a homopolar generator which produces high currents at low voltages has been abandoned for quite some time [34] as a method of transducing mechanical energy to electricity on the grounds that for transmission and many other uses, high voltage electricity is needed. For example, the resistance losses are less if the electricity is transmitted at high voltages over a power line than when it is transmitted at low voltages and high currents.

In electrolyzers, however, the reverse condition from that normally obtained is necessary: what is needed is low voltages and very high currents, and for this, the homopolar generator seems ideal.

The energy necessary to drive a homopolar generator could be calculated from a knowledge of the electromagnetic torque value [35] of the disc used, since the power (P) required is to overcome this electromagnetic torque (T_{el}). P , power, in watts, is given by

$$P = T_{el} \omega, \quad (17)$$

where ω is the angular velocity of the disc used (in rad s⁻¹). T_{el} is calculated [35] from

$$T_{el} = \int_{r_i}^{r_0} \int_0^{2\pi} \int_0^D \frac{IB}{2\pi D} (dD) (rd\alpha) dr \quad (18)$$

or

$$T_{el} = \frac{IB}{2} (r_0^2 - r_i^2), \quad (19)$$

where r is the radius and D is the width of disc, I is the total current flowing through the disc at a magnetic field of B . T_{el} is in Nm, I in amperes, B in Tesla, and r_0 and r_i are the outer and inner radii of the disc in meters.

There are several ways of using a homopolar gen-

erator for hydrogen production. One way is by using a disc rotating in a magnetic field.

The disc is made to rotate in contact with an electrolyte, and electrolysis occurs when sufficient potential difference is generated between two regions of the disc. In this method the generator and the electrolyzer are in one unit (Fig. 6).

Ghoroghchian and Bockris [36] have developed a homopolar disc electrolyzer based on the above concept. They use a stainless steel disc (30 cm dia.) in a magnetic field of 0.86 T. To produce the necessary potential for electrolysis the disc was rotated at a speed of 2000 rpm. At such speeds, in addition to the magnetic torque, there is also a viscous force which has to be overcome. The calculation of the viscous force is difficult due to certain assumptions to be made concerning the characteristics of the motion [36].

The possible routes to overcome the viscous force difficulty are either to increase the magnetic field or to rotate the disc and solution together in a cassette (i.e. to reduce the relative motion of the disc to the solution to zero).

To increase the magnetic field for an effective electrolysis, superconducting magnets could be used.

Theoretical calculations of the magnetic field necessary for various power consumption rate per cubic meter of hydrogen produced, Fig. 7, show that for the effective production of hydrogen a magnetic field of more than 11 T is needed (for the same geometry of the disc). Further, high values of IR drop in the cell due to the large separation between the cathodic and anodic regions of the disc have to be overcome. This could be achieved by increasing the field and reducing the size of the disc.

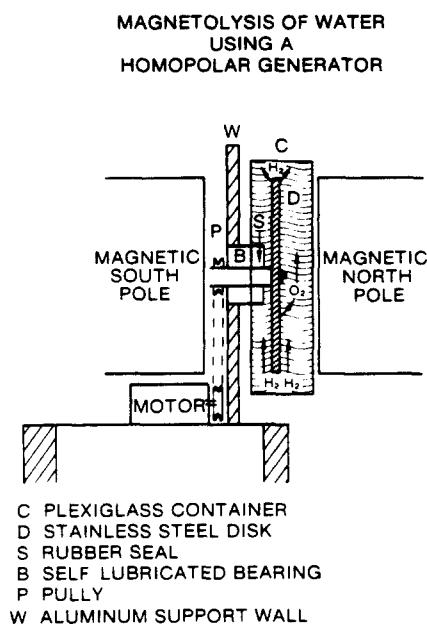


Fig. 6.

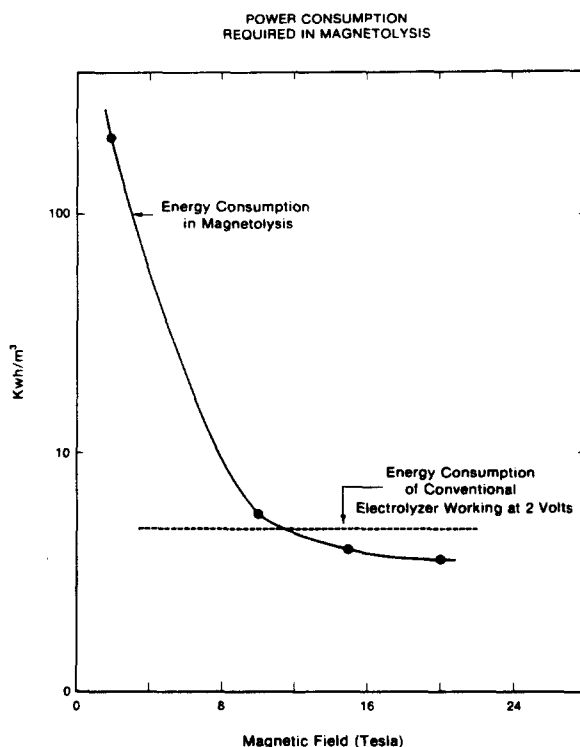


Fig. 7.

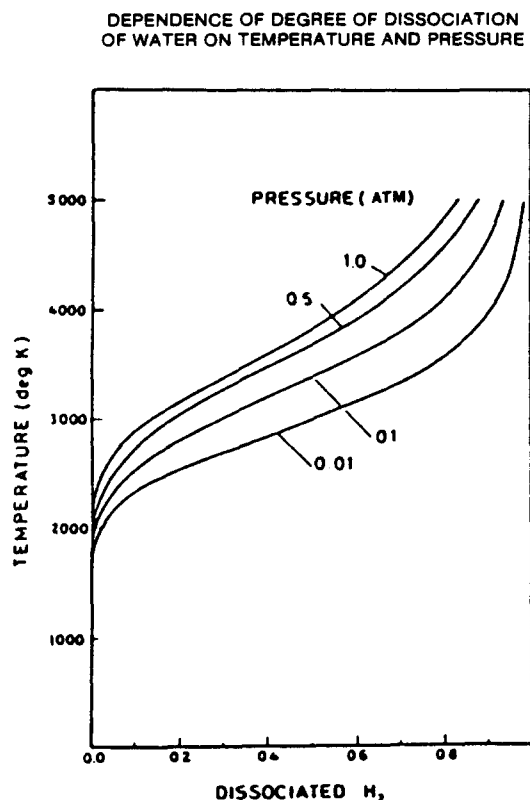
One way of beating the high field required is to use a homopolar generator as a source to drive an external electrolysis cell. Thus, the viscous drag of the solution is then eliminated. In this modification the potential generated could either be used in a continuous or pulse mode. To use it in a pulse mode a rotating propellor has been designed [36]. In this there are magnets (2.5 cm dia) at both ends of the propellor to give a magnetic flux density of 0.6 T. The propellor (mounted on the shaft) passes through a plexiglass loop and has a radius of 30 cm. The loop is laminated with copper strips (2.5 × 0.6 cm). The copper strips diametrically opposite to each other (when under a magnetic field) are connected in series to increase the output potential at a relatively low rotation speed of the propellor. Depending on the speed of the rotation of the magnets, pulses of 2–3 V with a duration of about 1 ms is achieved. Studies on the effect of pulsing on hydrogen evolution on nickel electrode has given [34] an effectiveness factor (i.e. $i_{\text{pulse}}/i_{\text{st. state}}$) value of 2. In similar studies by Tseung and Vassie [37], an effectiveness factor of 2 and 9 is obtained for teflon-bonded and platinized platinum electrodes, respectively.

The cost of producing hydrogen by magnetolysis depends largely upon the cost of electromagnets. At present, the available costs are for specific items made for laboratory use. If large electromagnets can be made at low cost, magnetolysis (particularly with pulsed

potentials which appear to double the current at low voltage) could be made some 15–20% cheaper than electrolysis. It would be particularly suitable in conjunction with hydropower or wind power. Whether superconducting magnets (10–20 T) could improve the situation seems doubtful because of their greatly increased cost. However, efforts are being made to get the cost of superconducting magnets down by using various alloys. Appleton [34] has suggested that Ti–Nb alloys in the form of filaments encapsulated in epoxy resin will give reasonably cheap superconducting magnets. Recently Gregory [38] has reported that niobium–tin alloys have the advantage of higher magnetic fields and elevated temperatures.

4. THERMAL APPROACH

The thermal approach to the dissociation of water has within it an attractive concept, in respect of the fact that, thermodynamically, by concentrating sufficient heat onto water, it is possible to dissociate it to hydrogen. Such a relationship between the temperature needed, in degrees K, and the degree of dissociation [39] is shown in Fig. 8.



Roughly speaking, to achieve a 10% dissociation of hydrogen at one atmosphere, a temperature of 3000 K is necessary and a 50% dissociation would take about 3500 K. However, at 0.01 atm, the dissociation of hydrogen can be obtained more readily, i.e. a 10% dissociation can be obtained at about 2000–2500 K.

4.1. Direct decomposition of water

If we say that 'at 2500 K the direct dissociation of water is possible' then we are looking for materials which are stable above about 2200°C and there are several of these, including tantalum boride, tantalum carbide, tungsten, and graphite. However, graphite would be chemically unstable at these temperatures in H_2 and O_2 and tungsten, tungsten carbide, etc. gets oxidized at these high temperatures. Only oxides are stable at these temperatures and the effect of hydrogen on the oxides at high temperatures is not clearly known. Perhaps ceramic materials like boron nitride (m.p. 2700°C) could be useful for these applications if oxidation could be controlled. The concepts which are involved in the direct dissociation of hydrogen have recently been discussed by Lede *et al.* [40, 41]. The initial dissociation to the 1% level can certainly be attained. The separation of hydrogen and oxygen is carried out with a semipermeable membrane of $ZrO_2-CeO_2-Y_2O_3$ which removes O_2 preferentially. A second method attempted by Lede *et al.* is the use of ZrO_2 nozzles through which steam is forced into the thermal stream and the decomposed and undecomposed water is quenched suddenly to remove O_2 and H_2O . The resulting gas contained only 1.2% molar fraction of hydrogen.

For a laboratory experiment, such methods might work. Assuming that hydrogen is produced at about 100 plants per state, in the United States, the production of plants would have to be in the region of 10 000 tons of hydrogen per day, and it is difficult indeed to see that exotic refractories and very high temperatures could be utilized in such a scale.

It is probably best to drop the direct conversion of water to hydrogen from heat as a possible method for the production of hydrogen.

4.2. Catalytic decomposition of water

Another approach to the thermolysis of water is to pass water through a 'getter' which will remove the oxygen. It must be noted that having obtained the hydrogen it is necessary to regenerate the 'getter'. (Thermal cycle operations at a temperature as low as 500° will have a low Carnot efficiency.) Such is the work of Kasal and Bishop [42, 43] who have used zeolites. Kasal and Bishop [43] have described a simple two-step thermochemical cycle to decompose water by cycling water over chromium or indium substituted aluminosilicates. For a two-step thermolysis process consisting of an endothermic step T_L where $T_H > T_L$, the thermo-

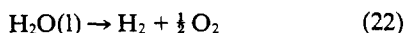
dynamics requires that

$$Q \left(\frac{T_H - T_L}{T_H} \right) > \Delta G_{\text{H}_2\text{O}}, \quad (20)$$

where Q is the heat absorbed at the T_H and $\Delta G_{\text{H}_2\text{O}}$ is the standard free-energy of formation of water. The minimum entropy change incurred during the first step is given by

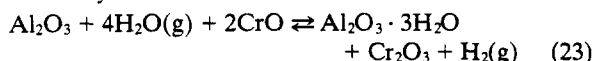
$$\Delta S = \frac{Q}{T_H} \approx 120 \text{ eu}, \quad (21)$$

where $T_H = 800 \text{ K}$ and $T_L = 300 \text{ K}$. Such a large entropy change is rarely found in a single chemical reaction. The standard entropy change associated with the reaction

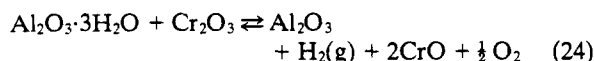


is 40 eu. A large entropy change can be realized by resorting to a cycle consisting of many reaction steps or to a single reaction involving many molecules. All the processes reported to date for the thermochemical decomposition of water consists of several chemical reactions, except for the zeolite process. The zeolite process resorts to a reaction involving many water molecules of hydration.

England [44] has proposed, based on Kasal and Bishop's results, a quantitative relationship approximated by the reactions.



at low temperatures with an entropy change of -128.5 eu and



at high temperatures with an entropy change of 139.1 eu . These indicate that the entropy changes for water splitting are consistent with the requirements mentioned earlier and it might be possible to run a purely thermal two-step cycle at temperatures as low as 500°C using strong chemisorbers such as zeolites. However, other researchers [45] have been unable to realize the same experimental results as those of Kasal and Bishop.

It is possible that such a method could be applied elsewhere and this gives rise to a research topic. Would it be possible, for example, to utilize a nonstoichiometric oxide as a catalyst? Preheated steam would be introduced onto the catalyst, maintained at a low temperature, say 1000 K , and the product then emitting from the catalyst could be rich in hydrogen above the equilibrium amount expected in the gas phase. A schematic representation of this method is shown in Fig. 9.

4.3. Cyclic decomposition of water

The cyclical decomposition has been mostly used till the present and more research has been done upon this method than upon any other. The temperature at which there can be interesting amounts of hydrogen obtained can be diminished to the region where atomic heat is available, $800\text{--}900^\circ\text{C}$, by carrying out the decomposition of water by a number of cycles. It is possible to show this is not possible in two cycles but possible in three and four cycles [46]. Cycles are well known and given in tables in books and it is only necessary here to point out some difficulties which make this method at present seem unlikely to succeed.

(1) The original concept [47] was that, because the method avoided the formation of electricity by the conversion of heat to mechanical work, it would avoid the Carnot cycle, and as this is a fundamental difficulty in increasing the price of electrolysis methods, the cyclical method was thought to be likely to give hydrogen at a cost of about half that of the electrolytic method.

This basic thought is fallacious because the method has to have reactions carried out at different temperatures in order that the entropic properties of the partial reactions in each cycle should be used to maximum advantage. Where the individual reactions have a positive entropy change, it is desirable to carry the reaction out at the highest temperature practical to minimize the overall ΔG^0 ; and conversely, were the entropy changes negative, the reaction should be carried out at the lowest temperature. However, this requirement of changing the temperature of the reactants in the various cycles gives rise to a requirement to change the pressure, too, and so it would have been necessary to pump gases

SCHEMATIC REPRESENTATION OF POSSIBLE CATALYTIC DECOMPOSITION OF WATER AT LOWER TEMPERATURES THAN THERMODYNAMIC GAS EQUILIBRIUM

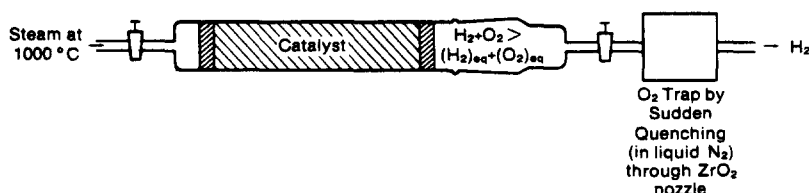


Fig. 9.

from one temperature and one pressure to another, and this is similar to the Carnot cycle as given in thermodynamics texts.

(2) With 3–4 cycles, and the need for separate apparatus for each, plant costs would be likely to be more, per unit of hydrogen produced, than those for electrolysis. Further, as some of the reactions would be carried out in the region of 800–900°C and all of them above, say 250°C, the corrosion of vessel walls would be considerable with a corresponding short life and expense of the plant.

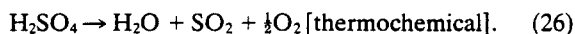
(3) It has been assumed by proponents of this method [47, 48] that the reactions would take place down a free-energy pathway but they take place down a reaction rate pathway, [49] and it is not reasonable to assume that the reactions follow the thermodynamic pathway. Since other reactions develop, the final product may not be what was intended.

(4) Because of (3), cyclicity fails, and if it fails even by 1%, considerable amounts of unwanted material build up and the economics of the process has been worked out on the basis that the process is cyclical.

Two cyclical methods are under detailed investigation at present. The first one is a hybrid cycle consisting of an electrochemical and a thermochemical step. Electrical energy is used in this method for one of the reaction processes as a means to overcome the positive free-energy barrier inevitably occurring in a pure thermochemical cycle. The second one is a purely thermochemical cycle.

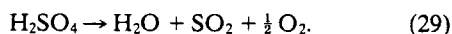
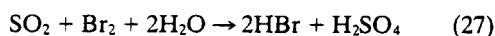
4.3.1. Hybrid cycle. The two main processes under this class are the Mark 11 cycle, also known as the Westinghouse sulfur cycle and Mark 13 cycle developed at Ispra establishment in Italy.

In the Westinghouse sulfur cycle [50] SO₂ is dissolved in aqueous solution and electrochemically oxidized to H₂SO₄ at the anode [51]. The idea of using SO₂ as an anodic depolarizer was originally suggested by Moulton and Juda [52]. The steps involved in the Mark 11 process which is the same as Westinghouse sulfur cycle are



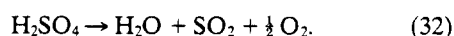
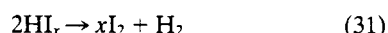
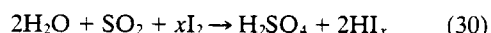
The H₂SO₄ produced is catalytically decomposed at a high temperature to give SO₂ which is cycled back into the electrochemical step. The main problem in this case is the compatibility of materials for withstanding H₂SO₄ at high temperatures.

Mark 13 process developed by Ispra [53] consists of the following steps.

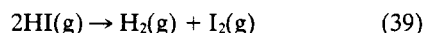
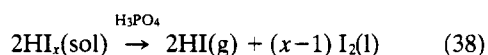
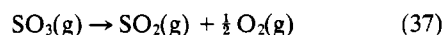
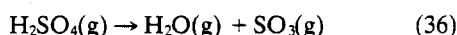
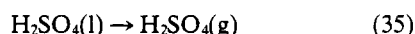
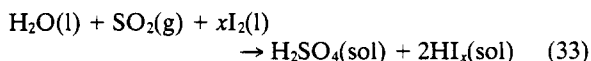


A bench-scale operation of this process has run for several years producing 100 l h⁻¹ of hydrogen [54] but a cost evaluation of the process is not available.

4.3.2. Thermochemical process. This method known as GA sulfur–iodine cycle was reported first by Russel [55]. It consists of the reactions:



The HI_x in (30) is a mixture of several polyiodides formed in reaction (31). A realistic description of the cycle is given by the following reactions [56]



The improvement made in this method is the counter-current operation with the SO₂–O₂ product and utilization of liquid iodine provide better efficiency and ease of operation. Further improvements reported [57] on this process involves the use of HBr for the recovery of HI instead of H₃PO₄. This requires that HBr be added to HI–H₂O–I₂ solution until the second phase is incipient and then countercurrently extracting the HI with liquid HBr. However, the HBr system is far from optimized and needs considerable work. In a process concept, based on 47% process efficiency, Besenbruch *et al.* [58] have predicted a large capacity production of 4.64 × 10⁵ m³ day⁻¹ (roughly 410 tons day⁻¹) of hydrogen by the GA sulfur–iodine process at a cost of \$17.96–21.58 MBTU⁻¹ based on 1980 dollars [59]. It is noteworthy that this is higher than most estimates of the cost of hydrogen from electrolysis.

4.3.3. High temperature electrolysis. The use of high temperatures (1000K and upwards) to electrolyze steam has been attempted [60, 61]. In this process, as the temperature increases, part of the energy for the electrolysis of water comes from the electrical energy. This energy, of course, is Carnot-limited in the sense that it has been produced by a Carnot process. For this reason, electrical energy—as it is well known—is more expensive than other forms of energy. As the temperature increases with water electrolysis, however, the amount of energy which comes directly from heat in contributing to maintaining the temperature of the reaction (which is endothermic below 1.47 V) means that increasing amounts of energy can be contributed

to the water splitting which are not dependent upon Carnot limitation.

Because of the endothermism of the hydrogen dissociation reaction, heat energy from outside is needed to maintain the temperature constant. At 1000 K the amount of this energy is 39% and at 2000 K, the percentage of the energy arising from the thermal contribution is 63%.

Thus neglecting other difficulties, the high-temperature electrolysis method should definitely give a cheaper hydrogen than electrolysis at room temperature because the total amount of electricity used is considerably less than 100% and cheap heat energy is being used for the rest.

It would, however, be naive to leave the situation at this stage without modification. It is clear that considerable difficulties in dealing with high temperatures will be associated with the high-temperature decomposition of water. Yttria-stabilized zirconia is practically the only material at the present time which is known to have the necessary high ionic conductivity (O^{2-} conductivity) so that water can impinge upon one side of the electrode, a side in which there are cathodic collectors, and hydrogen is evolved—while O^{2-} transports itself through the solid electrolyte (zirconia stabilized by yttria) until it reaches the other side where oxygen is evolved on the anodic collectors.

Another difficulty of the usual arrangement is the use of contacts as electrodes which do not themselves allow the diffusion of water or oxygen through them. This difficulty is overcome by Bevan, Pound and Bockris [62] who introduced the use of uranium oxide, U_3O_8 . This substance has unique properties. On the other hand it is highly electronic conducting at 1500 K and above. It does not dissociate in the presence of hydrogen and oxygen up to 1800 K. Lastly, it has both good ionic and electronic conductivity. It allows the permeation of water through its pores and the permeation of oxygen and hydrogen out of them.

U_3O_8 appears to be the ideal substance for use in water electrolyzers and its introduction on a massive scale should facilitate the situation with them.

On the other hand, insufficient work has been done to judge the cost of the refractories and although the cost of the use of electricity to produce hydrogen utilizing water electrolyzers is perhaps two-thirds of one half of that utilized for water electrolysis at room temperature, the net cost of electricity (because of the high cost of refractories) must be regarded as not definitely smaller than that for the water electrolyzers at room temperature.

Thermally assisted electrochemical production of hydrogen was examined by Bockris [63]. He calculated the value of the heat used which would make the thermally assisted electrochemical production of hydrogen to be advantageous. In 1984 dollars the calculation comes to about \$33 per MBTU, or about 5–6 times more than the price of heat at this time.

Thus, thermally assisted electrochemical methods do not have great encouragement for their development.

4.4. Magmalysis

A research project could be mounted toward what may be called magmalysis [64]. The basic idea is to find a part of the magma which is near the surface (presumably in tubes leading to a volcano) and inject steam into this. According to Northrup *et al.* [64] the following reaction would occur:



Fresh basaltic lava contains on the order of 10 w% ferrous oxide (FeO) and 1–2 w% ferric oxide ($\text{FeO}_{1.5}$). These components exist as dissolved constituents within the melt and in minerals suspended in the magma. Hydrogen concentrations resulting from the equilibration of water with a solid assemblage of hematite-magnetite for a total pressure of 100 MPa (1000 bars) calculated by Northrup *et al.* is given in Fig. 10. The H_2O curve refers to the percentage of hydrogen generated by the thermal dissociation of water. Experiments conducted by them with water vapor reaction on crushed basalt gave results close to the calculated values.

In a water rich system the basalt becomes progressively oxidized and a continual addition of water ultimately converts most of the FeO to $\text{FeO}_{1.5}$. Northrup *et al.* feel that before the oxidation is complete, the hydrogen concentration will drop to levels which would probably make recovery impractical [65]. Hydrogen production estimates made by Northrup *et al.* [64] at 1200°C are shown in Table 2. Lower temperatures resulting from the cooling effects of injected water may permit a greater amount of FeO to be oxidized and hence greater hydrogen production [66].

From Table 2 it appears (from a laboratory experiment for 7 h) that about 2.2×10^6 tons of hydrogen are potentially recoverable from water interacting with 1 km³ of basalt at high temperatures at 1000 MPa.

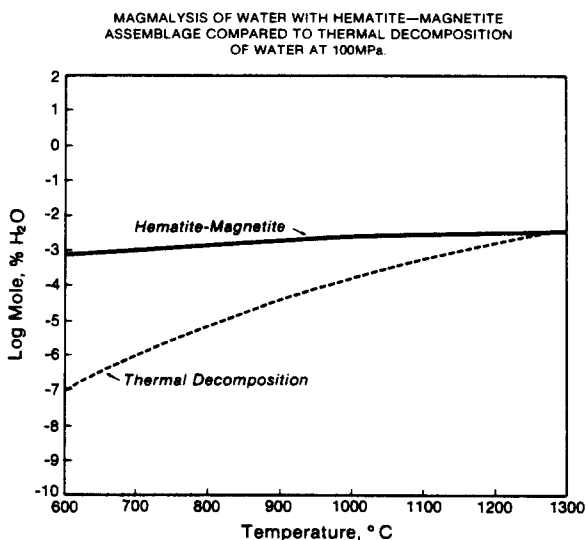


Fig. 10.

Table 2. Hydrogen production from water-basalt interaction at 1200°C and 100 MPa

Log ₁₀ f _{O₂}	$\frac{X_{\text{FeO}}}{X_{\text{FeO}_{1.5}}}$	Mole %H ₂	Mole H ₂ * km ³ Basalt
-9.0	7.40	3.000	0
-8.0	4.80	1.200	1.3×10^{11}
-7.0	3.20	0.450	3.0×10^{11}
-6.0	2.00	0.170	5.5×10^{11}
-5.0	1.30	0.070	8.0×10^{11}
-4.0	0.90	0.025	1.0×10^{12}
-3.0	0.58	0.010	1.3×10^{12}

* Cumulative yield for progressive oxidation of basalt.

Knowledge of the rates of magma emplacement into the crust, and cooling rates should permit estimation of the amount of magma available in an area and whether it should be considered to be a fixed or renewable resource. It is roughly estimated [64] that there exists 10⁵ km³ of magma bodies in areas of the U.S. where production of hydrogen by this method would be potentially viable.

5. USE OF LIGHT

Were it possible to use light to split water and to obtain hydrogen, the ideal method would have been reached because of the large amount of light available.*

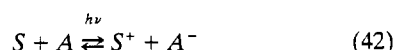
However, simple photolysis is not practical because the energy contained in the solar spectrum varies from a weak infrared portion to about 3 eV towards the u.v. side of the spectrum while to break the HO bond requires about 6 eV. It follows that any method which would attempt to use photolysis directly must give rise to a final product of H₂ and O₂, rather than the atomic constituents which come from direct dissociation. In this case, the energy needed for bond breaking is in fact compensated by the combination energy of the atoms and the overall heat of dissociation of water is then about 2.46 eV per molecule of hydrogen.

5.1. Photosensitized decomposition using dyes

Having stated the above, it is necessary to record that attempts have been made to undertake direct photolysis, outside the directly electrochemical situation.

Gray [68-71] has investigated polynuclear inorganic complexes in solution for irradiation and the production of hydrogen. Similar work using excited metal complexes have been published by Whitten [72, 73] and reviewed recently by Maverick and Gray [74]. Whitten [72] has reported that strong luminescence of a surfactant ruthenium complex could be quenched by immer-

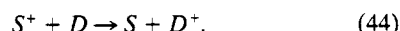
sion of assemblies containing the complex in water. The light-induced cleavage of water then yields hydrogen and oxygen. A recent review by Kiwi *et al.* [75] illustrates the homogeneous and heterogeneous photoproduction of hydrogen and oxygen. The majority of the photoredox systems (heterogeneous photolysis) involve a photosensitizer, an electron acceptor and an electron donor with the redox catalyst assisting in the gas evolution step. Excitation of the sensitizer (S) leads to an electron transfer



which is followed by the catalytic step



The back conversion of S⁺ to S may be achieved by sacrificing a donor D added to the solution



A schematic representation of the experimental set-up used [76, 77] is shown in Fig. 11. Koriakin *et al.* [78] have used acridine dyes as sensitizers, Eu³⁺, V²⁺ salicylates as electron acceptors and 'Adams' catalyst (PtO₂) as the redox catalyst. A wide variety of chromophores, redox reagents and redox catalysts have been investigated since then and the materials tried are given in Table 3. The photoredox system Ru(bipy)₃²⁺/MV⁺

BLOCK DIAGRAM OF DIRECT PHOTOLYSIS

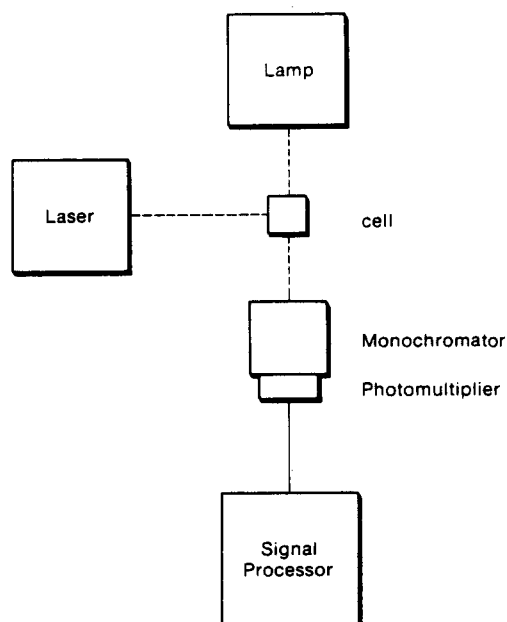


Fig. 11.

* Thus, were about 0.5% of the earth's surface to be covered with collectors, the present energy needs for the whole world could be obtained [67].

Table 3. Dye-sensitized redox reactions leading to H₂ evolution

Electron donor (sacrificial)	Sensitizer	Acceptor	Redox catalyst
EDTA	Bipy, phen. Complexes of Ru, Cr,* ...	Viologens (MV ²⁺)	Enzymes H ₂ -ase, N ₂ -ase
Cysteine, H ₂ S TEA and other	e.g. Ru(bipy) ₃ ²⁺ Acridine Dyes† Proflavine, Acridine Yellow	V ³⁺ , Cr ³⁺ , Eu ³⁺	Metal oxides PtO ₂ , IrO ₂ , Al ₂ O ₃ /Pt
Ascorbate, Eu ²⁺	Porphyrins‡ Phthalocyanines ZnPc§	Rh(bipy) ₃ ²⁺	Colloidal Pt, Au, Ag particles

*1. J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim.* **1**, 449 (1977).

2. M. Kirch, J. M. Lehn and J. P. Sauvage, *Helv. Chim. Acta* **62**, 1345 (1979).

3. G. M. Brown *et al.*, *J. Am. Chem. Soc.* **101**, 7638 (1979).

4. P. J. De Laive, D. G. Whitten and C. Giannotti, *Adv. Chem. Sci.* **173**, 236 (1979).

5. D. G. Whitten *et al.*, *Solar Energy Conversions and Storage*, (ed. R. R. Hatala). Humana Press (1979).

6. J. Kiwi and M. Gratzel, *J. Am. Chem. Soc.* **101**, 7214 (1979).

†1. B. V. Koryakin, T. S. Dzhabiev and A. E. Shilov, *Dokl. Akad. Nauk. SSSR* **298**, 620 (1977).

2. A. I. Krasma, *Photochem. Photobiol.* **29**, 267 (1979).

‡1. K. Kalyanasundaram and M. Gratzel, *Helv. Chim. Acta* **63**, 478 (1980).

2. M. W. W. Adams, K. K. Rao and D. O. Hall, *Photobiochem. Photobiophys.* **1**, 33 (1979).

§1. J. R. Darwent, *J. C. S. Chem. Comm.* **835**, (1980).

2. A. Harrison and A. M. C. Richoux, *J. C. S. Faraday II*, **76**, 1618 (1980).

(with EDTA or triethanolamine as the electron donor and Pt catalysts) has been investigated at length by Gratzel *et al.* [75] as a system leading to photolytic production of hydrogen. They have found that the hydrogen yields are maximum around pH 4.5 when EDTA is used as a donor with PtO₂ or colloidal Pt as a catalyst and falls off at either side of the pH value. The efficiency in generating hydrogen quantitatively and also kinetically depends on the nature of the protective agent used for the Pt particle and also on the aggregation of the catalyst (Pt particles coated with polyvinylalcohol) in the preparation. Though much work has been done on the kinetics of the photolytic process of hydrogen production, little has been done on the quantitative aspects of photolytic hydrogen production. An efficiency of up to 30% at a selected wave length for hydrogen production for a brief duration by photolytic process has been reported by Kalyanasundaram *et al.* [79].

5.2. Plasma-induced photolysis

It has been suggested [80] that plasmas could be used, not in the direct fashion discussed earlier, but to produce photons of appropriate energy so that water could be dissociated in the gas phase. Thus, in the hypothetical fusion of hydrogen, it would be possible to produce a light in the region of 1800–950 Å by the addition of aluminium to the plasma [81].

The main gain from the method proposed is that the

thermal energy adsorbed would be converted to electricity in a heat engine at about 30% efficiency. Thus, the hydrogen will be produced both by photolysis and by electrolysis, and this could give rise to a gain in efficiency.

The original suggestion of Eastlund and Gough [80] cannot be attempted until, and if, ignition of the hydrogen–tritium plasma is ever achieved. However, an investigation of the production of high-energy photons by injection of aluminium into other plasmas might be considered.

The difficulty may be here that the likelihood that one could attain 90% efficiency in the use of electricity, which is confidently expected from electrolysis, would be unlikely to be obtained (thus, among other difficulties, that of recombination would be paramount).

5.3. Photoelectrolysis

The basic concept [82] of photoelectrolytic hydrogen can be understood when it is realized that such a process involves what is in effect a light-driven electrolysis cell. Thus, the reactions which occur at the p-type cathode involve the evolution of hydrogen and at the n-type anode the evolution of oxygen. No external battery or power source is involved in this operation between the electrodes.

Hypothetically—neglecting at present considerations of efficiency—the current which flows could be used for the production of electric power and the hydrogen that

is produced during the process would be the fuel which would eventually replace carbon-based fuels.

The work which has been done up to now [83–94] shows an overall efficiency of the use of light in the production of hydrogen and electricity as being only about 1%.

The difficulties of the present situation in this field are threefold.

(1) The most important is the absence of a theoretical analysis. The only theoretical analysis carried out of the maximum feasible efficiencies in photoelectrolysis so far is that due to Scaife [95] and this cannot be relied upon because it involves the use of assumptions no longer realistic (e.g. the idea that photoelectrodes involved Schottky barriers, for many of them involve strong surface-state concentrations which diminished the internal field and greatly lower the barrier). However, a more important lack in the theoretical analysis is the absence of work which shows how the two electrodes should be combined in a manner which is helpful to the overall efficiency. This, in the earlier work of Ohashi *et al.* [83] the efficiency of one electrode depended upon the counter electrode, and these relationships—which involve taking into account the contact p.d. between the two materials at the semiconductor–semiconductor interface—have not yet been worked out.

(2) In analyses such as those of Memming [96] there is a reliance upon a principle which is now known to be untrue. Thus, for many years, electrochemists relied

upon the Fermi level in solution as an important aspect of the conditions under which cells would work. However, it is now known [97–100] that the Fermi level in solution is not given by the reversible potential of the redox couple on the absolute scale, as had originally been thought (Fig. 12).

Thus, most of the formulations which are given in photoelectrochemistry, upon which most American and German workers have relied, are not solid and need to be rethought.

(3) Another difficulty in photoelectrolysis is corrosion. This is the area in which photoelectrolysis has less to offer than photovoltaic contacts in air (and electrolysis as fed by the potential thereby produced) because corrosion of semiconductor surfaces in contact with solution is liable to be considerable, for it is caused not only by normal thermal corrosion, as determined by electrochemical equations, but may be promoted by extra photoelectrochemical reactions.

Natural photosynthesis has an efficiency of about 1%, and probably takes place by an electrochemical mechanism [101]. Photoelectrolysis has not exceeded natural photosynthesis, and the probability that significant (5–10%) efficient photoelectrochemical production of hydrogen from water can be achieved still lies in doubt.

One of the important achievements which has been obtained in recent times is that of photoelectrocatalysis. This has been carried out initially in terms of photoelectrochemical cells to produce hydrogen and oxygen by Yoneyama *et al.* [102] in 1975. They used TiO_2/pGaP

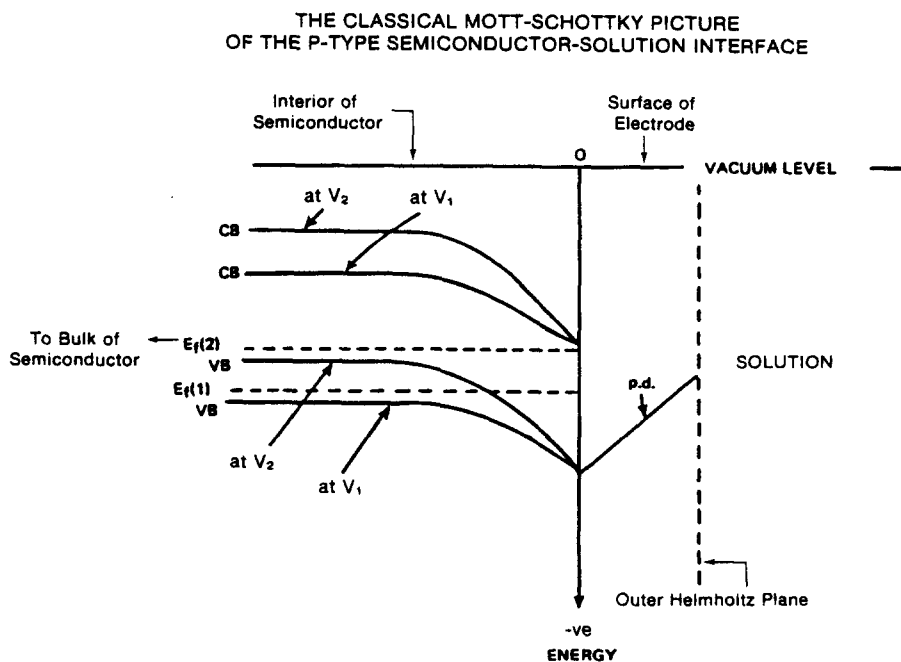


Fig. 12.

electrodes and reported that pGaP electrodes deteriorate with polarization time. Ohashi *et al.* [83] showed that the performance of a cadmium telluride electrode, coupled with strontium titanate, could be improved by the addition of small amounts of platinum to the surface and the SrTiO₃-GaP cells of these workers were the first stable photoelectrochemical cells.

Since this time, other workers have been able to show the effect of addition of metal atoms to the surface. This has been indicated at an early date by Tsubomora [103-105] and later by Gerischer [106] and Heller [107-109].

One of the more outstanding works in this direction has been that of Heller *et al.* [109] but this work was made more difficult to understand by the use of an unusual system for measuring the efficiency of performance.*

The work of Szklarczyk and Bockris [111] has established a remarkable relationship between photoelectrocatalysis and the nature of the metal on the surface. According to them (cf. Fig. 13) the change of potential of the position of the exponential section of the current-potential curve, caused by the addition of small metal objects to the surface, depends linearly upon the law of the exchange current density of the metal concerned in the dark. The work of Szklarczyk and Bockris [87, 111] means that photoelectrocatalysis is directly related to electrocatalysis. The rate-determining step in photoelectrocatalysis, in the region before the limiting current, is dependent upon the transfer of charge at the metal-solution interface and not at the semiconductor-solution interface.†

Other aspects of anodes are little known. Bockris and Uosaki [113] show that coatings such as TiO₂ on CdS could be successful in allowing semiconductors with suitable energy gaps but with too poor resistance to anodic dissolution to be effective. Gerischer [114, 115] has shown this same method is applicable, using tin oxide.

* One of the difficulties of the subject is that various measures of efficiency are used. These in general do not agree. Heller used an electrical energy savings efficiency which had nothing to do with the energy efficiency of the overall use of light. Such matters have been discussed by Bockris *et al.* [110].

† Other views have been expressed by different authors. Wrighton [89] stressed the dominance of the semiconductor-solution interface and thought that the metal had some effect on the internal structure of the semiconductor. Heller [109] pursued this theory in detail, and thought that the important aspect of the metal was to change the field inside the space charge region within the semiconductor [110].

The work of Szklarczyk *et al.* [112] extends now to five different semiconductors with seven different metals and conclusively demonstrates the dominance of the characteristics of the metal-solution interface in photoelectrocatalysis (Fig. 14), and the amount whereby the metal causes the rate of evolution of hydrogen to increase in photoelectrolysis is a function of the exchange current density for hydrogen evolution on the metal without photo effects. Some rationalization of this relation has been given [87].

THE SHIFT OF THE MIDPOINT OF A PHOTOELECTROCHEMICAL CURRENT-POTENTIAL RELATION AS A FUNCTION OF (DARK) EXCHANGE CURRENT DENSITY

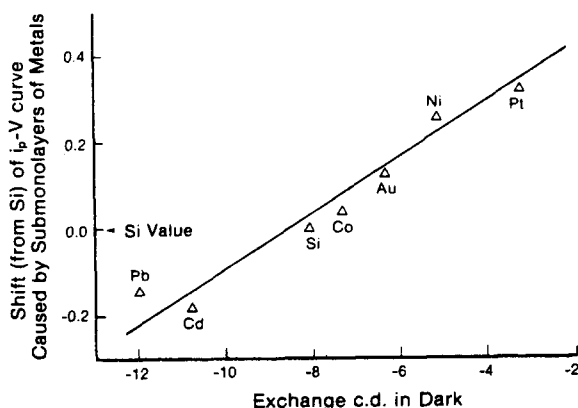


Fig. 13.

5.4. Photo-aided electrolysis

It is possible to get huge (100×) increases in current measured when light falls upon an electrode by applying to the electrode concerned a potential from an outside power source. Many workers have regarded the effi-

EFFECT OF VARIOUS SUBMONOLAYER TRACES OF METALS ON PHOTOELECTROCHEMICAL HYDROGEN EVOLUTION ON p-InP

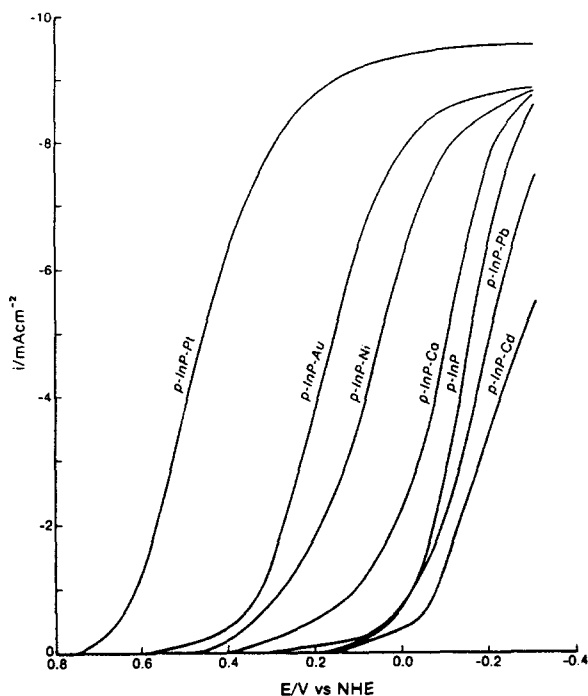


Fig. 14.

ciency of such devices in too simple a way. Thus the efficiency has been given by the expression:

$$\varepsilon = i_p V_{\text{rev}}/I, \quad (45)$$

where I is the intensity of illumination in watts per unit area, i_p is the photocurrent density under a bias potential, and V_{rev} is the reversible potential of the hydrogen-oxygen cell.

This expression gives high values (30–40%) for the overall conversion efficiency of light to hydrogen, but it is incorrect. It is, of course, necessary to take into account the electrical energy used so that in the expression the overall efficiency becomes

$$\varepsilon = \frac{i_p V_{\text{rev}}}{I + i_p V_{\text{bias}}}, \quad (46)$$

where V_{bias} is the shift in the potential of the cell caused by the external battery. If this comes, say, to 30–40%, it is not impressive when one realizes it is not the overall efficiency of conversion of light but light and electricity to hydrogen. After all, the conversion efficiency of electricity to hydrogen and oxygen may be as high as 90%. It is, therefore, necessary to remove from the top line of this expression the electrical energy used in causing the cell to function, in order to derive the efficiency of conversion of light to hydrogen and electricity. When the expression:

$$\varepsilon = \frac{i_p V_{\text{rev}} - i_p V_{\text{bias}}}{I} \quad (47)$$

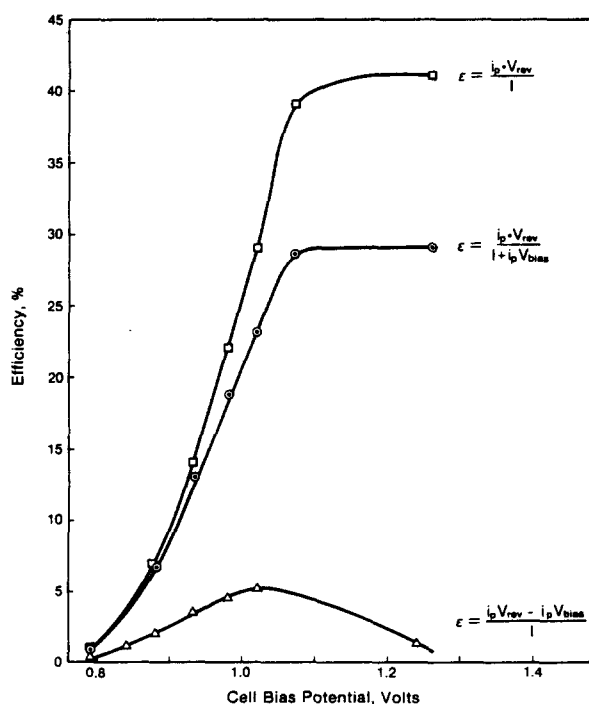


Fig. 15.

is used, smaller values are obtained for the conversion of light in photo-aided cells.

These relations can be seen in the accompanying diagram, Fig. 15.

Utilizing equation (47) it is possible to obtain efficiencies for the conversion of light to hydrogen which are higher than those obtained by present experiments on photoelectrolysis. It may be as high as, for example, as 3–4% [116]. However, it is not helpful to go in this direction because the principal point of obtaining hydrogen from photoelectrolysis cells is to avoid an electrical component which, in later years, could be very expensive. The main hope in the photoelectrolysis direction is in the development of the appropriate theoretical relationships which show the use of photo-electrocatalysts, and the development of new anodes to match the cathodes.

5.5. The indirect path towards hydrogen by photoelectrolysis; the photoelectrochemical reduction of CO_2

Water may be one source of massive hydrogen, but another possibility which must not be neglected is to start with CO_2 because this is available in large amounts and inexpensively (eventually, by means of extraction from the atmosphere). At first it does not seem reasonable that CO_2 could be a better source of hydrogen than water, but it might be via a path in which CO_2 is reduced to CO and then this is utilized to produce hydrogen by chemical reactions which are spontaneous.

Taniguchi *et al.* [120] have shown that CO_2 can be reduced on cadmium telluride electrodes at interesting efficiencies if aqueous solutions are used (these separate the reduction potentials of CO_2 and H in a way which is favourable to CO_2 reduction).

Remarkable effects have been observed [121] with ammonium mediator catalysis of the CO_2 reduction (Fig. 16).

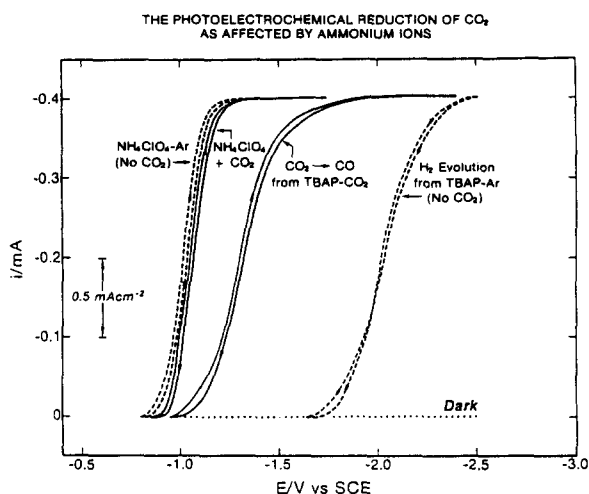


Fig. 16.

Although this CO_2 -related path may give hope, it is worthy of further investigation, it would involve a second stage (the reaction of CO with steam), and the likelihood that an overall more economic process could be obtained (in comparison say with the use of photovoltaics to produce electricity and then electrolyze water) seems improbable.

5.6. Photovoltaic electrolysis

A modification of the concept of a photovoltaic cell working in air, and electrolyzing a distant electrolyzer has been made by Murphy and Bockris [122] who have used two photovoltaic cells to create internal potential differences which directly feed electrochemical reactions taking place on electrocatalysts which are themselves applied to the photovoltaics. Such a device is shown in Fig. 17.

Photovoltaic electrolysis has advantages compared with photoelectrolysis. These include the fact that the semiconductor electrode is not in contact with the solution so that corrosion problems cease. Its contact is with air and the solution contacts with an electrocatalyst which are noncorrodable. Thus, long lifetime for these devices is expected.

With 8¢ kWh^{-1} for solar electricity one would have hydrogen at a cost of around $\$30 \text{ GJ}^{-1}$. Although this value is still 2–3 times too high it must be seen in relation to two aspects:

(1) We are not speaking here about immediate commercial applicability but about applicability which would be relevant in the 1990's, i.e. some 10–20 yr from now. In 1984 dollars a considerable rise in the corresponding price of fossil fuels would seem to be expected.

The price of electricity from solar plants should be independent of such factors. Thus, the competitive costs of solar-hydrogen may be reasonable in the time frame of the 1990's. Another factor is important, and that is the concept of 'Second Law Economics' and that of 'additional costs'. The latter topic has been developed by Bockris [123]. Thus the pollutive costs of utilizing hydrogen are zero while those of utilizing fossil fuels from coal, or from atomic plants, involve ancilliary costs which should clearly be prorated and added to the apparent first cost of the product. Such an accounting appears more rational than the accounting only for the costs of manufacture.

At the time of writing (1984) the best figures recorded in the literature for the decomposition of water by light is that given by a Murphy-Bockris cell using n-on-p gallium arsenide coated with ruthenium oxide, and p-on-n gallium arsenide coated with platinum. Such a cell gives about 8% direct conversion of light to hydrogen at current densities in the region of 10 mA cm^{-2} . Although tests for more than one week's use have not been made, there is no evidence that the cell's life would be less than that of the photovoltaics in air.

In respect of the economics of such devices, there might be two advantages compared with those of the normal photovoltaic cell in air combined with a distant electrolyzer.

- (1) The cell is in solution so that concentration of light upon the electrode, giving rise to high temperatures, can be met by using the heat to give household heat.
- (2) Only one device is needed and not two plants as in the normal concept (this would translate itself into improved economics in the building of a large plant).

AN ELECTROCHEMICAL PHOTOVOLTAIC CELL CAPABLE OF SPLITTING WATER INTO HYDROGEN AND OXYGEN GASES

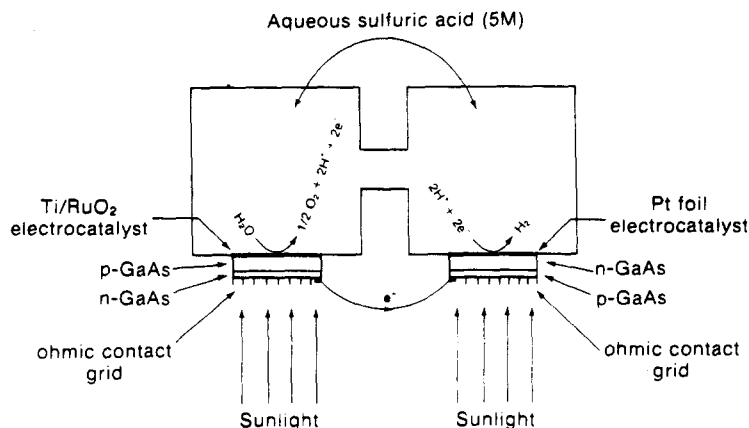


Fig. 17.

5.7. Particulate semiconductor systems

A novel way to tackle the problem of the splitting of water by light is to utilize microsystems, and this work has been promulgated particularly by Gratzel [124]. The colloidal particles are made up of suitable semiconductor materials, e.g. TiO_2 . On these colloids are induced two metallic substances, e.g. ruthenium oxide and platinum.

When the system is irradiated, hydrogen is evolved on the platinum and oxygen on the ruthenium oxide. A schematic representation of the process is shown in Fig. 18. Each colloidal particle is a micro photo-cell. The positive aspect is the large amount of area per gram of titanium oxide made available to light. The device is analogous to the use of porous electrodes in fuel cells. Some doubt has been expressed as to whether there is a true equal production of hydrogen and oxygen in these systems and whether oxygen is not perhaps taken up on some side reaction with an impurity, the consumption of which would decrease the rate of the anodic reaction. Further, it seems necessary to heat the systems in order to make them perform for longer than a few hours.

On the negative side is the absence of knowledge of the efficiency of such devices. Efficiency is more difficult to measure in the microsystems because of the difficulty of estimating the amount of light which falls directly upon solid materials (the area of these which are in the path of the light is difficult to estimate). However, there are two other difficulties.

- (1) The hydrogen and oxygen in this device come off together and their separation would present extra costs.
- (2) The fact that the hydrogen and oxygen are present together in the solution gives rise to chemical catalysis and recombination to water.

At present it is nugatory as to whether the advantage of the increased area obtained by utilizing microsystems can overcome the disadvantages of the recombination and separation.

Some other work in this area [125] carries out the

evolution of oxygen and the reduction of water to hydrogen by utilizing some auxiliary materials which are themselves consumed, and although such work may be of interest, using a fuel apart from light in photoelectrolysis is less likely to lead an economic device.

6. BIO-CATALYTIC DECOMPOSITION OF WATER

One of the attractive possibilities in the decomposition of water is to use materials (algae, bacteria) which themselves contain enzymes which decompose water under the influence of light. The potential advantage of such systems is that they could be self-reproducing, building themselves up on the basis of the presence of CO_2 and other natural materials. The most expensive part of photoconversion methods (e.g. photovoltaic cells together with an electrolyzer plant) is the materials themselves, and their supports over large areas of desert country. However, in the algal approach, the locale of water and the materials would have near-zero cost. The principal cost would appear in the collection of the hydrogen which would have to be separated from oxygen by means of membranes. A scheme of electron transport in biophotolysis is shown in Fig. 19.

The most outstanding work in this field has been that of Benemann [126]. Benemann has been able to show that by the use of *Anabaena cylindrica*, an algae, together with irradiation, hydrogen could be produced from water over the time of at least one day. Maximum hydrogen production has been observed with ascorbate 2,6-dichlorophenolindophenol (DPIP) and 1 nmol of ferridoxin. The crude ferridoxin preparation used by Benemann has saturated the ascorbate-DPIP dependent hydrogen evolution at remarkably low levels and high ferridoxin concentrations have been found to be inhibitory.

Analogous works have been carried out by Neil *et al.* [127] in 1976 and Hall *et al.* [128] in 1978. Neil *et al.* have found that hydrogen evolution begins after an incubation period of several hours. Thereafter, hydrogen evolution continues for about 24 hr. After the incubation period the rate of hydrogen evolution has been found to rise rapidly to a maximum rate in 12–20 hr and then falls to a low level. In some of the experiments they have found that the hydrogen evolution again increases to the maximum level and then falls off to a minimum in about 96 h. Hall *et al.* have worked extensively on the various factors affecting the hydrogen evolution in biophotolysis with a view to increase the efficiency of the process. They have found that scavengers of oxygen increase the rates and duration of hydrogen production. More work in this area is needed to make this process more viable since only micromolar quantities of hydrogen production per day is reported so far.

The mechanism by which these reactions occur has not been studied. However, work carried out by Bockris and Tunelli [101] on the mechanism of photosynthesis, with the production of hydrogen and oxygen, suggests

PRINCIPLE OF MICRO HETEROGENEOUS DECOMPOSITION OF WATER USING COLLOIDAL SYSTEMS

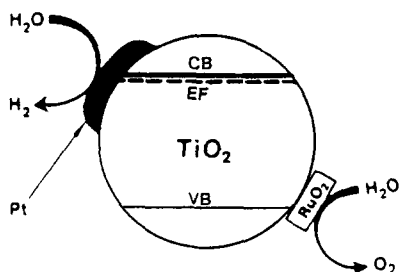


Fig. 18.

SCHEME OF ELECTRON TRANSPORT IN THE BIOPHOTOLYSIS OF WATER

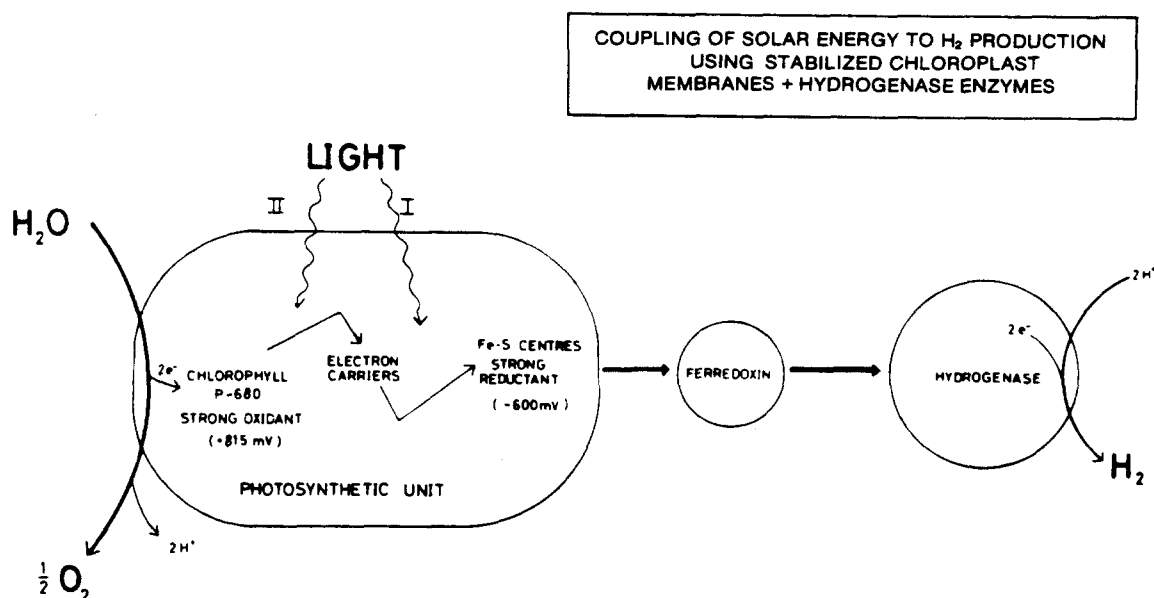


Fig. 19.

that the mechanism is similar to that of a photoelectrochemical cell. Thus, Bockris and Tunelli isolated photosystem I and photosystem II.

Each of these photosystems were placed upon platinum, and irradiated, hydrogen was obtained with photosystem II and oxygen with photosystem I, the currents being photoelectrochemical. Something similar to this probably occurs in the production of hydrogen utilizing algae which contains the enzyme hydrogenase. In this case the photosynthesis reaction goes to the formation of hydrogen from water instead of producing $NADPH_2$, which in a normal photosynthesis in turn reacts with CO_2 to form CH_2O .

Thus, in principle, any system which lives by means of photosynthesis, and contains hydrogenase, is a candidate for possible work on the production of hydrogen from water by biocatalytic means. At present in the work being carried out [129] the principal problem is the stability of the material. Thus, the current is produced for a short time, but after about 24 h, production lapses. This is due to the fact that exposure to light was too long and a cyclical exposure, 12 h to light and 12 h to CO_2 atmosphere, might make a more satisfactory system.

Another difficulty at present is the instability of hydrogenase in contact with air.

This subject has been little investigated from the mechanistic point of view and certainly justifies a research project. The ideal nature of the conversion, if efficiencies of 10% can be obtained, is attractive.

Another kind of photosynthetic research involves the

use of bacteria which consume materials and produce hydrogen. These are certainly not in the same class as those which consume only CO_2 and light. Utilizing these materials efficiencies of 5% have been claimed [129].

Some claims have been made [130] that 10% efficiency of photosynthesis (not however for the production of hydrogen) can be obtained from the work on plants under laboratory conditions. This gives hope that a greater efficiency can be obtained in photosynthetic results and the potential cost advantage of biocatalysis remains. Conversely, airborne CO_2 is not present in sufficient concentrations for a large rate of production of biocatalytic hydrogen, even if the efficiency were to be raised above 10%. The subject is, however, open to research.

7. RADIOLYSIS

Radiolysis involves the projection into water of radioactive substances (e.g. UO_2 (NO_3)₂), etc. which emit particles, e.g. alpha and gamma, which have an energy in the region of 10^6 eV . They would decompose some 10^5 water molecules per particle, and, were there no recombination, correspondingly large amounts of hydrogen and oxygen would be formed. What happens when the radioactive particles pass near molecules is that they strip them of parts of the electron shells so that protons are produced and the oxygen from the water becomes cationic. The mechanism of recombination is as yet unclear.

Between 1–5% production of the energy of the radio-

active materials in the form of hydrogen and oxygen is predicted [131]. An increase in efficiency could occur by rearrangements in a reactor, for example, the neutrons from the reactor leak into a blanket region and react with, e.g. Li^6 compounds. These produce particles which would ionize water. The potential value of the method depends upon the type of salts which could be used.

This method, similar to the micromethod used in photoelectrolysis or to biocatalysis, produces hydrogen and oxygen as a mixture which is a disadvantage. It is possible that it could be passed into a fuel cell, the hydrogen first being taken out at the anode and the oxygen being passed on to the cathode. There would be no explosion under appropriate conditions in solution.

The work of Kerr and Majumdar is suggestive of advance in this field [131]. They have shown that an increase in the efficiency of conversion can be obtained by adding B^{10} and Li^6 to the solution. The effects of B^{10} on the H_2 production rate (for 150 kW l^{-1} core power density) in the blanket region is shown in Fig. 20.

This field presents research prospects. If it is possible to increase the efficiency to more than 10% an impressive method would result so long as the radioactive materials used are wastes. At present these substances do not have known use but were they utilized to produce hydrogen a more positive future for some of them could be seen.

Recently, Gomberg and Gordus [132] have focused attention on the decomposition of water by radiation and heat at the same time to improve the efficiency of

producing hydrogen. According to them, nuclear fission can be used either in a solid fuel configuration where the radiation energy/heat ratio can be about $\frac{1}{4}$ or in a fluid fuel configuration where all the energy is available as radiation. They have attempted to produce hydrogen based on these concepts and claim [133] a better efficiency of hydrogen production than that of Kerr and Majumdar.

8. OTHER APPROACHES

There is in principle a possibility that water could be dissociated into hydrogen and oxygen by shock waves, mechanical pulses, etc. Extensive research has been done on the dissociation of diatomic molecules and organic compounds by shock waves [134]. This might be attempted in the case of water. This concept has not been subjected to theoretical or practical analysis. Further, it would be possible to introduce anharmonic oscillations into the molecules in such a way that the anharmonicity would introduce OH bond dissociation. A novel method for approaching this problem might be the excitation of adsorbed water species. One possibility would be the adsorption of water on the surfaces of fiber optics which could be made conducting and at the same time allow part of the light wave being transmitted to interact (through the system) with the adsorbed water.

CONCLUSIONS AND SUMMARY

(1) The methods used for the large-scale production of hydrogen should avoid carbon compounds because hydrogen from water will only be a viable technology when hydrocarbons are decreasingly available at reasonable costs; and (more importantly) their use injects an increasing amount of CO_2 into the atmosphere and could give rise to a decline in climatic conditions. Since only water is an admissible substance as a source of hydrogen, large-scale hydrogen production research is water-splitting research.

(2) The use of electricity should be avoided if it comes from a source of energy (e.g. coal) via the Carnot cycle because of a fundamental loss of about two thirds of the energy as heat. Methods, such as plasmolysis, which rely for the eventual energy source upon the production of electricity by means of a heat engine are not likely to be competitive with electrolysis. The latter is said to be inefficient but its inefficiency only relates to the production of electricity by means of Carnot processes and electrolysis itself can be reasonably assumed to have a 90% efficiency, with respect to the electricity used. No competing method uses electricity more efficiently.

(3) When mechanical power (as, e.g. in hydroelectric power or wind power) is available from sources other than heat, the best way to go would seem to be homopolar generators connected to electrolyzers, although this conclusion is subject to very considerable reduction in the cost of magnets.

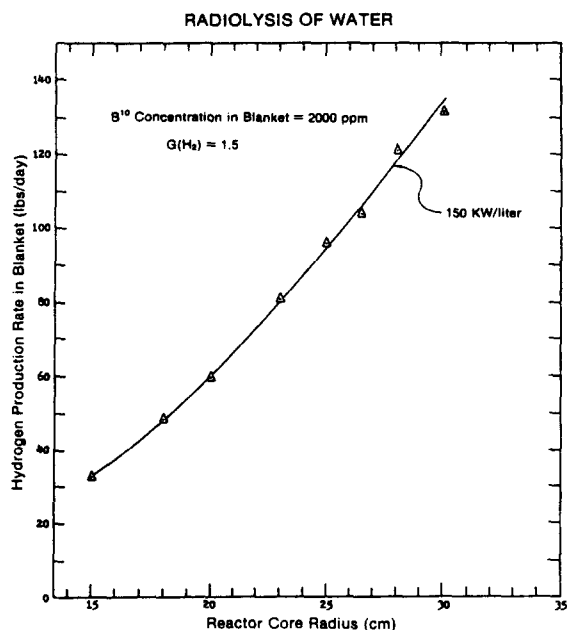


Fig. 20.

(4) Heat: the 1970's was a time in which the prospect of decomposing water by heat was intensely examined because of the hope given by Marchetti [47] that various chemical cycles could be used to attain hydrogen without the interference of a Carnot efficiency expression. This method may now be discarded because of misunderstandings connected with it. However, the equilibrium situation for water, hydrogen and oxygen is unfavorable, temperatures of at least 2500 K would be necessary (cf. material difficulties). On the other hand the possibility of changing the gas-phase equilibrium momentarily exists, the hydrogen produced now being frozen out of the mixture, should be researched.

(5) Use of light to split water seems to be potentially a favorable approach. The benchmark is the use of photovoltaic converters (e.g. amorphous silicon) coupled to water electrolyzers. This method will be difficult to beat. The only viable alternative seems to be photoelectrolysis. The progress of research in this topic has been held up by a misunderstanding as to the method by which one calculates the electron level in the solution. One of the difficulties is in the theory of matching the electrodes; and the last one is in the synthesis of new anode materials.

In respect to microsystems (colloidal suspensions) they offer some advantages which may be compensated by recombination losses.

(6) The bacteriological production of hydrogen has the potentiality of low cost owing to the absence of the costly impediments of solar energy collection.

(7) Radiolysis: increase of the efficiency of radiolysis to produce hydrogen can be obtained by the use of boron and other materials in the solution. Were this method to be coupled to the use of radioactive wastes, there might arise an important method for the large-scale production of hydrogen. This seems to be a potential research field.

At the present time the summary is that if mechanical power is available without the use of heat engines then homopolar devices and efficient (electrocatalyzed) electrolysis seems to be the best method to produce H_2 from water. When mechanical power is not available (and this will be the general situation) photovoltaics connected with electrolyzers is a solid possibility and photoelectrolysis is one which gives some hope but needs research. The situation with the biocatalytic and radiolytic approach are not sufficiently researched to offer conclusions but seem to have advantageous possibilities.

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