HYDROGEN PRODUCTION

CÉSAR A. C. SEQUEIRA*, DIOGO M. F. SANTOS

Chemical and Biological Engineering Department, Instituto Superior Técnico, 1049-001 Lisboa, Portugal
*cesarsequeira@ist.utl.pt

ABSTRACT: Possible means of producing hydrogen are discussed. Emphasis is given on the electrolytic hydrogen production from water electrolysis, at large scale, via the use of renewable electricity (solar, wind, tidal, etc.). Its storage, transport and possible end-uses are also considered.

Keywords: Hydrogen production; Electrolyser; Electrolytic hydrogen; Renewable electricity; Fuel cells.

RESUMO: Discutem-se processos de obtenção de hidrogénio. Em particular, considera-se a produção electrolítica de hidrogénio em meio aquoso, à escala industrial, e à custa de energia eléctrica renovável (solar, vento, marés, etc.). Fazem-se ainda algumas previsões acerca do armazenamento, transporte e possíveis aplicações do hidrogénio electrolítico.

Palavras chave: Produção de hidrogénio; Electrolisador; Hidrogénio electrolítico; Energia eléctrica de fontes renováveis; Pilhas de combustível.

1. INTRODUCTION

Hydrogen, the most common element on earth, is widely seen as the ultimate form of clean energy [1,2]. The proposition that hydrogen should be a sustainable energy medium has become known as the "Hydrogen Economy". This term is thought to have been coined in 1970 by Neil Triner at the General Motors Technical Laboratory in Warren, USA. But the concept of using hydrogen had in fact been suggested much earlier in such diverse publications as Jules Verne's science-fiction novel *The Mysterious Island* (1874) and J.B.S. Haldane's essay *Daedalus, or, Science and the Future* (1923) (Fig. 1). It is further notable that Haldane proposed the use of wind power to produce hydrogen via electrolysis of water; the gas would be liquefied and stored in vacuum-jacketed reservoirs that would probably be sunk in the ground. The overall scheme of the Hydrogen Economy is illustrated conceptually in Fig. 2, which outlines the many different possible routes to hydrogen from both conventional and novel primary energy sources, the storage and transportation modes for hydrogen, and its end-uses in fuel cells (Fig 3, Fig. 4), engines, and industrial processes. This is a broad canvas and many authors restricted the use of the term Hydrogen Economy (or "Hydrogen's Energy") to the production of hydrogen from non-fossil sources, its distribution and storage, and its combustion in a fuel cell to generate electricity.

Hydrogen has many potential attractions as a new fuel. It may be derived from non-fossil sources, it burns cleanly to water with no pollutants being emitted, it is suitable for use in a fuel cell to generate electricity directly, and it has a high
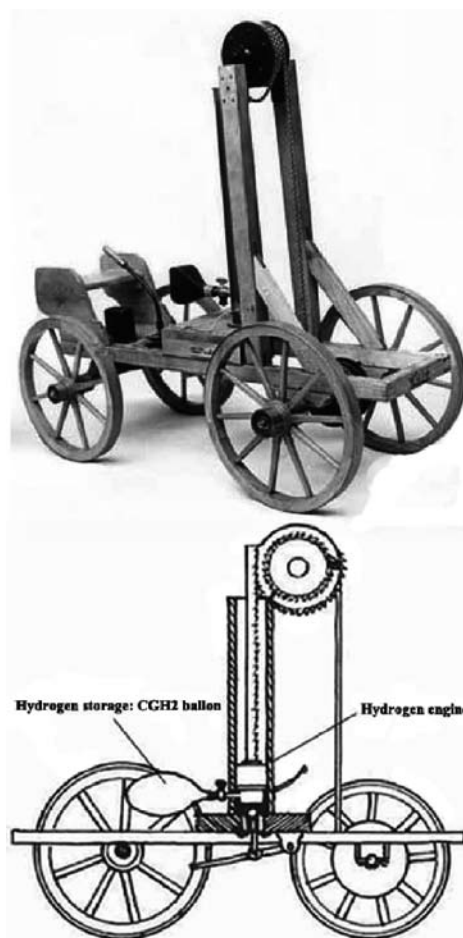

Fig. 1. First hydrogen car invented by Francois Isaac de Rivaz in 1807.

energy content expressed on a per mass basis (Table 1). Unfortunately, these attractive features are counter-balanced by many practical engineering and economic considerations that explain why hydrogen does not already find extensive use as a fuel.
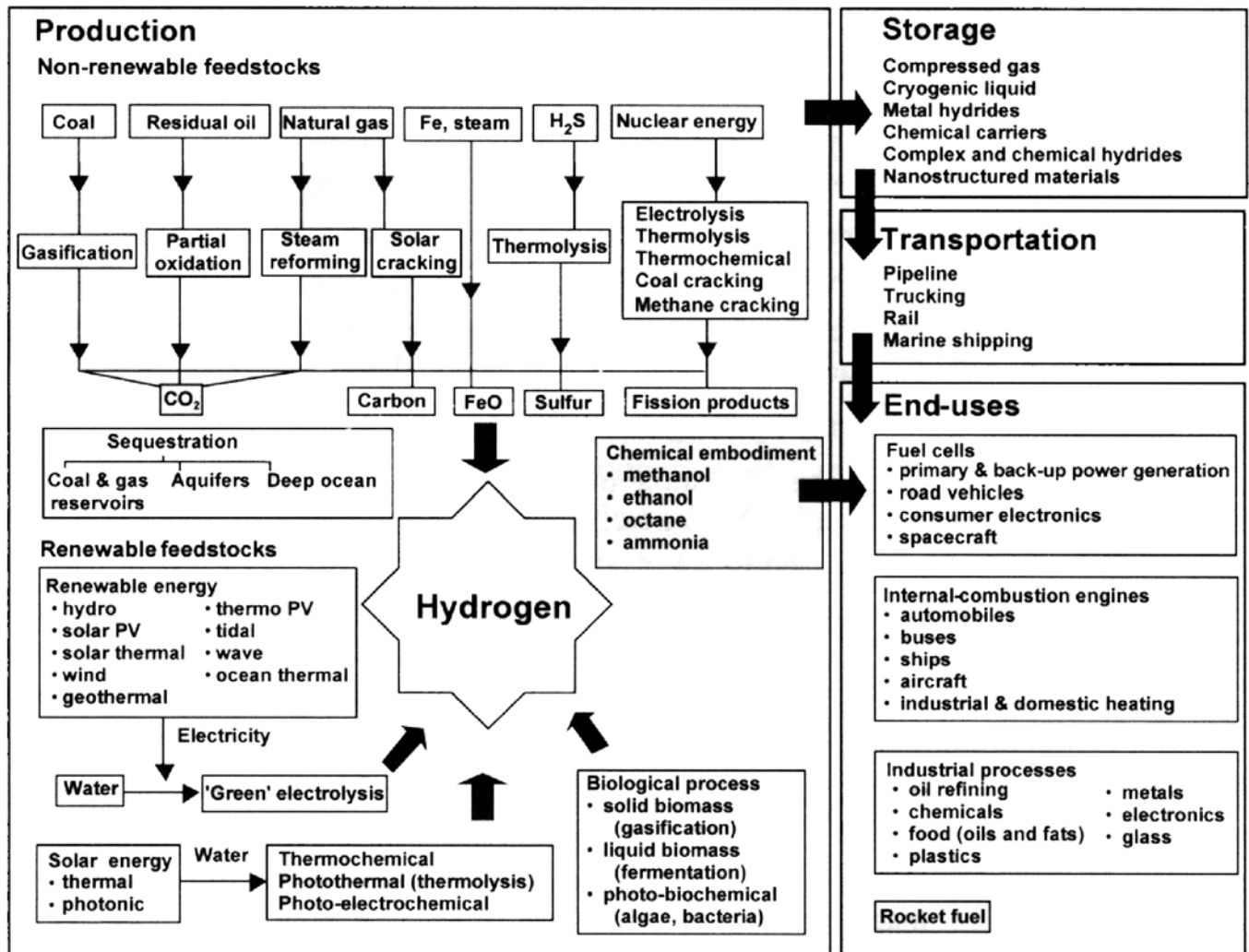

Fig. 2. The Hydrogen Economy: a summary diagram showing possible means of producing, storing and transporting hydrogen, as well as potential end-uses.

Table 1. Technical comparison of hydrogen with other fuels.

	Hydrogen	Petroleum	Methanol	Methane	Propane	Ammonia
Boiling point, K	20.3	350-400	337	111.7	230.8	240
Liquid density, kg m⁻³	71	702	797	425	507	771
Gas density, kg m⁻³, s.t.p.ᵃ	0.08	4.68	-	0.66	1.87	0.69
Heat of vaporisation, kJ kg⁻¹	444	302	1168	577	388	1377
Lower heating value ᵇ (mass), MJ kg⁻¹	120.0	44.38	20.1	50.0	46.4	18.6
Lower heating value (liquid, volume), MJ m⁻³	8960	31170	16020	21250	23520	14350
Diffusivity in air, cm² s⁻¹	0.63	0.08	0.16	0.20	0.10	0.20
Lower flammability limit vol. % (in air)	4	1	7	5	2	15
Upper flammability limit vol. % (in air)	75	6	36	15	10	28
Ignition temperature in air,ºC	585	222	385	534	466	651
Ignition energy, MJ	0.02	0.25	-	0.30	0.25	-
Flame velocity, cm s⁻¹	270	30	-	34	38	-

ᵃ s.t.p. = standard temperature (298.15 K) and pressure (101.325 kPa).

ᵇ There are two ways to define the energy content of a fuel. The "higher heating value" includes the full energy content by bringing all products of combustion to 25ºC. By contrast, the "lower heating value" neglects the energy in the water vapour formed by the combustion of hydrogen in the fuel. This water vapour typically represents about 10% of the energy content. The higher heating value represents the true (thermodynamic) heat of combustion, but the lower heating value is more relevant because a steam condenser is not used in most practical applications. In this table, the lower heating value is the heat of combustion (MJ kg⁻¹) of a fuel, based on complete combustion to carbon dioxide and steam at 100ºC.
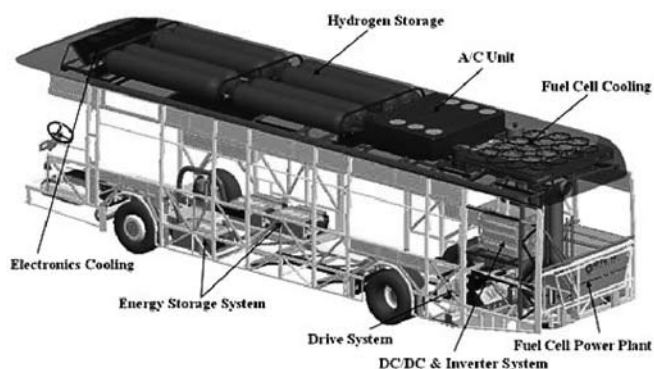
Fig. 3. Use of hydrogen in a modern fuel cell bus.

As discussed in a previous paper [3], hydrogen is produced today from fossil fuels by chemical reforming reactions, and its major uses are in the refining of crude oil and in the manufacture of ammonia. Lesser, non-energy, applications are found in the production of other chemicals, as well as in the food, plastics, metals, electronics, glass, electric power and space industries (Table 2). In contrast, the present use of hydrogen for electricity generation *via* fuel cells is still negligible. In the short term, however, there will be a significant environmental benefit in converting fossil fuels into hydrogen to serve as a clean fuel for fuel cells or internal-combustion engines. This benefit stems from the relative ease of pollution management at a central production facility compared with dispersed sites. Moreover, emissions of carbon dioxide are, in principle, more easily captured and sequestered at a single plant than when fossil fuels are deployed in the field. A prototype plant for the conversion of coal to hydrogen, with sequestration of carbon dioxide has been announced, in 2003, by the USA government. It is called FutureGen – a 10-year

research project to build the world's first coal-fired station to generate electricity with zero rate electricity and hydrogen with zero emissions.

Basically, when heated coal or coke is reacted with steam, the water-gas reaction occurs (Eq. 1).

$$C + H_2O \rightarrow CO + H_2 \qquad (1)$$

The gas produced by the water-gas reaction may be upgraded in terms of hydrogen content by the water-gas shift reaction. The gas is reacted with steam over a catalyst that converts carbon monoxide to carbon dioxide and increases the amount of hydrogen (Eq. 2).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

The carbon dioxide may then be separated in a form suitable for sequestration (*e.g.* in geological structures), while the hydrogen is used for power generation in gas and steam turbines, and/or in fuel cells. The equivalent gross electricity output for the USA project (FutureGen) was of 250 MW.

Fig. 4. The hydrogen car from Instituto Superior Técnico (IST) in the Shell Eco-Marathon competition.

Table 2. Principal non-energy uses of hydrogen

Industry	Uses
Oil	Removal of sulphur and other impurities ("hydro-desulphurisation"); conversion of large oil molecules to fuel distillates for blending with petroleum ("hydrocracking").
Chemical	Production of ammonia (for fertilisers), methanol, hydrogen peroxide, acetic acid, oxo alcohols, dyestuffs.
Food	Conversion of sugars to polyols (bulk sweeteners); conversion of edible oils (from coconuts, cotton seed, fish, peanuts, soybeans, etc.) to fats, *e.g.* margarine; conversion of tallow and grease to animal feed (and soap).
Plastics	Production of nylons, polyurethanes, polyesters, polyolefins; cracking of used plastics to produce lighter molecules that can be recycled in new polymers.
Metals	Reductive atmosphere for production of iron, magnesium, molybdenum, nickel, tungsten; heat-treatment of ferrous metals to improve ductility and machining quality, to relieve stress, to harden, to increase tensile strength, to change magnetic or electrical characteristics; oxygen scavenger in metal working; welding torches.
Electronics	"Epitaxial" growth of polysilicon; manufacture of vacuum tubes, light bulbs; heat-bonding of materials ("brazing").
Glass	High-temperature cutting torches; reductive atmosphere for float-glass process; glass polishing; heat-treatment of optical fibres.
Electric power	Coolant for large generators and motors; nuclear fuel processing.
Space	Rocket fuel.

In the present paper, a different future, possibly 20-30 years away, is looked ahead, in which hydrogen is produced by the electrolysis of water on a large scale *via* the use of renewable electricity (solar, wind, tidal, etc.). It would then be stored

in one of several different forms, distributed to where it is needed, and then reconverted to electricity in a fuel cell. The technology for this vision is still in embryonic form, mainly because the economics of such energy production and use are

not favourable. Nevertheless, for almost 30 years, much attention has been focused on the considerable challenges that would confront the practical introduction of hydrogen as an energy vector. Many conferences have been held and a specialist journal, the *International Journal of Hydrogen Energy*, is devoted to the subject.

At first, the interest in hydrogen energy arose from the shortfall in fossil fuels – especially oil – that was anticipated in the mid-1970s, and from a projected surplus of off-peak electricity from nuclear power stations. At that time, it was envisaged that nuclear power would expand much more rapidly than it has, and that surplus night-time electricity would be available because nuclear plant normally operates on base-load and is not really switched on and off. In parallel, there was a large interest in using hydrogen to store electricity from renewable energy sources. The attractions of using hydrogen as an energy storage medium came from the fact that:

- it is universally available in the form of water, from which it may be extracted conveniently by electrolysis;
- it may be transmitted over long distances in buried pipelines, which are cheaper to construct and operate than electricity grids, and have no visual impact;
- the gas in the pipeline provides a storage component within the electricity-supply system;
- hydrogen is the ideal fuel for use in fuel cells to regenerate electricity;
- hydrogen is oxidised cleanly to water, therefore the cycle is closed and no significant pollutants are formed.

While these attractions are still true, in principle, many extraneous events have conspired to delay the widespread introduction of hydrogen-based energy systems, irrespective of whether the hydrogen is to be produced from fossil fuels or from renewables. Chief among these events have been the demise of nuclear energy programs, and the discovery of far more petroleum and natural gas than was foreseen in the 1970s [4-7]. Technological advances in conventional power production have also played a role, such as modern combined-cycle gas/steam turbines that are over 50% efficient in electricity production from natural gas. A comparison of the advantages

and disadvantages of using natural gas to generate electricity is given in Table 3 [8,9].

Other factors that bear indirectly on this situation are the widespread privatisation of electricity utilities and the general imperative of short-term profitability that now pervades industry (deregulation of electricity markets) [10,11]. Quite simply, there is yet no economic case for hydrogen energy and the timescale on which it may become affordable is uncertain. Despite all these difficulties, interest in hydrogen energy is reawakening, especially in the USA where there is acute appreciation of the forward supply position for oil and natural gas. Many industrial companies, as well as the government and academia, are becoming involved.

Several automotive companies are developing vehicles powered by fuel cells [12,13] (Fig. 5). There is also considerable interest in fuel cells for the distributed generation of electricity. In fact, there is greater activity in the advancement of fuel cells than there are of electrolysers or hydrogen stores, which are the two other key components of the hydrogen-from-renewables scenario. Since fuel cells and electrolysers are essentially complementary, much of the technology for fuel cells is likely to be applicable to electrolysers.
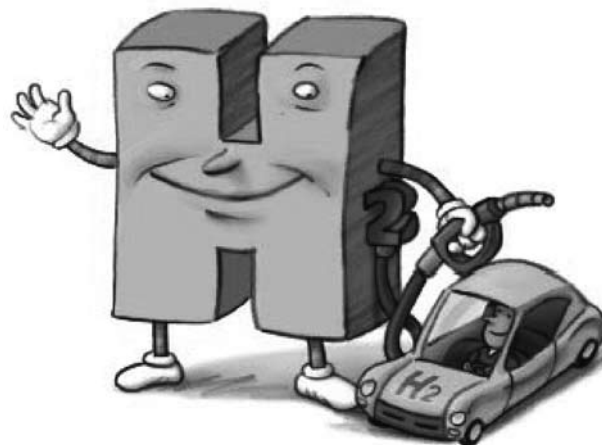

Fig. 5. Fuel cell vehicles powered by hydrogen. A growing tendency.

Table 3. Advantages and disadvantages of electricity generation by natural gas.

Advantages	Disadvantages
Natural gas is widely available	
Natural gas has the highest H:C ratio and, therefore, the least CO_2 generation per kWh	It may be argued that, where supplies are limited, natural gas is too valuable as a fuel to be used for electricity generation and should be reserved for space heating and chemical manufacture.
Methane is distributed by buried pipeline or LNG tanker with no environmental impact	For a country with indigenous coal, but no natural gas, the use of imported gas for electricity generation will place a strain on the nation's balance of payments
By using a gas turbine combined with a steam turbine, high efficiencies are achieved	Liberation of CO_2
Natural gas contains almost no polluting impurities	

From this discussion, it seems that the short-term prospects for electrolytic hydrogen on a global scale are not so great. Nevertheless, it is necessary to look ahead beyond a decade or two, when many of the premium fossil fuels are expected

to be in short supply and expensive, and when there may be even greater concern over greenhouse gases and associated global warming. At that point, electricity generation from renewable energy sources should become more generally

desirable and competitive, and the requirement for energy storage on a larger scale will emerge. Electrolytic hydrogen must then be considered as one option. In the meantime, circumstances in different countries and in different locations are sufficiently diverse that, in some regions, electricity from renewable sources is becoming the preferred technology. For this reason, it is expedient to continue the development of hydrogen energy, which should include research aimed at increasing the efficiency of hydrogen production from water electrolysis, improving methods for hydrogen storage, and perfecting electricity generation from hydrogen in fuel cells – and all at reduced cost.

2. ELECTROLYTIC HYDROGEN PRODUCTION

By providing electrical energy from an outside source, water can be decomposed ("electrolysed") into molecules of hydrogen and oxygen. Under thermodynamically reversible conditions, *i.e.* maximum efficiency, the expenditure of electrical energy results in the performance of maximum work, that is, in the maximum amount of water decomposed. Under conditions of constant temperature and constant pressure, this maximum amount of work equates to the change in the so-called "Gibbs free energy" of the system, ΔG. In thermodynamics theory, ΔG is defined as

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

where ΔH is the change in heat content, or "enthalpy", of the system and is calculated by adding up the amount of energy released or used to form or break chemical bonds during the reaction, T is the temperature, and ΔS is the change in the amount of disorder, or "entropy", that occurs in molecules involved during the reaction. Eq. 3 may be expressed in words as: "the change in free energy of a system that is acting reversibly at constant temperature and constant pressure is equal to the change in heat content of the system less than the heat absorbed by the system during the reversible change". This is the Second Law of Thermodynamics.

The change in the Gibbs free energy, ΔG, is a useful indicator of the spontaneity of electrochemical (or chemical) reactions: (i) if ΔG is positive, the process is not spontaneous, but can be driven by application of sufficient energy from the surroundings; (ii) if ΔG is negative, the process can take place spontaneously and do work on the surroundings; (iii) if ΔG is zero, the system is at equilibrium since the amounts of work being done on the process and by the process itself are equal. Clearly, category (i) applies to the electrolysis of water, and category (ii) to the reverse process, which takes place in a fuel cell.

The ΔG may be expressed in terms of the electrical voltage of a reversible galvanic cell, V_r, *i.e.*

$$\Delta G = -nFV_r \qquad (4)$$

where n is the number of electrons required in either electrode during completion of a molar quantity of the overall reaction and F is the Faraday constant (the charge of one mole of electrons, 96484 C). Under the arbitrarily chosen "standard" conditions of 25ºC (298.15 K) and 101.325 kPa (1 atm), the thermodynamic decomposition voltage of water is 1.229 V. This theoretical or reversible voltage required to split water at 25ºC concerns the hydrogen production at the negative electrode and the oxygen production at the positive electrode.

During the operation of an electrolysis cell, *i.e.* a cell driven by the application of an external voltage, the positive electrode sustains an oxidation (or "anodic") reaction with the liberation of electrons, while a reduction (or "cathodic") reaction takes place at the negative electrode with the uptake of electrons (Fig. 6a). For this reason, the positive electrode is often known as the "anode" and the negative electrode as the "cathode". The internal circuit between the two electrodes is provided by the electrolyte, in which negative ions ("anions") move towards the positive electrode, and positive ions ("cations") move towards the negative electrode.

A fuel cell operates in the reverse manner to an electrolysis cell, *i.e.* it is a "galvanic" cell that spontaneously produces a voltage. The anode of the electrolysis cell now becomes the cathode and the cathode becomes the anode (Fig. 6b). Nevertheless, the positive electrode remains a positive electrode and the negative electrode remains a negative electrode. The same also holds true for a secondary battery, whether it is being charged (*i.e.* as an electrolysis cell) or being discharged (*i.e.* as a galvanic cell) (Fig. 6c).
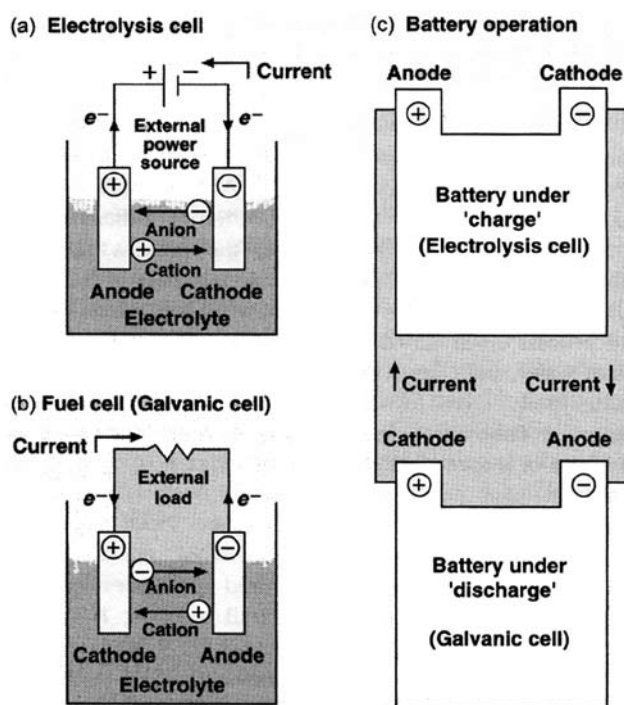

Fig. 6. Terminology used in the operation of electrochemical cells.

The voltage for water decomposition decreases, almost linearly, to 1.088 V at 200ºC (473 K) (Fig. 7). The decrease in ΔG with increasing temperature is largely offset by an increase in the entropy term TΔS, so that the enthalpy of the reaction, ΔH, is almost independent of temperature. Since electrolysers are essentially adiabatic (*i.e.* little heat is absorbed from the surroundings), the energy corresponding to the entropy term is also supplied electrically. At 25 ºC, this increases the minimum cell voltage for water electrolysis to 1.47 V, and

the electrical energy consumed in the reversible reaction is almost temperature-independent. In other words, the voltage is "thermoneutral" (upper line in Fig. 7). Many electrolysers operate at enhanced pressure in order to increase the hydrogen production rate and to avoid the need of using compressors after the electrolysis (without compression, the storage volumes would be enormous). Raising the operating pressure from, for example, 0.1 to 2.5 MPa ($\approx$ 1 to 25 atm) leads to a further increase of about 0.7 V in the reversible voltage. This corresponds to the free energy required to compress the product gases.
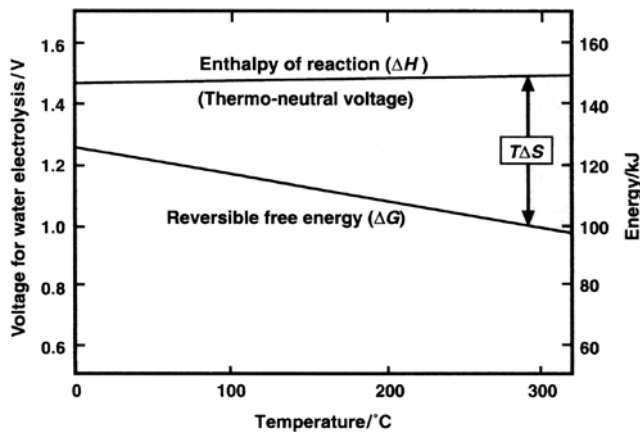

Fig. 7. Theoretical voltage versus temperature relationship for water electrolysis.

In practice, the operating cell voltage exceeds the theoretical value by an amount that represents the electrical losses in the cell. These arise from four different sources: (i) the resistive ("ohmic") losses in the electrolyte; (ii) the overpotential at the oxygen electrode; (iii) the overpotential at the hydrogen electrode; and (iv) the resistive losses in the electrodes.

For an electrode reaction to proceed at an appreciable rate, the potential of the electrode must be changed in such a direction that will sustain the flow current. The greater the current, the more is the change in potential, and the greater is the "irreversibility" of the electrode process. The degree of irreversibility is measured by the difference of the electrode potential from the reversible value (no current flowing) under the same experimental conditions. An irreversible electrode is said to exhibit "overpotential" [14].

Figure 8 shows the voltage-current characteristics of a cell operating at 90°C, together with the various components that give rise to the extra voltage required above and beyond the thermodynamically reversible value.

It is seen that the cell voltage increases sharply with current density, predominantly because of resistive loss in the electrolyte. For this reason, it is important to choose an electrolyte of maximum conductivity. In most cases, a concentrated (30 - 40 wt.%) aqueous solution of potassium hydroxide (KOH) is employed. This must be prepared from very pure water, otherwise impurities will accumulate during electrolysis; chloride ion, which is a common impurity in water, is particularly harmful in that it causes pitting of the protective films formed on metal surfaces in alkaline solutions.
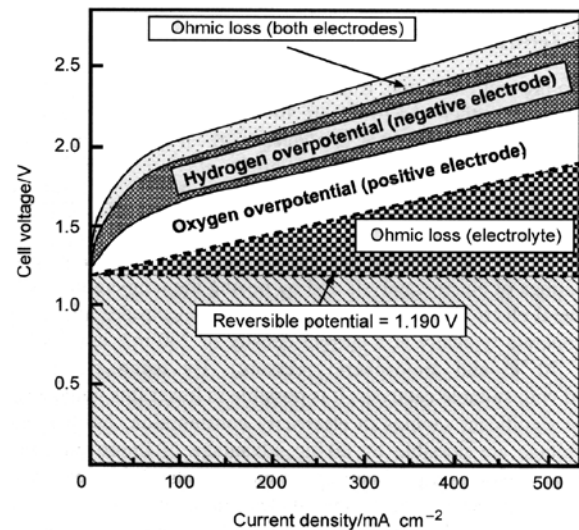

Fig. 8. Performance (voltage-current density) of a basic (unactivated) unipolar electrolyser operating at 90°C.

The overpotentials at the hydrogen and oxygen electrodes, *i.e.* at the cathode and at the anode, respectively, may be reduced by applying coatings of electrocatalysts and/or raising the temperature. Alkaline cells with base-metal electrodes (*e.g.* mild-steel negative electrodes and nickel positive electrodes) operate at a typical current density of 200 mA cm^{-2} when 2.1 V is applied (at 70°C and atmospheric pressure). By using electrodes that are electroplated with suitable catalysts, it is possible to lower this voltage to 1.7 V and thus achieve significant savings in electricity consumption. Further reductions in operating voltage are possible by taking advantage of improved precious-metal electrocatalysts – based on platinum-group metals – that have been developed for use in fuel cells [15,16]. Nevertheless, in order to reduce the capital cost of the electrolyser plant, it is necessary to operate at a current density as high as possible, often greater than 500 mA cm^{-2}. This leads to lower electrical efficiency and a trade-off must be made between capital costs and operating (electricity) costs.

Early electrolysis cells (Fig. 9) were about 60-75% efficient, but the small-scale, best-practice figure is now closer to 80-85%. Larger units are usually a little less efficient at 70-75%. It should be noted that when using electricity generated from thermal power stations, the overall efficiency is only about 25-30% for the conversion of fossil fuel to hydrogen. This is not a very attractive return on the invested energy.
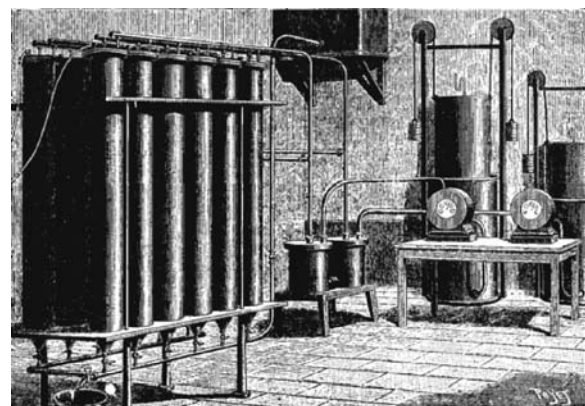

Fig. 9. Primitive plant for the industrial electrolysis of water.

Electrolysers, like batteries, may be constructed in either monopolar or bipolar designs. The monopolar (or "tank-type") electrolyser (Fig. 10a) consists of alternate positive and negative electrodes held apart by porous separators. The positives are all coupled together in parallel, as are the negatives, and the whole assembly is immersed in a single electrolyte bath ("tank") to form a unit cell. Cells based on aqueous KOH are often of this type. A plant-scale electrolyser is then built up by connecting electrically these units in series (this is analogous to the construction of a typical automotive lead-acid battery). Bipolar electrolysers and batteries, on the other hand, have a metal sheet (or "bipole") that connects electrically adjacent cells in series. As seen in Fig. 10b, the electrocatalyst for the negative electrode is coated on one face of the bipole, and that for the positive electrode of the adjacent cell is on the reverse face.

Fig. 10. Didactic scheme of (a) monopolar and (b) bipolar electrolyser modules.

A series-connected stack of such cells forms a module that operates at a higher voltage and lower current than the tank-type (monopolar) design. To meet the requirements of a large electrolysis plant, these modules are connected in parallel so as to increase the current. Bipolar cells may employ either liquid electrolyte or a solid polymer membrane.

Whenever hydrogen is formed by electrolysis, there is also formation of by-product oxygen in the ratio of 1 mole of oxygen to 2 moles of hydrogen (Fig. 11). If electrolysis starts being carried out on a very large scale, it may prove difficult to find a market for the oxygen. Substantial amounts of oxygen are used in steel making, but this supply is already well established. Other possible major uses of oxygen are in the partial oxidation of hydrocarbons to form syngas [17,18], or in the underground gasification of coal. For these applications, oxy-

gen is much preferable to air, as the resulting gas is of higher calorific value since it is not diluted by nitrogen.

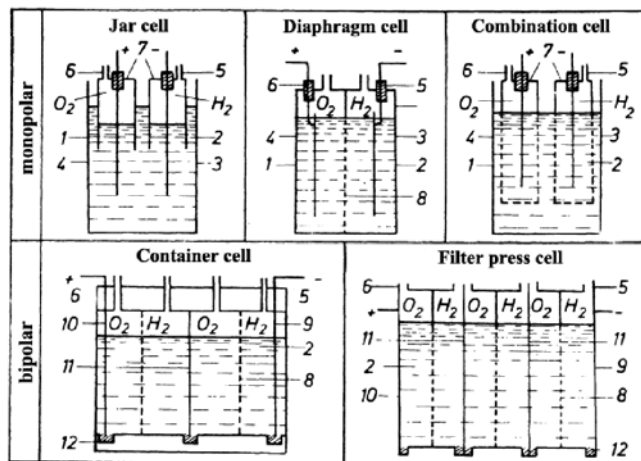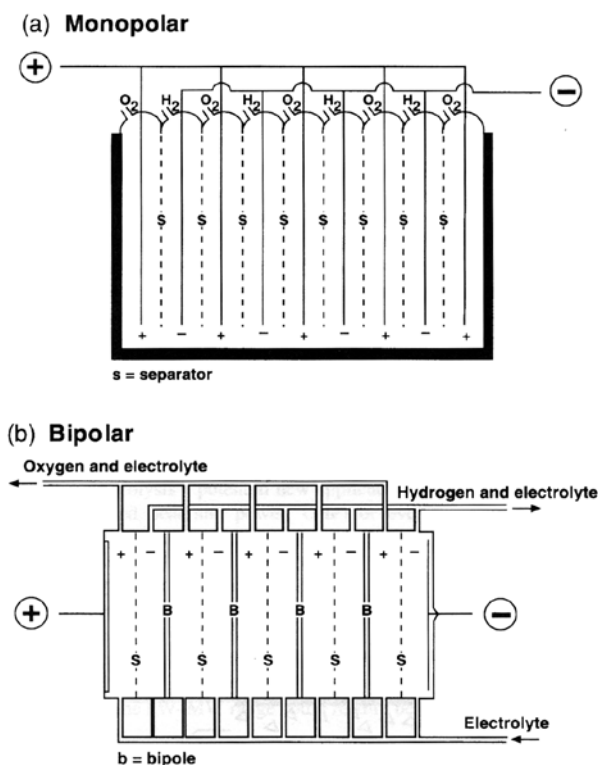Fig. 11. Several different types of water electrolysis cells.

A concentrated KOH solution at temperatures around 100°C is not an easy material to handle, especially in high-pressure systems. It poses some difficult materials science problems, which arise from stress-corrosion cracking of steels, degradation of gaskets and sealants, etc. In order to avoid these problems, many years ago, in the USA, the General Electric Company introduced a new concept for an electrolyser based upon the use of a solid polymer electrolyte (SPE), Nafion®, that was manufactured by the DuPont Corporation [19-21]. This is a perfluorosulphonic acid polymer that exhibits good mechanical properties and is highly conductive for cations, which include hydrated protons. It is acidic and available as thin sheets to form a membrane electrolyte. Appropriate electrocatalysts are coated on each side of the membrane and a metal mesh contacts these in order to complete the electrical circuit. Electrolysers based on this technology are very successful, although there is a cost problem associated to the high price of the SPE membranes. Some applications for these electrolysers, however, are relatively insensitive to the cost, when compared to other considerations such as reliability and safety. Thus, they are used to generate oxygen for life-support in manned satellites and space probes, and also in nuclear submarines that remain submerged for many days at a time.

A detailed drawing of a design for a bipolar proton-exchange membrane (PEM) electrolyser stack is shown in Fig. 12. This type of unit is also known as an SPE electrolyser. The conducting bipole is made of carbon (graphite) and is corrugated, or ribbed, to form channels through which the gases produced during electrolysis escape from the cell stack. A thin sheet of titanium is used to protect the carbon positive electrode from oxidation. The polymer electrolyte is in the form of a thin, plastic membrane. Sophisticated electrocatalysts have been developed for use in proton-exchange membrane fuel cells (PEMFCs) [22,23] and should be equally applicable to PEM electrolysers. New techniques for applying the electrocatalysts to the membranes of PEMFCs have also been formulated. These advances have resulted in improved performance at reduced loadings, which is especially important when using expensive electrocatalysts.
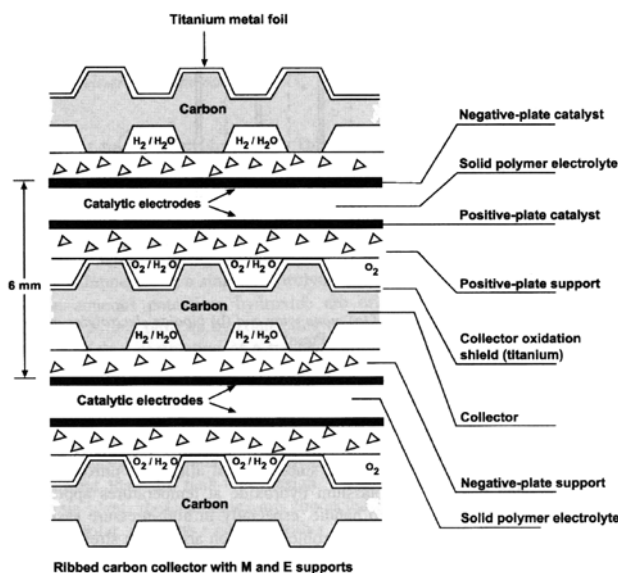
Fig. 12. Cell stack configuration of a PEM electrolyser.

Consideration has been given to operating fuel cells in reverse as electrolysers. The dual-function system has been termed as "regenerative fuel cell". Such technology would save on weight and costs compared with a system that employs a separate fuel cell and electrolyser. It would also offer the prospect of using renewable energy (*e.g.* solar, wind, geothermal) to generate hydrogen that would be stored in the same unit for subsequent production of electricity. Although the feasibility of the regenerative concept was demonstrated at the 50 W level in the 1990s, reliability problems with bifunctional electrodes and efficiency limitations of the "charge-discharge" process (new ways have to be found to optimise the catalyst for both processes) have resulted in little further progress. In general, PEM electrolysers are best suited to small plants, especially those powered by renewable energy where the electricity supply is variable, while alkaline electrolysers are more practical in larger systems that are connected to the grid.

Drawing also on fuel-cell research, there is the possibility of developing water electrolysers that are incorporated in furnaces and operate at high temperatures (700-1000ºC) – the so-called "steam-electrolysers". They use a ceramic ion-conducting electrolyte similar to those developed for high-temperature (HT) fuel cells [24,25]. Moreover, as shown in Fig. 7, HT operation favours electrolysis (*i.e.* improves efficiency) since some of the energy required to split water is supplied by heat. This substantially reduces the electricity demand (at least 25% of the electricity can be saved) but material requirements are more severe. Of course, corresponding amounts of heat must be supplied, which makes water electrolysis a potential new application for a dedicated co-generation unit (*i.e.* combined heat and power, CHP) or even, on a huge scale, a high temperature nuclear reactor [26,27].

Commercial water electrolysers are today manufactured in varying sizes, with power consumptions ranging from kW to MW (Fig. 13). The larger sizes are limited to alkaline electrolysers, and a unit capable of producing 500 m^3 of hydrogen per hour might consume about 2.3 MW of power. Though it seems large, it is less than 1/400th of the size that would be

suitable for coupling to a typical 100 MW pressurised water reactor (PWR) [28,29]. In contrast, solar arrays with power outputs in the kW-MW range could readily be coupled to present-day water electrolysers.

Fig. 13. A commercial water electrolyser.

Large-scale water electrolysis plants have long been installed in certain countries (*e.g.* Norway, Canada) to make use of the surplus hydroelectric capacity. The hydrogen generated was produced for the manufacture of ammonia-based fertilisers rather than for electricity storage. With the advent of cheap natural gas as a source of hydrogen, this process has become much less significant. In 2003, a filling station for hydrogen-powered vehicles opened in Iceland (Fig. 14). The hydrogen is produced by electrolysis using electricity generated from hydropower and geothermal springs. Over 90% of Iceland's electricity is derived from these two sources.
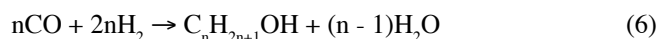
Looking to the future, there are possible situations in which it might prove economic to generate bulk hydrogen electrolytically, for instance:

* in remote regions of the world where the supply of renewable energy exceeds the local demand of electricity;
* as a means of load-levelling in the electricity utility network;
* using nuclear power plant dedicated to hydrogen production.

Fig. 14. A filling station in Iceland for hydrogen-powered vehicles.

Although electrolytic hydrogen would be used first in the chemicals market, this need not continue to be the case. For example, a country that has a high installed capacity of nuclear power, but is short of indigenous hydrocarbon fuels (*e.g.* France), might find it economic to use nuclear electricity to generate electrolytic hydrogen, which could then be combined with carbon monoxide to manufacture synthetic fuels and chemicals, as expressed by Eqs. 5 and 6.

$$nCO + (2n + 1)H_2 \xrightarrow[\text{Ni, Co or Th catalyst}]{200°C} C_nH_{2n+2} + nH_2O \quad (5)$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n - 1)H_2O \quad (6)$$
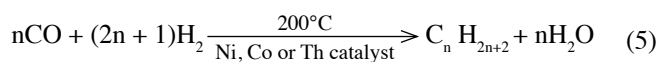
This brings us a new concept of a hydrocarbon or alcohol molecule that is in part fossil and in part nuclear in its origins! At the moment, this situation is far from being implemented as there is still plenty of natural gas remaining worldwide to manufacture inexpensive hydrogen (Table 4).

Table 4. Production and reserves of natural gas by the end of 2002.

Countries: major producers[a]	Annual production			Countries: greatest reserves	Reserves (10^{12} m³)	Reserves/ Production (years)
	(10^9 m³)	(Mtoe)	% World total			
Russian Federation	554.9	499.4	22.0	Russian Federation	47.6	81
USA	547.7	492.9	21.7	Iran	23.0	>100
Canada	183.5	165.2	7.3	Qatar	14.4	>100
UK	103.1	92.8	4.1	Saudi Arabia	6.4	>100
Algeria	80.4	72.3	3.2	United Arab Emirates	6.0	>100
Indonesia	70.6	63.5	2.8	USA	5.2	10
Norway	65.4	58.9	2.6	Algeria	4.5	56
Iran	64.5	58.1	2.6	Venezuela	4.2	>100
Netherlands	59.9	53.9	2.4	Nigeria	3.5	>100
Saudi Arabia	56.4	50.7	2.2	Iraq	3.11	>100
Rest of the world	741.2	667.0	29.3	Rest of the World	37.9	44
Total	2527.6	2274.7	100.2[c]	Total	155.8	

[a] Iraq is omitted because in 2002 its production was low for political reasons; [b] Mtoe stands for a million tonne oil equivalent; [c] Data have a rounding error of 0.1%.

3. OTHER MEANS OF HYDROGEN PRODUCTION

In principle, there are several other ways of decomposing water to form hydrogen without having to generate electricity first. These avoid the need for an electrolyser. The first route, which has been extensively investigated, is to use thermal energy to decompose water by means of cyclic chemical reactions, so-called "thermochemical cycles". These indirect routes offer the potential for producing hydrogen at lower temperatures than that required for the direct thermolysis of water. Without the intermediate production of electricity, overall efficiencies of around 40% are expected, which are higher than the overall efficiency of electrolysis. Although several thermochemical cycles have been experimentally demonstrated (*e.g.* the calcium bromide-iron oxide, the copper-chloride, and the sulphur-iodine processes), they are still far from practical implementation. The remaining options are specific to the use of solar radiation and here there are at least three possibilities. The first uses a solar-thermal power plant to decompose water directly *via* a "photothermal process". In such a plant with a central collector, the temperature can reach over 2000°C and this is sufficient to breakdown water into hydrogen and oxygen. Research is being conducted on the use of catalysts to reduce the temperature for water dissociation, and on the development of methods for the efficient separation of the two gases at high temperatures to prevent their recombination.

The second solar route is through a "photoelectrochemical process" whereby a suitable semiconductor, such as titanium oxide (TiO_2) or cadmium selenide (CdSe), in the form of a thin layer with electrodes attached, is immersed in an aqueous solution and irradiated with sunlight. When the external circuit is completed, water starts to decompose, liberating hydrogen at one electrode and oxygen at the other. This process is still at the research stage and, as yet, the efficiency is very low, just a few percent.

An intriguing idea has been advanced to employ solar-thermal radiation to facilitate and improve the photoelectrochemical decomposition of water. Much of solar radiation lies in the infrared spectrum and is of too low energy (below the band-gap energy of most semiconductors) to be used in photoelectrochemical reactions and is therefore wasted. The idea proposed involves the photoelectrolysis of water at high temperatures and pressures where, as seen from Fig. 7, the required voltage is lower and the entropy of reaction can be supplied thermally. A field of heliostats would be used to focus solar radiation on a receiver mounted on a tower. The radiation would then be split into an infrared component to heat the pressurised water to at least 300°C, and into visible/ ultraviolet radiation to carry out the photoelectrochemical water splitting reaction. Thermody-

namic calculations suggest that at high temperature and high pressure, the required voltage is substantially reduced and it should be possible to reach overall efficiencies approaching 20% for the conversion of solar energy to hydrogen. This approach to water splitting is usually termed as "thermally-assisted photoelectrochemical decomposition" [30,31].

The final approach to the direct solar decomposition of water is to use natural bacteria, or biological organisms such as blue algae, that have the propensity to decompose water under the action of sunlight and release hydrogen freely into the air. In theory, algae can produce hydrogen with an efficiency of up to 25%. The problem is that oxygen is also formed and inhibits the hydrogen-producing enzyme, hydrogenase, so only small amounts of hydrogen are actually generated. Research is in progress to moderate the release of oxygen and to increase both the general feasibility and cost efficiency of such photobiochemical processes [32,33].

All of the above solar-based approaches are too speculative, futuristic and complex to discuss in detail in this paper, although conceivably they might become important before 2030.

4. CONCLUSIONS

The principle of producing hydrogen in an electrolyser (using a renewable electricity source), storing it, and regenerating the electricity in a fuel cell when needed, sounds attractive at first acquaintance. However, the practice and the economics are quite a different matter. In the early days of the dream, cheap abundant nuclear power seemed the most practical means of generating hydrogen. As this does not seem likely in the next decades, it will be necessary to fall back on solar- or wind-generated electricity. The requirement for these separate devices (electrolyser, hydrogen container, fuel cell) merely to store and use small quantities of electricity is not efficient at all from an energy viewpoint. Such an approach would therefore be a gross misuse of renewable energy. Moreover, the activity would be capital intensive and there would be the added cost of the power-conditioning equipment.

We do not see hydrogen being produced from renewables on a significant scale in the next 20 years. Rather, hydrogen for fuel cells will be produced, as it is now, from fossil fuels. Meanwhile, electrolysers will continue to be used mostly for the production and processing of chemicals and metals, and for life-support oxygen in submarines and manned spacecraft. From the point of view of greenhouse emissions, however, the use of fossil fuels to generate hydrogen for chemical manufacture or for use in fuel cells is useful only if the carbon dioxide, that is inevitably produced, can be sequestered. Practical technology for this does not yet exist and its development is an area for immediate attention [34-36]. Alternative possibilities of decomposing water to form hydrogen, as well as other means of hydrogen production have been briefly analysed in this article.

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