

CHAPTER 1

Introduction to Electrolysis, Electrolysers and Hydrogen Production

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1.1 Introduction

An electrochemical cell involves the transfer of charge, by the movement of ions in a liquid or solid phase and the movement of electrons in a solid phase, through which electrochemical transformation of species can be achieved. An electrochemical cell is formed by placing two conducting materials (conductors or semiconductors), referred to as electrodes, into an ionically conducting electrolyte and electronically connecting them. In the cell, two sets of reactions take place at the separate electrodes, oxidations at the anode and reductions at the cathode, both of which are linked by the flow of current (Figure 1.1). This current flows in the form of electrons in the electrodes and as ions in the electrolyte, separating the electrodes.

A broad classification of electrochemical cells is based on as either Galvanic devices, which involve spontaneous reactions, or electrolysis cells, which require electrical energy input. In Galvanic cells, such as batteries or fuel cells, the chemical reactions or transformations are coupled to suitable half-cell reactions to produce a negative free energy change for the overall cell process which can then result in power production *via* electricity generation. Electrolysis cells require an applied potential field which forces

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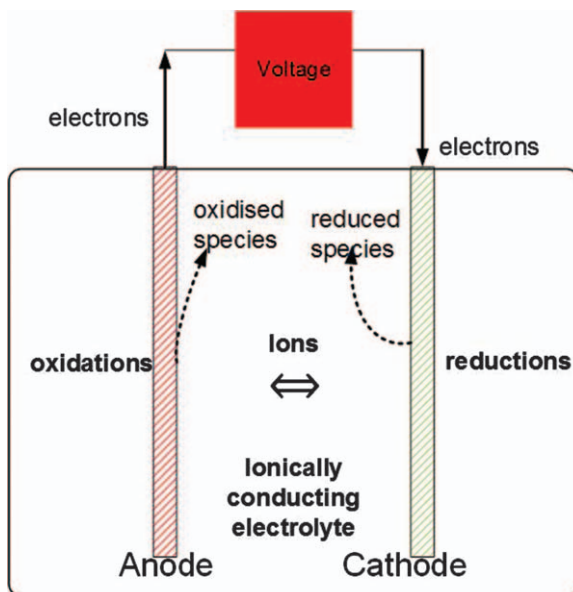


Figure 1.1 An electrochemical cell.

the non-spontaneous electrochemical and chemical changes to occur at the electrodes. The magnitude of applied potential voltage will generally determine the rate of the charge transfer and ionic flux.

Electrolytic processes or electrolyzers are used for a diverse range of applications including synthesis of chemicals and materials, extraction and production of metals, recycling, water purification and effluent treatment, metal and materials finishing and processing, energy storage and power generation and corrosion protection. Electrolysis is used for production of organic and, notably, inorganic chemicals. The two largest industries (in terms of tonnage) are for combined chlorine and caustic soda (NaOH) production (chlor-alkali) and aluminium electrowinning. The chlor-alkali industry is based on the electrolysis of aqueous brine solutions at relatively low temperatures and involves the formation of hydrogen gas at the cathode. Another important inorganic electrolysis process is the production of hydrogen by water electrolysis. The use of electrolysis for the production of organic chemicals is mainly within the fine chemical industries where somewhere in the region of a hundred industrial processes have been developed. Any oxidative electro-synthesis involving an aqueous electrolyte will typically lead to the formation of hydrogen as a useful by-product at the cathode. Furthermore, any loss of efficiency in a cathodic synthesis can also lead to hydrogen formation. Such operation provides an opportunity to capitalise on hydrogen as a very useful fuel.

Electrolysis can be seen as a tool for green chemistry, which is “concerned with the utilisation of a set of principles that can reduce or eliminate the use

of hazardous substances in the design, manufacture and application of chemical products”.¹ Electrolysis can provide a selective and environmentally friendly procedure for synthesis² and offers alternative approaches to the recycling of chemicals and achieving improved sustainability. Electrolysis presents a powerful method for promoting reactions through the generation of large electrochemical potentials, and the generation of powerful oxidants, such as superoxide and ozone, and powerful reductants, *e.g.* solvated electrons. Electrons are clean and versatile redox agents, able to perform clean and fast reactions. Contrary to popular belief, electrons are an inexpensive reagent to use in most applications; the cost of electrons compares extremely favourably with the cheapest oxidants and reductants, *e.g.* £10 per mole (@ £0.1 per kWh, 3.5 cell voltage).

1.2 Electrolysis and the Hydrogen Economy

The worldwide demand for energy puts increasing pressure on the available carbon sources. The combustion of carbon-based fuels, *e.g.* natural gas and coal, cannot be sustained indefinitely, as carbon resources become depleted, unless effective technology is developed to recover and re-use the carbon dioxide combustion product. Solutions proposed for this re-use include electrolysis or photo-electrolysis of carbon dioxide with water to species such as carbon monoxide and hydrogen, known as “synthesis gas” (syngas), formic acid or methanol, and the production of methanol, catalytically from carbon dioxide and hydrogen. Such approaches require the use of electricity, either directly or indirectly (hydrogen formed from water electrolysis) in electrolysers, for which currently production is dominated by fossil fuel combustion. Hence for sustainable electrolysis, its future use would need to be based on “renewable” sources (hydro, solar, wind and wave) or on photochemical or photo-biological methods using solar energy sources. Notably such energy sources can be used to generate hydrogen *via* electrolysis or by use of other technologies.

A concept called the “hydrogen economy” based on a H₂ energy system was put forward in the 1970s in which hydrogen was proposed as the major energy vector.³ In practice this could mean that water is used to generate hydrogen and oxygen by, for example, electrolysis, which are able to be used in fuel cells to generate power. Thus, we have an energy system based on the re-use of water. Additionally, because of its abundance in the form of water and because it is distributed in most habitable regions throughout the world, hydrogen is thus considered an alternative to fossil fuels for energy systems.⁴

Using an energy system based on hydrogen and electricity could be less constrained by geographical boundaries, as current fossil fuel supplies are. Hydrogen, when reacted with oxygen releases, energy in combustion engines or in fuel cells to produce water as the only by-product. A major attraction of hydrogen is its compatibility with fuel cells and their high energy efficiencies in converting chemical hydrogen (with air (oxygen)) to electricity (and heat) generation.

The hydrogen economy is an energy system based on hydrogen for energy storage, distribution and utilisation (see Figure 1.2). The concept was conceived because of concerns over the stability of petroleum and gas reserves and the potential lack of stable energy sources. This situation made governments and industries in several countries consider alternative strategies to implement an energy system based on hydrogen as a clean, potentially renewable, fuel. Hydrogen was thus considered an ideal candidate as a carrier of energy, in much the same way as electricity. To be sustainable it must be produced from a natural resource using renewable energy or materials.

Hydrogen is a suitable basis for an energy system because it has a number of attractions:

- It is the most abundant element in the world, although almost exclusively in combination with other elements, notably oxygen as water
- It can be obtained readily from water
- It has very good chemical activity
- When combusted or reacted with oxygen it has zero emissions characteristics – the product is water
- It has the highest gravimetric energy density of any known fuel
- It is compatible with both electrochemical and combustion processes
- It has very good electrochemical activity
- It is very compatible with fuel cell applications

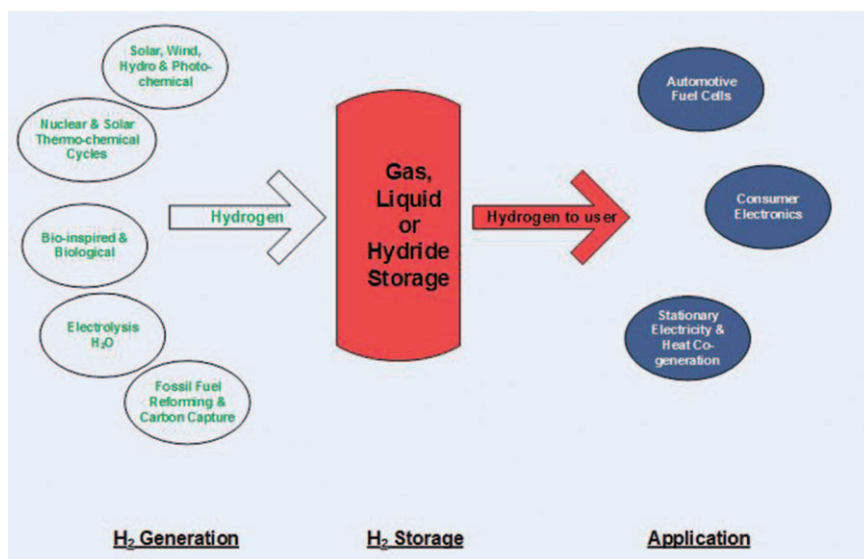


Figure 1.2 The hydrogen economy or hydrogen energy system. A network of primary energy sources geared to hydrogen generation and storage to support multiple power applications.

There are of course several challenges to the implementation of hydrogen into an energy system and these include both societal and technical barriers such as:

- Hydrogen occurs almost exclusively in combination with other elements and is not immediately accessible as fuel without significant energy input.
- Hydrogen buoyancy and flammability must be accounted for in its safe use and storage.
- Hydrogen production is currently mainly from non-renewable fossil fuels.
- Hydrogen's energy storage and distribution infrastructure is limited worldwide.
- Hydrogen containment at technical levels on a volume basis is lower than liquid fuels.
- Hydrogen has unique permeability characteristics through many materials and can result in material embrittlement.
- Hydrogen is a "greenhouse" gas.
- Hydrogen has large investment costs in its manufacture and production for worldwide, large-scale use.
- There are potentially higher consumer costs with the use of hydrogen.
- Hydrogen's use is in competition with other energy sources and storage systems, such as batteries, redox fuel cells, compressed air and pumped water storage.

The majority of the world's hydrogen production is from natural gas using a process called steam reforming. Steam reforming is the reaction of a carbon-based fuel with water to produce a gas mixture of hydrogen and carbon dioxide. The hydrogen is then separated and used as the energy vector and the carbon dioxide is released into the environment, unless carbon capture or abatement methods are used to prevent its release. Hence the realisation of a sustainable hydrogen energy system requires the development of alternative means of hydrogen production, from renewable sources, together with effective networks of storage, distribution and use, as either a fuel or as a chemical feedstock, for example as syngas (a mixture of hydrogen and carbon monoxide). The move towards a hydrogen economy is being partly driven by the use of hydrogen in fuel cells. This drive is regardless of the current methods for hydrogen production and is mainly due to the fact that fuel cells are one of the cleanest and most efficient technologies for generating electricity. Fuel cells electrochemically convert hydrogen into water by reacting it with oxygen, typically contained in air.



They do not use the direct combustion of H_2 with air and thus the pollutants commonly produced by boilers and furnaces are not formed. The

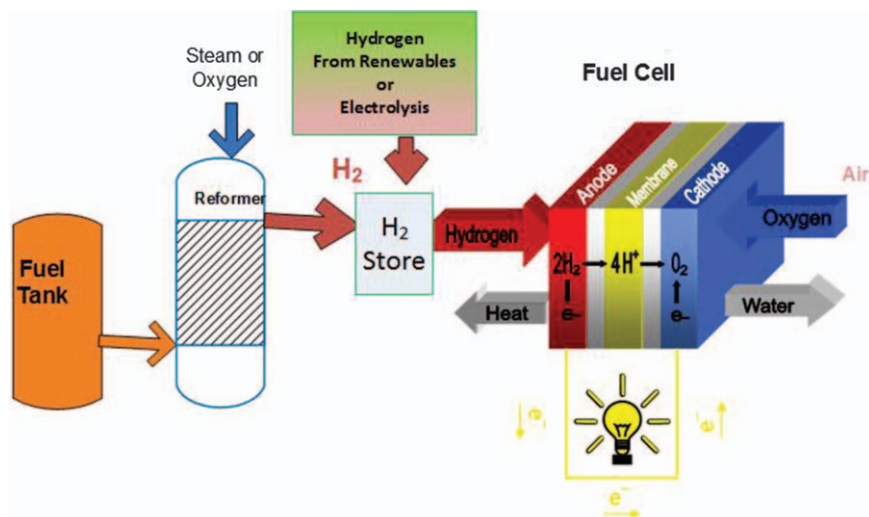


Figure 1.3 Fuel cells energy conversion system (a link between hydrogen and efficient electricity generation).

only products are electricity, water (or steam) and heat (Figure 1.3). Heat is generated because of electrical inefficiencies, as discussed in Chapter 2. This heat can be captured and used for heating or in energy recovery systems, such as steam turbines. The form of energy recovery will depend on the type of fuel cell used, but notably whether it operates at low temperature (<100 °C) or higher temperatures of 200–900 °C.

1.3 Hydrogen Generation, Storage and Use

Progress towards a hydrogen economy is slow, as developments in related technologies are largely based on reforming carbon-based fuels. Advances in technology include lowering the cost and increasing the efficiency of fuel reforming, improving the storage capability of H₂, and development of more efficient hydrogen fuel cells and also internal combustion engines.

1.3.1 Storage of Hydrogen

Hydrogen must be conveniently stored and readily available for dispensing for a range of applications, including transportation, portable devices and large-scale stationary power generation. The storage of hydrogen is one of the fundamental requirements for the evolution of the hydrogen energy system. There are currently three principle methods available for hydrogen storage: as a pressurised gas, as a cryogenic liquid and as a metal hydride.⁵ A major challenge for effective hydrogen storage is related to its physical properties.

Hydrogen is a light gas with a molar mass of 2, and thus has a high energy density availability based on the mass principle. However, it has one of the lowest energy storage densities based on unit volume. For example, at ambient

temperature and pressures of 10 and 100 bar, the density of hydrogen gas is only approximately 0.8 and 7.5 kg m⁻³ respectively, compared to methane which is 6.5 kg m⁻³ at only 10 bar pressure. Hydrogen storage requires the reduction of an enormous volume of gas and an objective in hydrogen storage is to pack hydrogen as close as possible, *i.e.* to reach the highest volumetric density, using as little additional material and energy as possible. To increase the density of hydrogen, either work must be applied to compress the gas, or the temperature must be decreased below the critical temperature to liquefy it. Alternatively, the molecular repulsion can be reduced by the interaction (chemically or physically) of hydrogen with another material. Storage of hydrogen as a gas uses very high pressures. Cryogenic storage of hydrogen as a liquid is not straightforward, requiring a reduction in temperature to 22 K, and even then, the density is still modest at 71 kg m⁻³.

Hydrogen occurs in many forms. It can occur as an anion (H⁻) or cation (H⁺) in ionic compounds, form covalent bonds *e.g.* with carbon, and behave like a metal to form alloys or inter-metallic compounds at ambient temperature. The chemical storage of hydrogen with other elements can be achieved with reasonable volumetric energy densities, but an important issue for a hydrogen storage system is the reversibility of the chemical combination and the release of hydrogen from the “host” material. The reversibility criterion excludes all covalent hydrogen-carbon compounds, as with these, hydrogen is only released when they are heated to temperatures above 800 °C or if the carbon is oxidised. The methods for reversible hydrogen storage which provide a high volumetric and gravimetric density known today are:

- conventional storage methods, *i.e.* high-pressure gas cylinders or as liquid hydrogen;
- the physi-sorption of hydrogen on materials with a high specific surface area [many forms of carbon (nanotubes, nanofibres, fullerenes, activated charcoals, other forms of nanoporous carbon, *etc.*); other inorganic nanoporous materials];
- hydrogen intercalation in metals and complex hydrides;
- storage of hydrogen based on metals and water;
- as inorganic and organic liquids and solids.

For storage in stationary systems, steel tanks are a suitable method, as weight and size are not important. For transportation, the traditional tanks do not represent an adequate solution due to their additional weight, which can be more than the weight of the stored hydrogen, and volume needed to store the gas. Over recent years there have been significant developments in new types of composite storage tanks that can store hydrogen at 300–800 bar pressure, at which hydrogen can reach a gas density of 36 kg m⁻³, which is approximately half that of its liquid form at its normal boiling point. These types of storage tank have a capacity of 10–18 wt% of hydrogen. Further developments are taking place to use lightweight composites that will meet the requirements for an acceptable driving range for automobiles, as well as safety

requirements related to potential collision damage. Of course, the issue of compression of hydrogen to these pressures is an important consideration due to the associated energy costs and the need for specialised compressors. Storage of hydrogen above pressures of 1000 bar would on first sight seem to be a way of increasing capacity. But hydrogen is a non-ideal gas and its compressibility factor increases with pressure applied such that at such high pressures it approaches a maximum in volumetric storage capability.

As an energy store, hydrogen has high energy storage capabilities (Figure 1.4) with a gravimetric storage capability of 38 kWh kg^{-1} as a liquid. Unfortunately, hydrogen has a relatively low volumetric energy storage capability which is one of the major challenges in its use, when space is at a premium. Hence for transportation applications and other applications where volume is at a premium the storage of hydrogen is a greater challenge. Sufficient fuel must be stored to make it practical to drive distances comparable to petrol- or diesel-powered cars. For example, the energy content of 1.0 kg hydrogen is approximately equal to 3 kg petrol (~ 4 litres). Thus, an average tank of some 60 litres requires an equivalent storage for 15 kg H_2 . An 800 bar storage tank (hydrogen gas density = 40 kg m^{-3}) would thus need to have a volume for hydrogen of 375 litres, *i.e.* some six times that of a petrol tank.⁴

One positive feature of using hydrogen in conjunction with fuel cells is that the efficiency of fuel cells can be a factor of two or more greater than that of internal combustion engines. Hence for cars, the hydrogen container is only required to store around half the energy required from petrol.

However, the challenge faced for hydrogen storage is trying to compete with the energy density of petrol, which is much greater than hydrogen, in either liquid, hydride or gaseous form. For hydrogen, that added weight of the container is an additional and major factor which significantly affects its ability to compete with petrol. As a means of comparison to illustrate the

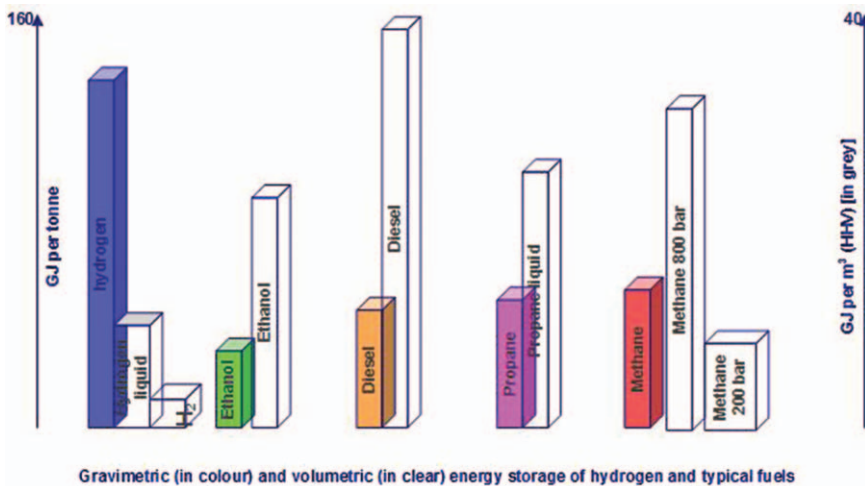


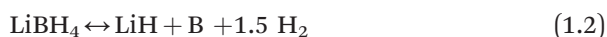
Figure 1.4 Comparison of energy storage of hydrogen with other fuels.

Table 1.1 Comparison of energy density storage characteristics for hydrogen.

Method	Storage capacity, wt% of hydrogen	Volumetric capacity, Mass kg _{H₂} per litre
Metal hydrides FeTiH ₂ and LaNi ₅ H ₆ , Mg ₂ NiH ₄	~2	0.115–0.145
Pressurised H ₂ gas (330 bar)	5	0.05
Cryogenic liquid H ₂ (20K)	100	0.066
Solid H ₂	100	0.08
Methanol	12.5	0.1
Methane (liquid)	25	0.105
Gasoline (C16)	15	0.12
Ammonia	17	0.103
LiBH ₄	18	0.125
NaBH ₄	11	0.115

challenge faced in hydrogen storage, Table 1.1 shows the volume density of hydrogen stored in several compounds and liquid hydrocarbons.⁶ The volumetric energy densities of those compounds (except graphite monolayers) are higher than that of hydrogen as liquid or as compressed gas (at approximately 700 bar). The most effective hydrogen storage media (ignoring the organic chemical compounds) which provide the highest mass fraction and volume density for hydrogen are based on light elements such as lithium, nitrogen, boron and carbon. Ammonia is considered a potential storage compound for hydrogen because of its known chemistry of formation from nitrogen and hydrogen, which is the basis for its formation for the synthesis of fertilisers. Hydrocarbon-based compounds, *e.g.* methanol and octane, are both liquid and high-density hydrogen storage compounds and high energy density fuels. An alternative to the storage of hydrogen in chemical compounds is to store it by adsorption onto a solid surface.

The compound with the highest gravimetric hydrogen density today is LiBH₄ (18 mass%). This complex hydride could, therefore, be the ideal hydrogen storage material for mobile applications. LiBH₄ desorbs three of its four hydrogens upon melting at 280 °C and decomposes into LiH and boron.



The desorption of hydrogen on these compounds can be catalysed by adding SiO₂ and significant thermal desorption has been observed, starting at 100 °C.

1.3.2 Generation of Hydrogen

Hydrogen can be produced by several methods which include chemical, electrochemical, catalytic, thermal and biological processes.⁷ Hydrogen production routes can be put into four general categories, namely:

- Fossil fuels
- Electrolysis

- Renewable energy, which can include electrolysis
- Biological and biomass systems
- Nuclear fission and fusion, which can include electrolysis

1.3.2.1 Fossil Fuel-based Hydrogen Production

Hydrogen has historically been produced from coal, gasoline, methanol, natural gas and other fossil fuels. Some fossil fuels have high hydrogen to oxygen ratios, making them good candidates for reforming processes. The fossil fuel with the highest hydrogen to carbon ratio is natural gas (CH₄). Natural gas is not simply methane, but a mixture of mainly methane with other hydrocarbons (ethane, propane, butane) and various amounts of carbon dioxide, nitrogen, helium and sulphur (mainly as H₂S); the composition of which varies greatly from region to region. The processing of natural gas includes removal of higher molecular weight hydrocarbons, inert and acid gases, water, liquid hydrocarbons and sulphur. For the transmission of natural gas, odour compounds such as mercaptans, thiophenes and di-ethyl sulphide are added for safety.

The principle behind any hydrogen production method is to efficiently remove the hydrogen and exclude other elements present in the original compound. In most fossil fuels, hydrogen is a major constituent and some have high hydrogen to oxygen ratios, making them good candidates for hydrogen production. The hydrogen is produced from these materials by processes such as gasification or reforming. The dominant method is endothermic catalytic steam reforming, which combines a fuel, such as methane, with steam and catalytically reacts them together at high temperatures in a two-stage process:



Hydrogen is then be separated from the mixture using, for example, pressure swing adsorption. A drawback of steam reforming is that it is endothermic, and thus heat is required, meaning energy is consumed. Another type of reformer is the partial oxidation (POX) reformer which reacts the methane with oxygen to produce hydrogen:



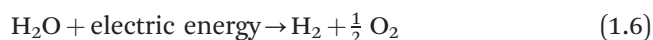
Reforming hydrocarbons inevitably leads to CO₂ emissions, and consequently it is not a pollution-free process. The production of hydrogen is often linked to its use to generate power using fuel cells which generally run on hydrogen, but any hydrogen-rich material can serve as a possible fuel source. However, this latter type of fuel is only really suitable for higher temperature fuel cells (650–900 °C) such as molten carbonate or solid oxide systems, whereas for low temperature fuel cells gas “clean-up” is required

mainly to remove carbon monoxide to levels of around 20 ppm (parts per million) and lower.

1.3.2.2 Hydrogen via Electrolysis

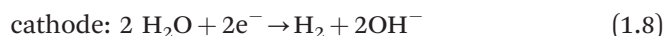
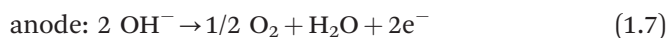
Electrolysis currently produces pure hydrogen for use in the electronics, pharmaceutical, food and other industries and is also considered a potential method of hydrogen production for fuel.⁸ Water electrolysis is also a safe option for the use of hydrogen at the point of use, in relatively small quantities, as it does not demand a substantial storage requirement. The electrolyser systems are expensive compared to, for example, steam reforming plants, and also, depending upon the scale of production, the electricity used can account for up to 75% of the cost of hydrogen generation. Potentially, electrolysis, when coupled with a renewable energy source, can provide a clean and renewable source of chemical energy. In other circumstances, electrolysis can capitalise on off-peak electricity to reduce the cost of electrolysis. Both scenarios are under detailed study in several countries as a means of electrical grid supply energy balancing.

In water electrolysis a voltage is applied to the cells and a DC current passes between two electrodes (Figure 1.5), in contact with an ionic conducting medium, with hydrogen and oxygen produced by water decomposition:



Most of the larger scale, commercial, electrolysers are based on alkaline electrolysis and operate with aqueous electrolytes containing approximately 30% KOH; which gives the maximum ionic conductivity, at operating temperatures between 70–90 °C. Cell technologies are often based on elevated pressure operation of approximately 30 bar, as electrolysis is the most energy efficient means for compressing the gas. This reduces the need for external gas compression and offers slightly lower energy consumption. Electrolysis also produces commercially-valuable oxygen gas which has many industrial applications.

The individual electrode reactions that produce hydrogen, by alkaline electrolysis, at the cathode and oxygen at the anode are:



In operation the cell contains a separator to isolate the hydrogen gas from oxygen gas, to avoid formation of a potentially explosive mixture. An alkaline electrolyte enables the use of low cost non-precious metal catalysts, such as nickel, for the electrodes, which helps to keep cell capital costs relatively low.

In more recent years, commercial development has actively focused on an acid electrolyte, typically using a solid polymer electrolyte (see Chapter 3) and not an aqueous electrolyte, such as sulphuric acid, as this enables a

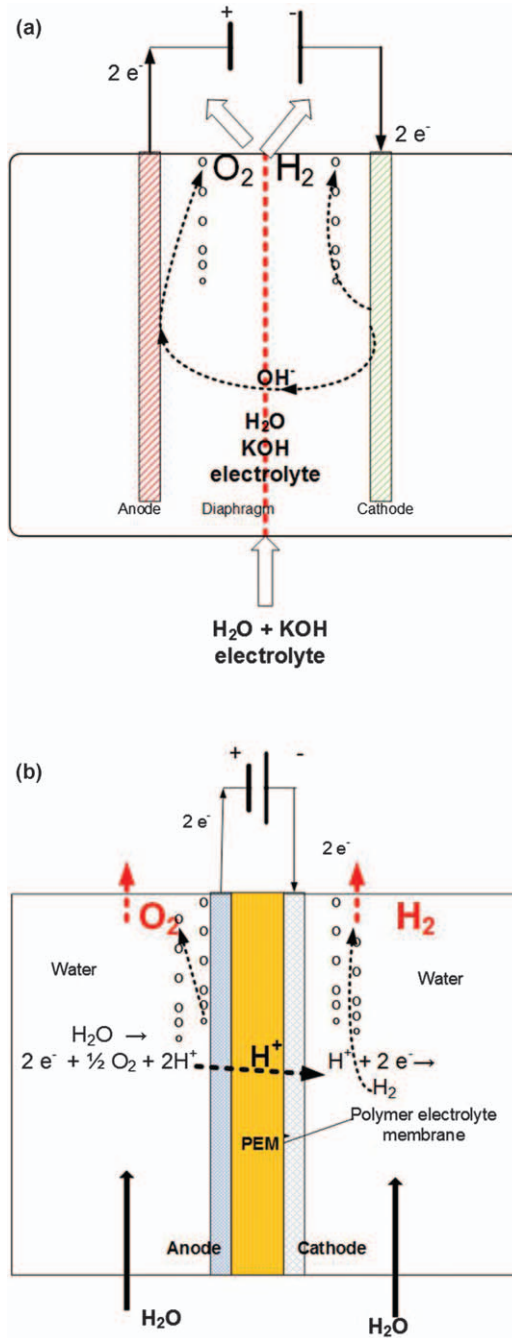
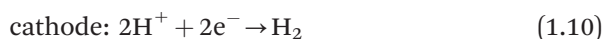
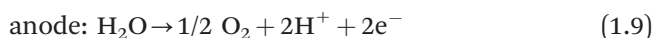


Figure 1.5 Electrolyzers for production of hydrogen from water. (a) Alkaline electrolyser. (b) Solid polymer membrane electrolyser.

compact and higher efficiency system than an alkaline system. In these so-called polymer electrolyte membrane (PEM) electrolysers the electrode reactions are:



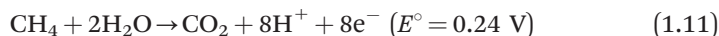
In these systems the PEM is the means for separating the two gas products. Presently, there is limited large-scale use of polymer membrane water electrolysis systems, with only a few commercial systems available. In more recent years, two other very promising electrolyser technologies have been under investigation for hydrogen production: the alkaline polymer membrane (see Chapter 6), and the high-temperature, solid oxide, or similar ceramic-based (see Chapter 5) cells.

The alkaline PEM system development has been driven by the relatively high capital cost of proton exchange membrane electrolysers; this is largely dictated by the high material costs of membranes (perfluorinated polymers) and precious-metal-based (Pt, Ir, Ru) catalysts. Alkaline electrolysers use lower cost electrode materials based on Ni. However, PEM water electrolysis systems offer advantages over liquid alkaline technologies: greater energy efficiency, higher production rates (current density per unit electrode area), and more compact and flexible design operation. Adopting alkaline anion-exchange membrane (AEM) systems provides the opportunity to combine the attractions of both electrolysers, to create lower cost polymer membrane electrolyser systems, through low material costs. Recent research has demonstrated the potential of alkaline membrane electrolysers, achieving performance similar to acid systems, *e.g.* cell voltage of 1.8 V at 1.0 A cm⁻² using a copper cobalt oxide anode catalyst and Ni cathode at 25 °C.⁹

High-temperature electrolysis of steam has been driven by considerable attraction to increasing the temperature of operation of electrolysers from the perspectives of thermodynamics, *i.e.* lower energy input and electro-catalytic activity and electrolyte resistance. Current interest in the development of higher temperature electrolysers is based on solid oxide ionic conductor technology, as used for solid oxide fuel cells (SOFCs). Typical system development is based on yttria-stabilised zirconia (YSZ) electrolytes and nickel zirconia cermet (ceramic-metal) cathode and the anode is strontium-doped lanthanum manganite.¹⁰ In high-temperature electrolysis, high-temperature steam is separated at the anode into hydrogen and oxygen ions which pass through an ion-conducting membrane (such as zirconium oxide) to the cathode where they are converted to oxygen. In high-temperature electrolysis a significant part of the energy needed to split water is thermal, instead of electrical, thus reducing the overall electrical energy required and improving process efficiency. Subject to the source of thermal energy both the previous factors can reduce capital and running costs. The process can also provide waste heat recovery.

1.3.2.3 Electrolysis Using Organic Fuels

Although water or steam electrolysis is well known, widespread use is hindered by high operating costs related to electricity consumption. A decrease in the electrical power requirements in electrolysis may be achieved by using an alternative anode reaction to O₂ evolution, with a lower value of equilibrium potential. This may be achieved using several reactions, but one potentially attractive route is using an organic chemical fuel. One such approach uses methane gas as an anode depolariser:



At the cathode:



This is equivalent to electrochemical steam reforming, and essentially replaces one unit of electricity with one equivalent energy unit of natural gas at lower cost. The use of natural gas in the electrolyser enables very high system efficiency with respect to primary energy; voltage reductions of up to 1.0 V compared to conventional electrolysers, are possible and thus the electricity consumption can be around one third of that used in conventional electrolysers. However, this process uses natural gas and is thus not sustainable.

An alternative system can be based on alcohol, which may be formed *via* fermentation technologies. In one such cell using methanol, an aqueous solution is circulated past the anode, where methanol and water react to form carbon dioxide, as in a direct methanol fuel cell:¹¹



In this cell hydrogen is produced at the cathode by reduction of protons (H⁺) which are formed at the anode:



The net reaction in the cell is:



Applications using biological fuel cells are also under scientific evaluation in which wastewater provides the energy source at the anode, while hydrogen is evolved at the cathode¹² (see Chapter 11).

Electrolysers not only produce hydrogen but also produce pure oxygen, which is a useful industrial gas. Water electrolysers produce oxygen for applications such as breathing air maintenance in submarines and manned space missions.

1.3.2.4 Photo-electrolysis

The conversion of sunlight to H₂ is one of the most important developments in water splitting.¹³ Established technology splits water in two

steps: photovoltaic cells convert solar radiation to electricity which is then used in separate electrolysers to generate hydrogen from water. Photovoltaic conversion occurs with varying efficiency depending upon the semiconductor material used. An efficiency of up to 32% with expensive single crystal semiconductors, used in multi-junction stacks, or around 3% with much cheaper organic semiconductors, can be achieved. The cost of the delivered electricity is similar in both cases.

The conversion of solar energy into electricity and the water splitting reaction can be combined in a single process in which photon absorption creates electron-hole pairs that electrochemically split water molecules. The efficiency of this integrated photochemical process is around 8–12% and can be much greater than the two sequential processes. The technical challenge is to create robust semiconductor materials that satisfy the competing requirements of photon absorption and water splitting.

In the process, solar photons are absorbed directly into an absorber material, without complete conversion to heat. The absorber can either convert part of the photon energy to electricity (as in a photovoltaic cell) or use it for the decomposition of water to hydrogen and oxygen, *i.e.* the solar photo-electrolysis of water (Figure 1.6). Fujishima and Honda¹⁴ were the first to report generation of hydrogen and oxygen in a photo-electrochemical cell (PEC) using a TiO₂ photo-anode illuminated with near ultraviolet light. The electrons generated at the anode passed to a Pt cathode, at which hydrogen was evolved.

Photo-electrochemical (PEC) or photo-electrolysis systems use solar light energy for the electrolysis of water. In PECs, photovoltaics, semiconductors and an electrolyser are combined in one unit that generates hydrogen. The operation of PECs is based on the conversion of light energy into electricity,

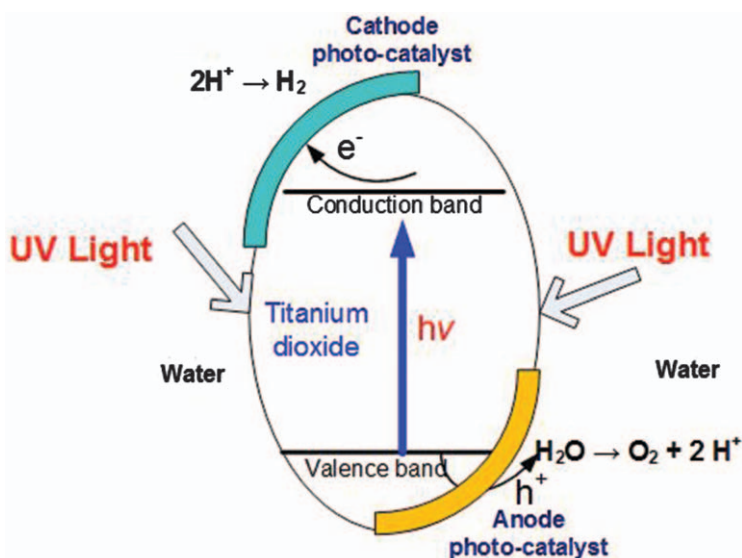


Figure 1.6 Photo-electrochemical hydrogen production.

within a cell involving two electrodes, which is then used for water electrolysis. A light-absorbing semiconductor is used as either the anode, the cathode, or both in the cell. There are essentially three options for the arrangement of photo-electrodes in the assembly of PECs:

- photo-anode made of a n-type semiconductor and a metal cathode;
- photo-cathode made of a p-type semiconductor and an metal anode;
- photo-anode made of a n-type semiconductor and a photo-cathode made of a p-type semiconductor.

Catalysts, as with other hydrogen generation electrochemical technologies, can play an important role in improving efficiency and production rates in photochemical based processes. The behaviour of photocatalysts is influenced by the band gap of the semiconductor. The term “band gap” refers to the energy difference between the top of the valence band and the bottom of the conduction band (see Figure 1.7). Electrons are able to jump from a valence band to a conduction band, but this requires a minimum amount of energy for the transition, which depends upon the specific photo-electrode materials. Electrons can gain enough energy to jump to the conduction band by absorbing a photon of light (or a phonon (heat)). The band gap is a major factor determining the electrical conductivity of a solid. Substances with large band gaps are generally insulators, those with smaller band gaps are semiconductors, while conductors either have very small band gaps, or none, because the valence and conduction bands overlap. In silicon, for example, sunlight can provide enough energy to push an electron out of the lower energy valence band into the higher-energy conduction band. Electrons in the conduction band are free to move about the silicon and, when a load is placed across the cell, they will flow out of the p-type side into the n-type side, lose energy while moving through the external circuit, and then back into the p-type material where they recombine with the valence band hole they left behind. In this way, sunlight creates an electrical current.

A major factor with photocatalysts that use sunlight is that the photons are primarily in the visible part of the light spectrum and thus have a wavelength that requires semiconductors with small band gaps, below 1.7 eV, for efficient absorption. Oxide semiconductors, *e.g.* titanium dioxide, that are robust in aqueous environments, have wide band gaps and require higher-energy photons for excitation. To improve performance in PECs, several approaches have been developed that involve controlling or altering the band gap of a material through changing the composition of a semiconductor:

- modification of the TiO₂ microstructure (such as porous nanocrystalline TiO₂);
- use of other stable, non-oxide semiconductors such as GaAs, InGaAs, MoS₂, WSe₂ and MoSe₂ as the n-type electrode;
- illuminated organic dyes can be used to generate electricity at oxide electrodes in electrochemical cells.¹⁵

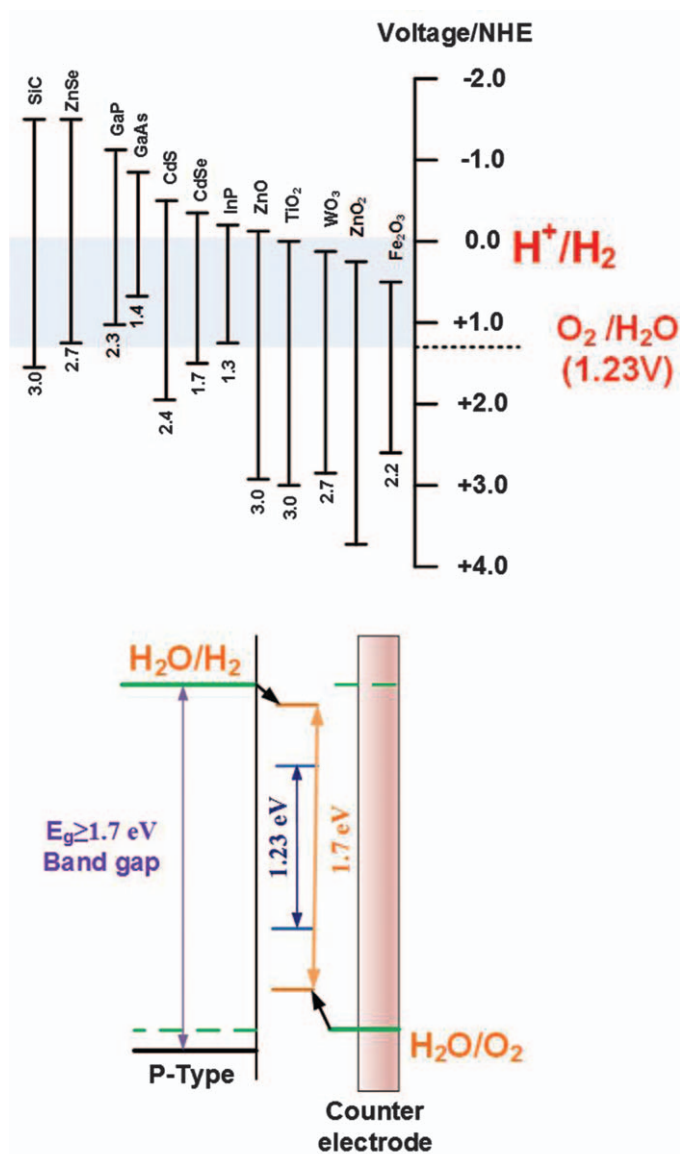


Figure 1.7 Band gap in photocatalysis. (a). Band width and band edge criteria for photocatalytic production of hydrogen. (b). Position of valence and conduction band edges for a range of semiconductors (pH = 1).

The use of dye-sensitised photocells that can accumulate energy from low energy photons and inject higher-energy electrons into the semiconductor can be used to match the solar spectrum and semiconductor band widths (Figure 1.8). In 1991 a version of a dye solar cell was invented by Grätzel and O'Regan, and is known as the Grätzel cell.¹⁶ The cell was significantly less

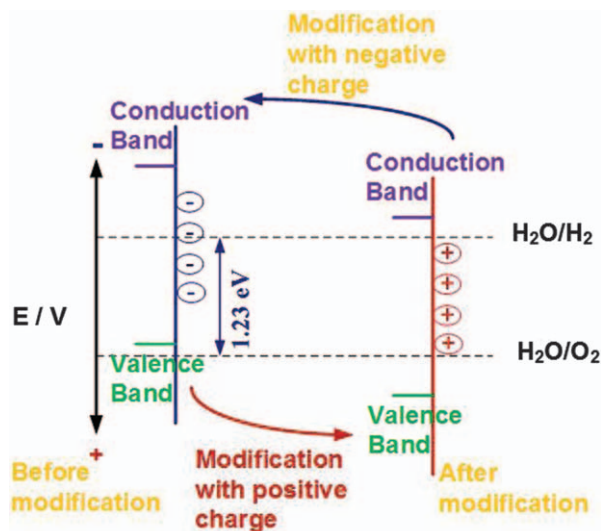


Figure 1.8 The matching of the band edges for semiconductor and water splitting using dye-sensitised cells. The shifting of band edges using surface modification can achieve the energetic positions for water splitting – above and below the conduction and valence bands.

expensive to manufacture than older solid-state cell designs and can also be engineered into flexible sheets, giving it a price and performance that was attractive enough to be considered as a potential competitor to fossil fuel electrical generation.

Commercial applications of such cells are not developing rapidly due to chemical stability problems, notably from degradation when exposed to ultraviolet radiation. A barrier layer may be used to improve stability. These include UV stabilizers and/or UV absorbing luminescent chromophores (which emit at longer wavelengths) and antioxidants to protect and improve the efficiency of the cell. Replacing the liquid electrolyte with a solid has also been a field of research.

The Grätzel cell is a single junction device operated as a photo-anode (n-dye sensitive cell (DSC)), where photocurrent arises from electron injection by the sensitised dye. Tandem cells combining a p-DSC and a n-DSC in a simple sandwich configuration with an intermediate electrolyte layer have been developed to offer greater solar to electricity energy efficiency.

The tandem cell design relies on dyes which respond over a wide range of frequencies of the solar spectrum. One dye, gallium indium phosphide, has a band gap of 1.8–1.9 eV and meets the band gap energy criteria of a solar cell, but its band edges are 0.2 to 0.4 V – too negative to achieve the band edge overlap criteria. This can be resolved by chemical modifications of the semiconductor electrode surface – which shifts the band edges to appropriate energetic positions which catalyse the interfacial charge transfer. Adsorption of organic and inorganic molecules, such as metallated porphyrins and

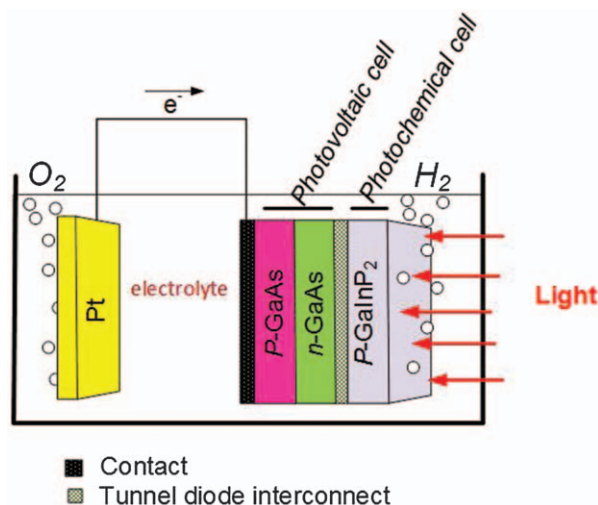


Figure 1.9 A double junction GInP₂/GaAs PEC system.

transition metals, at p-type GaInP₂ can shift the band edges of the semiconductor to positive or negative values.¹⁵ A double junction GInP₂/GaAs PEC system (Figure 1.9) has been able to produce hydrogen at a 12.4% efficiency from solar light; and has very good corrosion stability, but it is relatively expensive.¹⁷

In comparison to conventional two photon PEC systems, the PV/PEC systems are more elaborate but have achieved the highest solar to hydrogen water splitting efficiency of all PEC systems, *i.e.* around 16%. The maximum theoretical efficiencies for photo-electrolysis of water are approximately, 31, 42 and 52% for a single band gap absorber, two and three bandgap systems respectively.

1.3.2.5 Biological and Biomass Processes

The use of biological processes to produce methane by anaerobic fermentation is an established technology and indeed using the methane-containing biogas to produce hydrogen by a series of process steps of gas cleaning and reforming is seen as one method to use biomass to generate hydrogen. However, it would, in principle, be more efficient to generate the hydrogen directly from the biomass material, thus removing the reforming step. The biological production of hydrogen (biohydrogen) can be achieved by several approaches, including biophotolysis, indirect biophotolysis, photo-fermentations and dark fermentations.¹⁸ However, none of these approaches are used commercially and a large amount of research and development remains to be completed if applications are to be realised.

Gasification and pyrolysis of biomass and biological waste materials, agricultural residues, agricultural and municipal wastes, and biomass specifically grown for energy use as feedstock, present a route to more

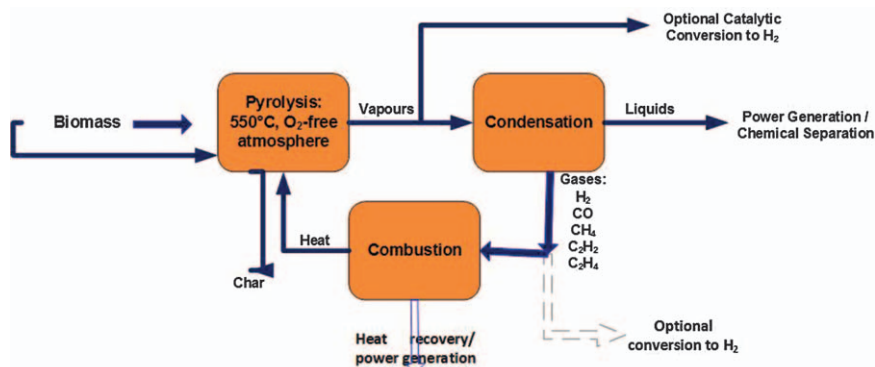


Figure 1.10 Schematic diagram of a process for biomass liquefaction by pyrolysis.

sustainable hydrogen production.¹⁹ The thermal processing techniques of pyrolysis and gasification for plant material (biomass) and fossil fuels are similar in many respects (Figure 1.10) with both using heating in a limited oxygen environment. This process produces a range of potential liquid and gaseous fuels and biochars that can be used in combustion of can be converted into hydrogen by reforming.

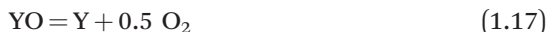
In photo-biological systems, photosynthetic organisms carry out a reaction that stores the solar energy in fuel production. Under normal conditions photosynthetic systems do not evolve hydrogen, but rather reduce CO_2 to carbohydrates. However, it is possible to modify the conditions if the reducing end of the photosynthetic process is coupled to a hydrogen-evolving enzyme, such as hydrogenase or nitrogenase. The more effective photo-biological systems for hydrogen/oxygen generation are those based on microalgae, such as green algae and cyanobacteria. Efficiencies under ideal conditions approach approximately 10%, but an issue with algal systems is they tend to saturate at solar irradiances above 0.03 suns.

The above approaches are not used commercially and thus a large amount of research and development is required for the future. One system for hydrogen generation is based on an indirect photo-biological process,¹⁶ in which sunlight and CO_2 are used to produce algae (aerobically). The produced algae are then concentrated and used to form H_2 , anaerobically. The projected cost of hydrogen generation would be $\sim \$10$ per GJ hydrogen based on a solar to hydrogen conversion efficiency of 10%. The photo-bioreactor costs are of the order of $\$100 \text{ m}^{-2}$ and amount to 50% of the total cost.

1.3.2.6 Thermal-Electrochemical Generation of Hydrogen from Water

Hydrogen can be produced from water in a number of ways using solar energy. An example is the high-temperature thermochemical coupling processes with concentrated solar power. This technique uses thermochemical cycles operating at elevated temperatures which facilitate fast reaction

kinetics. Heat sources include solar collectors operating up to 3000 °C or nuclear reactors designed to operate between 500 to 900 °C. Many chemical cycles have been proposed, including systems based on zinc – oxygen operating at 1500 °C, sulphur – iodine at 850 °C, calcium – bromine at 750 °C, and copper – chlorine at 550 °C. A thermochemical process uses heat to indirectly split water *via* a sequence of intermediate chemical reactions as in eqn (1.16)–(1.18).²⁰

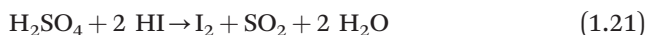


For example, when energy (in the form of heat) is applied, chemical XH liberates hydrogen and chemical YO liberates oxygen. The species X₂ and Y recombine with water to form XH and YO and liberate heat. The gas generation reactions operate in separate reactors, at high temperatures, and thermochemical cycle processes must balance the favourable reaction kinetics at high temperatures against the aggressive chemical corrosion of process vessels.

One of most researched cycles is based on sulphur–iodine (SI) chemistry.²¹ An energy input for a thermochemical cycle is required for the heat of reaction of one or more of the endothermic reactions. In the SI cycle the heat is mainly for the dissociation of sulphuric acid and also for the dissociation of hydrogen iodide.



The sulphuric acid and hydrogen iodide are formed from the exothermic reaction between SO₂, H₂O and I₂.



Hydrogen is generated by the decomposition of hydrogen iodide (eqn (1.20)).

There have been several proposals to incorporate electrolysis into this.²² For example, in the SI cycle, the high-temperature thermal decomposition of H₂SO₄ (essentially the SO₃ species) can be carried out by a lower temperature electrolysis:



The benefits of lowering the maximum operating temperature of the SO₃ to SO₂ reaction to 500–600 °C in the cycle are that it allows the use of a lower temperature heat source and product gases are produced at separate electrodes thus solving a separation problem. The theoretical cell potential is very low (0.17 V), although in practice it will be greater due to the usual internal resistance and polarisation losses (see Chapter 2).

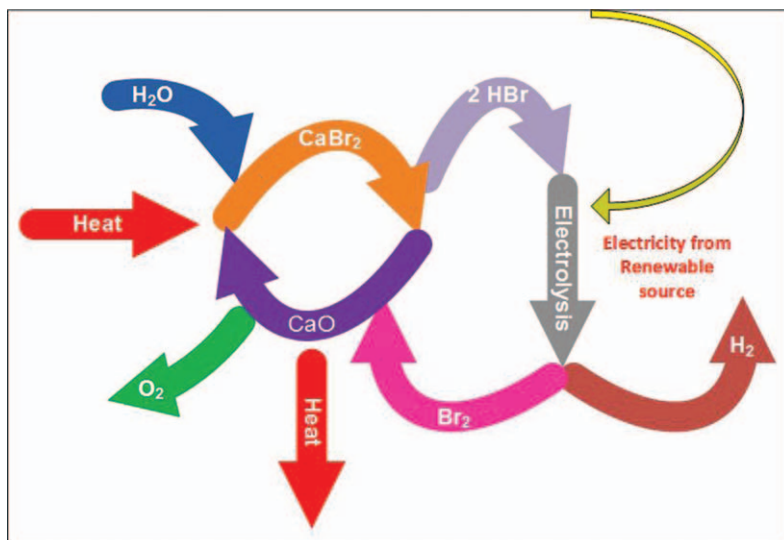
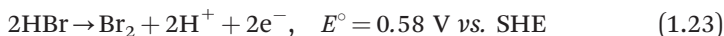


Figure 1.11 The modified Ca–Br cycle. CaO and CaBr₂ are recycled at a high temperature and the HBr is converted to Br₂ by an electrolyser at a low temperature.

Another cycle which uses an electrolysis step is based on calcium–bromide (Figure 1.11) also offer the potential for high efficiencies but with lower temperature requirements ($\sim 750\text{ }^{\circ}\text{C}$) than the sulphur-based cycles. The stages in this cycle are:

- i) conversion of calcium oxide (CaO) and Br₂ to CaBr₂ and O₂ at approximately $550\text{ }^{\circ}\text{C}$
- ii) conversion of CaBr₂ back to CaO and HBr at $730\text{ }^{\circ}\text{C}$
- iii) conversion of HBr directly to Br₂ and H₂ in a single step which can be performed in a HBr electrolyser: on the anode side, the HBr is converted to Br₂



Protons pass through the membrane and recombine at the cathode to produce hydrogen.



The Westinghouse Electric Corporation developed a hybrid sulphur process, which eliminated the use of iodine completely.²² The sulphur cycle hydrogen production process combines two steps: a thermochemical and an electrochemical reaction in which sulphur dioxide, dissolved in aqueous solution, is oxidised at the anode while hydrogen is produced at the cathode.

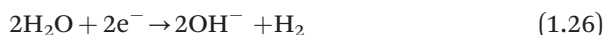
1.3.3 Hydrogen as a By-product from Electrolysis

There are several electrolyses which are based on anodic oxidation which is accompanied by hydrogen evolution at the cathode. Notably this includes a range of chemicals from the electrolysis of the halides chloride, bromide and iodide. A major area of commercial activity is in chlorine electrochemistry.²³ The reactions involved in the chemistry and electrochemistry of the halides (Br, Cl and I) are quite similar but the values of the kinetic and thermodynamic parameters are different.

A major example is the production of chlorine and sodium hydroxide by the electrolysis of sodium chloride (the chlor-alkali process). In the electrolysis of a solution of sodium chloride the desirable reaction is the generation of chlorine:

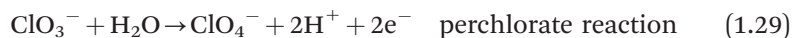


In chlorine production the cathode reaction involves the formation of hydroxide ions and hydrogen gas, in alkaline solution:



By separating the products of the anode and cathode reactions they will not react and this enables the collection of hydrogen gas.

Under different conditions, other electrolyses of NaCl can produce chemicals such as sodium hypochlorite, chlorate and perchlorate, in conjunction with hydrogen (at the cathode):



Similarly, smaller-scale production of bromates and iodates and periodates have been realised.

Table 1.2 gives examples and conditions of operation, of other inorganic synthesis⁸ which result in the generation of hydrogen at the counter electrode (cathode).

1.4 Conclusions

Currently around 95% of the hydrogen produced worldwide is from hydrocarbons typically using reaction with steam, with the remainder mainly from the electrolysis of water. A hydrogen-based energy system will need to rely on inexpensive and efficient routes to create hydrogen in sufficiently large

Table 1.2 Inorganic electrolyses that form by-product hydrogen.

Chemical product	Reaction	Anode (A) and cathode (C)	Conditions	Temperature
Chlorine, sodium hydroxide	$2 \text{NaCl (aq)} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Cl}_2(\text{g}) + 2 \text{NaOH}$ $E^\circ = 1.36 \text{ V}$	Noble Metal Oxide/Ti (A) Steel or Hg (C)	Aqueous NaCl; asbestos or ion-exchange Membrane. 200–1000 mA cm ⁻²	80–95 °C
Hypochlorite and chlorate	$2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ $E^\circ = 1.35 \text{ V}$ $\text{Cl}_2 + 2\text{OH}^- \leftrightarrow \text{OCl}^- + \text{Cl}^- + \text{H}_2\text{O}$ $2 \text{HClO} + 3\text{OCl}^- \leftrightarrow \text{ClO}_3^- + 2\text{Cl}^- + 2 \text{H}^+ + 2\text{e}^-$	Noble Metal Oxide/Ti (A) Steel (C)	Aqueous NaCl (310 g dm ⁻³) Na ₂ Cr ₂ O ₇ (1–6 g dm ⁻³) 150–400 mA cm ⁻²	60–80 °C
Perchlorate	$\text{H}_2\text{O} + \text{OCl}_3^- \rightarrow \text{ClO}_4^- + 2\text{Cl}^- + 2 \text{H}^+ + 2\text{e}^-$ $E^\circ = 1.18 \text{ V}$	Pt/Ti, PbO/Graphite (A) Steel or Ni (C)	Aqueous ClO ₃ ⁻ 150–500 mA cm ⁻²	35–50 °C
Permanganate	$(\text{MnO}_4)^{2-} \rightarrow \text{MnO}_4^- + 2\text{e}^-$ $E^\circ = 0.54 \text{ V}$	Ni, Monel (A) Fe or Steel (C)	Aqueous K ₂ MnO ₄ (25–100 g dm ⁻³) 1–4 mol L ⁻¹ aq. KOH 5–150 mA cm ⁻² undivided cell	60 °C
Persulphate	$2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2\text{e}^-$ $E^\circ = 2.01 \text{ V}$	Pt or Pt/Ti (A)	Conc. H ₂ SO ₄ , 500–1000 mA cm ⁻² divided cell	Cold < 10 °C
Fluorine	$2\text{F}^- \rightarrow \text{F}_2 + 2\text{e}^-$ $E^\circ = 2.87 \text{ V}$	Carbon (A) Mild steel (C)	KF-2HF (eutectic) at 13 mA cm ⁻² undivided cell	82 °C
Manganese dioxide	$\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4 \text{H}^+ + 2\text{e}^-$ $E^\circ = 1.23 \text{ V}$	Graphite, Pb or Ti (A)	MnSO ₄ (0.5–1.2 mol L ⁻¹) in aq. H ₂ SO ₄ 7–12 mA cm ⁻² undivided cell	90–100 °C
Ozone	$3\text{H}_2\text{O} \rightarrow \text{O}_3 + 6\text{H}^+ + 6\text{e}^-$ ($E^\circ = 1.51 \text{ V}$)	Vitreous carbon (A), lead dioxide, Tin oxide (Ni doped)	Solid polymer electrolyte. Conc. aq. HBF ₄ 500 mA cm ⁻² divided cell	Room temperature or lower

quantities from non-fossil natural resources. Only around 5% of hydrogen is produced using electrolysis of water mainly from renewable energy sources. Estimates of hydrogen requirements vary from country to country, but the quantities are massive and orders of magnitude greater than current production. To eliminate fossil fuels from this cycle, the electrical energy must come from renewable sources, such as hydropower, wind, solar radiation or heat from a nuclear reactor or solar collector.

From a sustainability perspective, the most promising route to hydrogen is splitting water, which is an ideal carrier of hydrogen. Electrolysis is a convenient and developed technology for splitting water into hydrogen and oxygen and currently produces very pure hydrogen for use in the electronics, pharmaceutical and food industries. Water electrolysis is a safe option for the generation of hydrogen, at point of use, in relatively small quantities, as it does not demand a substantial requirement for storage. Compared to steam reforming, electrolysis is expensive; the electricity required to split the water into hydrogen and oxygen accounts for around 80% of the cost of hydrogen generation. Potentially, electrolysis, when coupled with a renewable energy source, can provide a clean and renewable source of energy. In other circumstances, electrolysis may also capitalise on off-peak electricity to reduce the cost of electrolysis.

However, electrolysis alone will not be sufficient to generate all the hydrogen predicted to be needed for future energy demands. Exploitation of solar radiation in the form of heat and/or in photocatalysis holds considerable promise but requires more research and development, although pilot systems are under investigation. As advances are made in water splitting processes, using high temperatures generated from solar radiation, they may replace the fossil fuel processes as cleaner, long-term energy solutions. Photo-electrochemical catalysts with the ability to produce hydrogen under visible light irradiation are currently under research and development to enhance their durability and efficiency and cost of materials.

Biological routes for hydrogen are under development and set to impact the hydrogen energy sector. The use of such techniques to produce methane have been development and provide an indirect route to hydrogen. Furthermore, the use of biomass is set to make a significant impact through gasification, pyrolysis and fermentation. Current technology that produces alcohols, mainly ethanol, by fermentation could also be seen as a route to hydrogen, by for example electro-reforming.

Overall there is a significant number of options and technologies for hydrogen production that are potentially sustainable and avoid this use of fossil fuels. However, their development requires significant R&D and notably large investments in plant as well as motivation driven by political legislation. This book attempts to put electrolysis in this context and provide detailed information on its industrial and development status and economics.

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