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Introduction to Electrochemical Sustainable Processes

1.1 Introduction

Electrochemistry is a fundamental process in life and plays an important role in a range of commercial technologies in industry. Electrochemistry is concerned with the transfer of charge, by the movement of ions, in a liquid or solid (or gaseous) phase through which electrochemical transformation of species can be achieved. Electrochemistry can be used to synthesize materials and chemicals, to generate power and to analyse and detect compounds and components. The applications of electrochemistry are quite diverse and span over a wide range of industries, including:

- Energy storage and power generation
- Synthesis of chemicals and materials
- Extraction and production of metals
- Recycling, water purification and effluent treatment
- Corrosion protection
- Analysis, sensors and monitors
- Metal and materials finishing and processing
- Semiconductor technology

Corrosion is an important industrial issue as great efforts and cost are required to minimize its effects. The majority of corrosion processes involve some form of electrochemical reaction of a metal component, which leads to a gradual loss of function or property of a device or component. Although the subject of corrosion is outside the scope of this book, its influence is important in the context of the selection of electrode materials. Electrode material selection must recognize that corrosion may occur during operation both in 'current-on' conditions and in standby, or open circuit, conditions. Current-on conditions can induce cathodic reduction of coatings and anodic dissolution of so called 'inert anodes'. At standby conditions the electrodes are at different potentials to the current-on situation. This may result in a loss of protection of the material in the cell environment or an increased possibility of corrosion, for example in the case of fuel cell cathodes where potentials are higher at open circuit conditions. Such effects can be aggravated by the presence of corrosive chemical products and reagents, dissolved oxygen or other impurities. Electrochemical processes, by their very nature, involve the flow of current which can induce leakage or parasitic currents and thus cause and accelerate corrosion of components of the electrolytic systems.

Sustainable and Green Electrochemical Science and Technology, First Edition. Keith Scott.

Electrochemistry plays a vital part in sensors, analytical detection and in monitoring. Important applications include in polarography and anodic stripping voltammetry for trace metal ion analysis, ion selective electrodes, electrochemical biosensors and detectors.

Electrochemistry is used in the metal and material processing and semiconductor industries, producing components which are otherwise difficult to produce by mechanical means. The methods include machining, grinding, deburring and etching. Electrochemistry is used in the finishing of many components through the deposition of coatings (metallic, polymer) and through anodizing to produce surface oxide films. Electrophoretic painting is used widely in the motor industry for bodywork protection. Other applications are in electropolishing and in electrochemical cleaning, pickling and stripping.

Energy storage and generation through the application of electrochemical processes are provided by batteries, capacitors and fuel cells. The generation of electrical energy is caused by two 'redox' reactions (with a negative free energy) which occur spontaneously within a battery or fuel cell or from the liberation of an accumulated charge in a capacitor. There is a wide range of batteries for low, medium and high power applications and three of the most common are the lead/acid, nickel/metal hydride and lithium ion.

Fuel cells are devices for generating electrical power by the continuous supply of a fuel to one electrode and an oxidant to the other electrode. There are a variety of these devices which operate at low or high temperatures. The electrodes in fuel cells are different to those in batteries as they must generally be permeable to gases. In low temperature cells, catalytic gas diffusion electrodes are therefore used which are typically a composite structure of electrocatalyst, carbon, hydrophobic binder and a coating. Applications of fuel cells are in large scale power (combined electricity and heat) generation, vehicle traction and small scale remote site energy generation.

Electrochemical synthesis is used for production of both organic and inorganic chemicals. The two largest industries (in terms of tonnage) are for combined chlorine and caustic soda (NaOH) production (chlor-alkali) and aluminium electrowinning. These two processes use radically different cell technology, aluminium production being based on molten salt electrolysis at temperatures around 1000 °C, whilst the chlor-alkali industry is based on the electrolysis of aqueous brine solutions at relatively low temperatures. Other inorganic electrochemical processes include the production of hydrogen by water electrolysis, molten salt electrowinning of sodium, lithium and magnesium and electrowinning from aqueous electrolyte of copper, zinc and nickel. The purification of several metals is carried out by 'electrorefining' in which the impure metal is dissolved anodically in an electrolyte bath and the pure metal simultaneously electroplated onto a cathode. Furthermore, many species such as hydrogen peroxide and ozone, can be safely produced on-site electrochemically without the need for bulk storage of the hazardous reagent. The electrosynthesis of organic chemicals is mainly located in the fine chemical industries where the advantages of this technique have seen somewhere in the region of a hundred or so industrial processes developed. In bulk organic chemical manufacturing, electrochemical technology is used in relatively few syntheses as there is often a relatively large equipment cost associated with its use and a strong presence of heterogeneous catalysis. An important exception to this is the production of adiponitrile from acrylonitrile (an intermediate in the production of nylon) which competes well on the open market with a gas phase catalytic route.

An important part of electrochemical technology is that associated with the use of ion-exchange membranes. Membranes are both a vital component of many electrolytic cells and also a means of carrying out specific separations of ionic and non-ionic species and the formation of chemical products.

Areas where electrochemistry can play a major role are in sustainability of energy and chemical supplies. A significant area for the application of electrochemical technology is water purification and the recycling of materials and remediation of effluents (Comninellis and Chen, 2010).

1.2 Effluent Treatment and Recycling

The process industries are under environmental and economic pressure to make more effective use of the material resources used in the manufacture of commercial products. This impacts in several areas of process and product planning; the selection of the most appropriate starting materials and end product and the overall design of the process steps. Due to the inherent inefficiencies of physical and chemical processes there will be species and streams generated which are not a desirable part of the envisaged manufacturing process. If these materials are seen to have some immediate economic value, methods will be implemented to recover and re-use them. If the economics of re-use are not directly apparent then procedures are generally adopted to dispose of the material at short term minimum cost. In many cases these materials are potential pollutant and/or hazardous materials and their disposal should be looked at in a much larger context. The safe management of these materials, especially the more toxic and hazardous, is a major problem and is fraught with many issues; economic, social, political and technological. Nevertheless there are methods and procedures currently available, and in use, which can improve approaches to waste management based on strategies of re-use and recycling. The simple recovery of material and disposal without its re-use is less satisfactory; suitable ways, or alternative use, should ideally be found, for example the incineration of organic materials to produce process heat.

Electrochemical methods can be applied to the treatment of and recycling of many species present in solid, liquid or gaseous phases and compete commercially with many other methods not based on electrochemistry (Bersier *et al.* 1994). For example, conventional biological processes have been used in industrial waste treatment for many years and utilise either aerobic or anaerobic bacteria. New technologies are now being investigated which use the electron transfer ability of certain micro-organisms to generate electrical power in microbial fuel cells or to synthesize chemicals.

There are several established processes such as those for metal recovery by electrodeposition, ion separation by electrodialysis, water treatment using hypochlorite and the treatment of liquors bearing chromium species (Scott, 1995).

1.3 Green Electrochemistry

Electrochemistry can be seen as a branch of green chemistry which is '"concerned with the utilization of a set of principles that can reduce or eliminate the use of hazardous substances in the design, manufacture and application of chemical products' (Bernando

et al., 2010). Thus electrochemistry covers processes which relate to a reduction in the environmental impact of chemicals (and fuels) using improved production methods and delivery systems, the use of sustainable resources, or product substitution. Green electrochemistry solutions include improvements in process engineering and applications of bio-electrochemistry. Electrochemistry plays an important role in the development of cleaner/greener and more efficient processes in all chemical manufacturing industries. Electrolysis can provide a selective and environmental friendly procedure for synthesis (Luzzi *et al.*, 2004) and offers alternative approaches to recycling of chemicals and improved sustainability. It presents a powerful method for promoting reactions: through the generation of large electrochemical potentials, and generation of powerful oxidants, such as superoxide and ozone, and powerful reductants, for example solvated electrons. Benefits in using electrochemistry for greener and more sustainable processes include mild chemical/process conditions, ease of control and safer operation, high process selectivity and novel chemistry.

Importantly the electron is an inexpensive reagent to use in most applications. Electrons are cheap, pure and versatile redox agents able to perform clean and fast reactions (Scott, 2002). The cost of the electron compares extremely favourably with the cheapest oxidants and reductants, for example £10 mol^{-1} (at £0.1 kWh^{-1}, 3.5 V (cf. hydrogen peroxide at £50 mol^{-1} and potassium permanganate at £500 mol^{-1}).

Electrochemistry can make a significant contribution to sustainability through satisfying a range of targets for green chemistry (Figure 1.1):

- Clean synthesis: By direct oxidation and reduction
- Enhanced atom utilization
- Replacement of stoichiometric reagents: Regeneration of a wide range of redox oxidants and reductants
- New solvents and reaction media: Solid polymers, ionic liquids, supercritical fluids
- Water-based processes and products: Predominate in electrochemistry
- Replacements for hazardous reagents: Solution phase oxidants and reductants can be generated *in situ*
- Intensive processing: Application of ultrasonics, centrifugal fields, and so on.
- Novel separation technologies: electrochemical enhancement of ion exchange (IX), adsorption, gas phase separation and water filtration
- In many cases allows alternative feed-stocks
- New safer chemicals and materials: *Insitu*, reagent can be generated on demand
- Waste minimization/reduction through reagent regeneration and material recycling

The use of electrochemistry in synthesis can establish new syntheses processes that are greener and more sustainable than alternative processes using new solvents and electrolytes based on ionic liquids, micro (and nano-emulsions) and solid polymers (Bernardo *et al*., 2010).

1.4 Electrochemistry and Energy Sustainability

The worldwide demand for energy puts increasing pressure on carbon sources, the combustion of such fuels, for example natural gas and coal, cannot be sustained indefinitely, as carbon resources become depleted, unless effective technology is developed

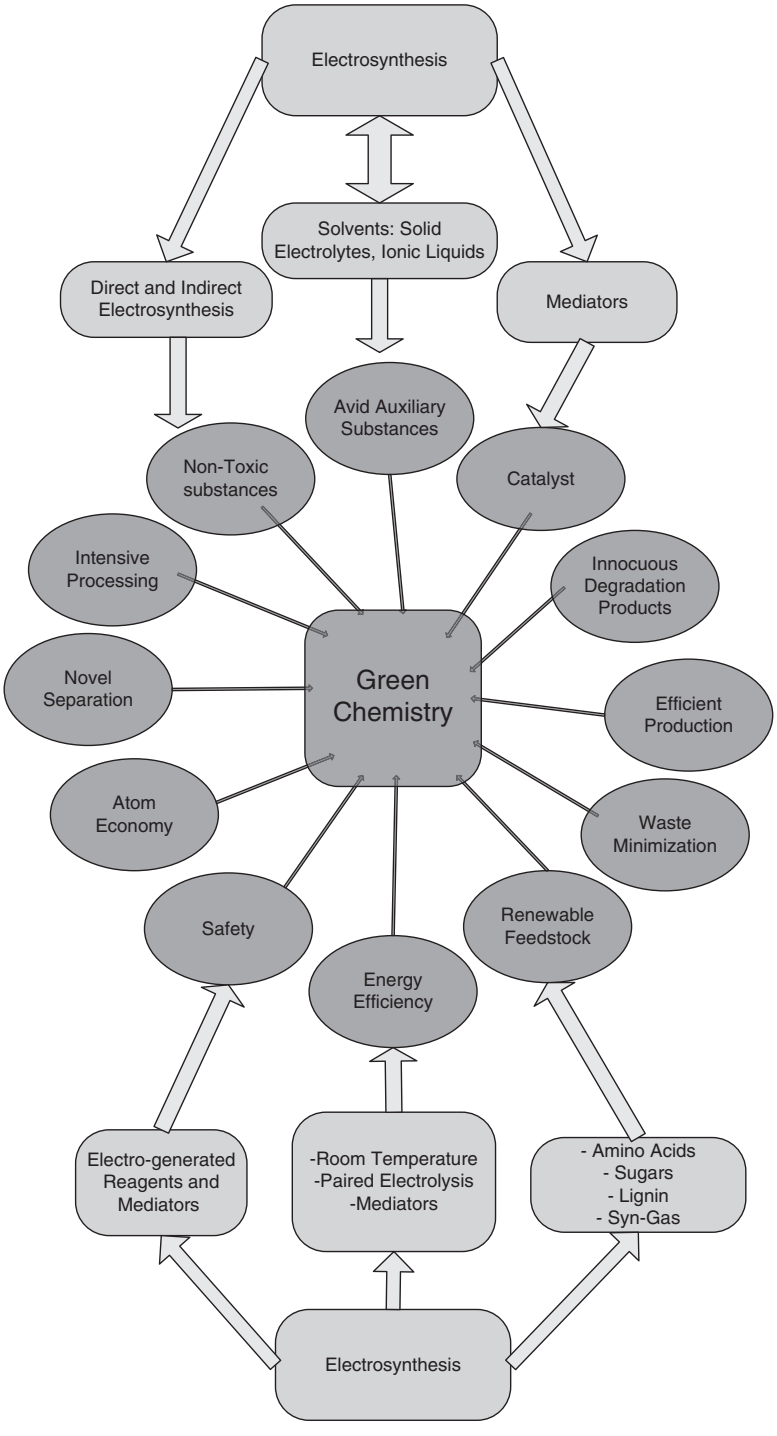

Figure 1.1 Electrosynthesis as a major contributor to green chemistry.

to recover and re-use carbon dioxide, the combustion product. Solutions proposed for this re-use include the catalytic reaction between carbon dioxide and hydrogen to produce methanol, and the catalytic or electrochemical formation of formic acid from carbon dioxide and water. Thus 'Energy Cycles' are envisaged in which hydrocarbon based fuels (methanol, formic acid) are used to produce, for example, electric power by fuel cells and the carbon dioxide generated is reconverted back to fuel. These cycles are energy inefficient as more energy is used in chemical production than is obtained from the chemicals use as fuel. Thus unless the fuel is produced by, say, fermentation, for example ethanol or wood alcohol (methanol) they are not sustainable. Thus a potential fuel cycle based on methanol could be developed in which, for example, methanol is used in a fuel cell.

A similar concept called the 'Hydrogen Economy' was put forward in the 1970s in which hydrogen was proposed as the major energy vector. In practice, water can be used to generate hydrogen and oxygen, by electrolysis. These gases can then be used in fuel cells to generate power. Thus we have an energy system based on water or a 'Water Energy Economy' (Figure 1.2). Although the majority of electricity is generated by fossil fuel combustion, its future generation would need to be based on 'renewable' sources (hydro, solar, wind and wave) or on photochemical or photobiological methods.

Electrochemistry can play a major role for energy and power production and generation in the future and covers applications in storage batteries, super-capacitors, redox batteries, solar cells and fuel cells. The function of the battery for energy storage in portable devices is well established in many markets for medium and small scale power generation. Exciting new battery couples continue to be developed including lithium air and sodium/nickel chloride. For the sustainability of battery technology methods are required to recycle and re-use, in particular, the active battery components. Recycling of lead acid batteries is well established and efficient whilst other battery recycling techniques (e.g. for nickel cells, etc.) are developing.

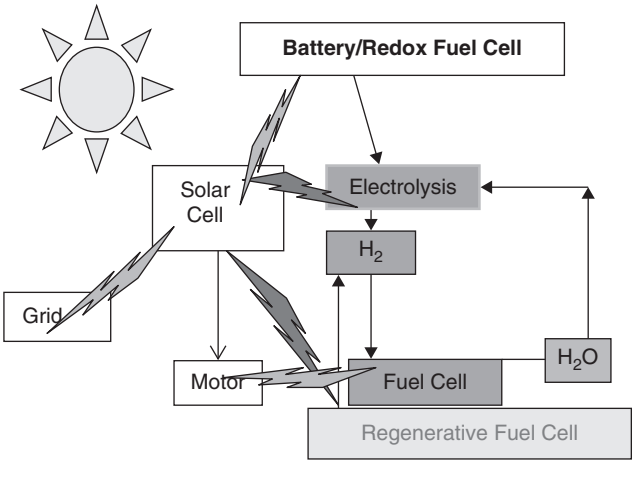

Figure 1.2 Cycle for renewable energy based on solar generation of electricity and water.

1.5 Hydrogen Economy and Fuel Cells

Reliance on fossil fuels, for technology and transportation networks that drive society, puts the world under increasing economic, health and environmental pressures. Fossil fuel supplies are finite and with the projected increased demand due to population growth and industrialization of developing countries, major shortages are inevitable. The use of fossil fuels puts the world population's health at risk through the chemical and particulate pollution it creates. The stability of the earth's climate is threatened by carbon dioxide and other greenhouse gas emissions associated with global warming. Critically, the simple burning of fossil fuels will deprive the world of major materials resource, for example plastics, that underpins technological development and limit our ability to manufacture (Crabtree, 2004).

Commercially available alternatives to the use of fossil fuel reserves that can supply energy in quantities demanded by an increasing world population will only be developed over a relatively long timescale as they will have to be competitive in cost to a large extent with fossil fuels, and based on an appropriate economic infrastructure. Alternatives to fossil fuels do exist, for example in the form of biomass, but production is relatively small, and the ability to provide increasing amounts of such materials to meet the world's demand is uncertain. One promising alternative to fossil fuels is hydrogen, particularly because it can be produced in a number of ways and notably from electricity generated from renewable sources such as hydro, wind, wave, solar energy and biologically (Luzzi *et al*., 2004).

Hydrogen is abundant, in the form of water, and distributed in most habitable regions throughout the world. Using it in an energy system based on hydrogen and electricity would be less constrained by geographical boundaries, as for the current fossil fuel supplies. Hydrogen when reacted with oxygen releases energy in combustion engines or in fuel cells and produces water as the only product. A major attraction of hydrogen is its compatibility with fuel cells and the potentially high efficiencies in electrical (and heat) generation possible.

1.5.1 The Hydrogen Economy

Energy is vital for human prosperity on a global scale, although most countries depend upon fossil fuels as the primary energy source. A move to the use of hydrogen would offer great potential for clean and renewable energy use. Hydrogen technologies, including hydrogen fuel cells, can provide the essential link between renewable energy production and sustainable energy supply and systems. The 'hydrogen economy' is an energy system based on hydrogen for energy storage, distribution and utilization (Figure 1.3) (Crabtree, 2004). The concerns over stability of petroleum and gas reserves and the potential lack of stable energy sources has increased the momentum for government and industry to implement strategies for introduction of hydrogen into an energy system. Hydrogen gas is thus a carrier of energy, in much the same way as electricity, and to be sustainable it must be produced from a natural resource using renewable energy or materials.

Hydrogen is a suitable basis for an alternative energy system because it has a number of attractions but of course there are several challenges to the implementation of hydrogen

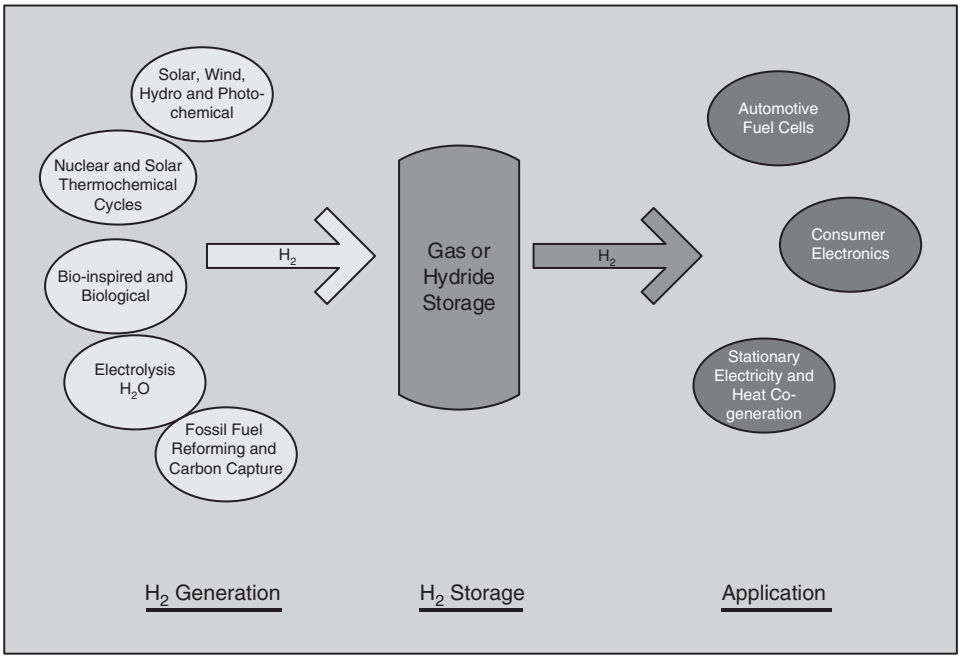

Figure 1.3 The hydrogen economy. A network of primary energy sources geared to hydrogen generation, using hydrogen as an energy carrier to support multiple power applications.

into an energy system and these include both societal and technical barriers as described in Table 1.1.

Hydrogen does not occur in nature as molecular hydrogen, but rather, in chemical compounds such as water, hydrocarbons and carbohydrates. Hence, unlike fossil fuels, it is not directly accessible by extraction or mining and to produce hydrogen, chemical compounds have to be transformed with input of energy. To achieve the benefits of a sustainable hydrogen economy, hydrogen must ultimately be produced from non-fossil fuel resources, such as water, using a renewable energy source. Moreover, more effective means for its storage and distribution to enable its efficient use are needed. Additionally, hydrogen itself is a greenhouse gas that can rapidly scavenge ozone and thus safe and effective containment is required for the minimization of climate change within a hydrogen economy.

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 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 this release. Using reforming and similar fuel conversion processes to produce hydrogen as fuel, does not reduce the use of fossil fuels; they merely change the energy vector. Fuel conversion processes are intrinsically energy inefficient, that is they result in a net loss of usable energy in the conversion process. Hence the realization of a sustainable hydrogen economy requires the rapid development of alternative means of hydrogen production, from renewable sources, together with effective networks of storage, distribution and use, as either a

Table 1.1 Attributes of hydrogen as an energy vector.

Attractions of hydrogen	Challenges for hydrogen
It is the most abundant element in the world, although almost exclusively in combination with other elements, notably water	It occurs almost exclusively in combination with other elements and is not immediately accessible as a fuel without significant energy input
It can be obtained readily from water	Its buoyancy and flammability must be accounted for in its safe use and storage
It has very good chemical activity	Its production is currently mainly from non-renewable fossil fuels
When combusted or reacted with oxygen it has zero emissions characteristics, the product is water	Hydrogen's energy storage and distribution infrastructure is limited worldwide
It has the highest gravimetric energy density of any known fuel	Its containment at technical levels on a volume basis is lower than liquid fuels
It is compatible with both electrochemical and combustion processes	It has unique permeability characteristics through many materials and can result in material embrittlement.
It has very good electrochemical activity	It is a greenhouse gas
It is very compatible with fuel cell applications	There are large investment costs in its manufacture and production for world-wide, large scale use
	There are potentially higher consumer costs in its use
	It is in competition with other energy sources

fuel or as a chemical feedstock for example as Synthesis gas (mixtures 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 due to the fact that fuel cells are one of the cleanest and most efficient technologies for generating electricity. Fuel cells do not directly combust hydrogen with air and thus pollutants commonly produced by boilers and furnaces, are not formed: the only products are electricity, water and heat (Figure 1.4). Fuel cells are an important technology for a wide variety of applications including on-site electric power for households and commercial buildings; auxiliary power to support car, truck, naval and aircraft systems, power for personal, mass and commercial transportation and for portable and mobile power generation. Clearly they are in competition with electrical energy supplied by national grids but can be seen as complementary to a network of energy supply and localized electrical energy production.

There is currently a large gap between the present technologies for hydrogen production, storage and use and that needed for a competitive hydrogen economy. This gap is there because the basic technologies to achieve each of these steps cannot generally compete with fossil fuels in terms of cost, performance, or reliability. For the equivalent amount of energy, hydrogen produced by steam reforming of methane is more expensive than gasoline. The production cost of fuel cells remains high: thousands of pounds per kilowatt of power produced, with mass production set to reduce this cost

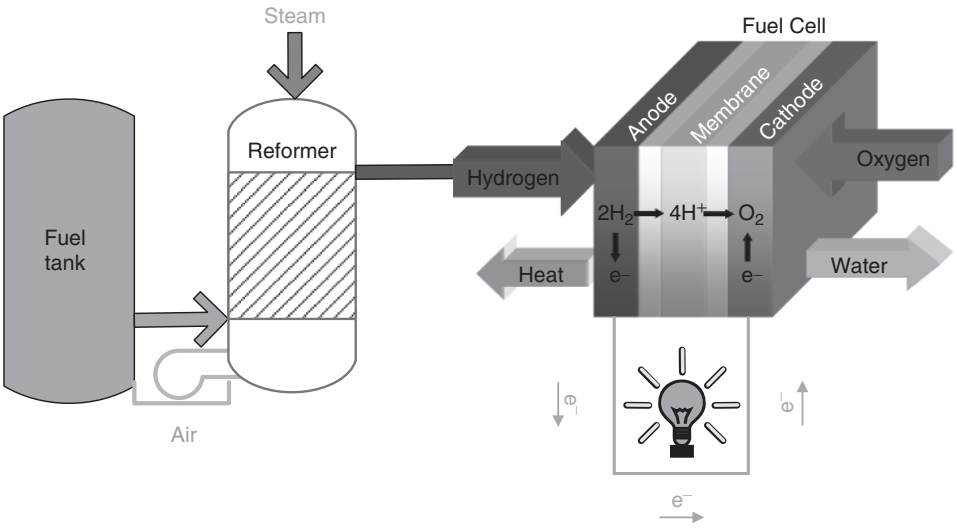

Figure 1.4 Fuel cell energy conversion system (which provides a link between hydrogen economy and efficient electricity generation).

by a factor of 10 or more; compared with around £20 per kilowatt for gasoline engines. The low volumetric energy density of hydrogen stored as pressurized gas or in cryogenic containers, imposes limitations for practical applications, for example to meet the requirement to drive a car up to 500 km on a single tank requires much greater storage volume than when using petrol.

Regardless of these economic and technical constraints the hydrogen economy has enormous appeal, both social and technical, as a solution to the fundamental concerns over future energy supply and environmental impact. Ultimately, a hydrogen economy will be driven by market forces, and consequently governments must play a key role in the move away from fossil fuels to hydrogen technologies. The investments in research and development are large and governmental support in establishing goals, providing research and sharing risk are necessary to see the emergence of a hydrogen economy.

Public acceptance of hydrogen as a fuel is needed for effective implementation of a hydrogen energy system and will be determined by its commercial appeal, ease of use, the convenience and accessibility to supply and filling stations and its record of safety in widespread use. The flammability, buoyancy and permeability characteristics of hydrogen present challenges to its safe use, which are different from, but in principle no more difficult to those of other fuels. Public acceptance of natural gas and other fuels such as liquid petroleum gases (LPG) in transportation and portable and stationary appliances is not an issue and hence hydrogen should not be.

1.5.1.1 Hydrogen Generation, Storage and Use

Progress towards a hydrogen economy is slow, as developments in related technology are largely based on reforming carbon based fuels. Advances in technology include lowering cost and increasing efficiency of fuel reforming and improving the storage capability of, for example, high pressure hydrogen storage and development of efficient hydrogen fuel cells and internal combustion engines. To significantly increase the world's energy

supply, and to decrease carbon emission and air pollutants, efficient hydrogen production must replace fossil fuels using, for example, solar radiation and thermochemical cycles to split water. Hydrogen must also be conveniently stored and readily available for dispensing, using for example portable solid state media.

1.5.1.1.1 Storage of Hydrogen

Electricity is and will remain central to our energy infrastructure. Electricity, when produced from renewable sources, must be used in some way at the rate it is produced. If not converted to power, then the alternative is to store the electricity, for example, in batteries or similar larger devices known as redox batteries (or fuel cells) or to generate hydrogen (or other chemical energy stores). The redox battery, as the name suggests, stores the energy in a similar way to a conventional battery. In this case the store is a liquid (electrolyte), and is analogous to storing the electrical energy in water pumped up hill to a storage reservoir (pumped storage). The energy can then be released on demand, by flowing water through a generator. In the case of the redox batteries, energy is released by running the cell in reverse mode (discharge). Redox batteries offer higher electrical efficiency than pumped water storage, or other systems, but have a greater capital cost of the cell and associated plant.

The storage of hydrogen is one of the fundamental problems facing the evolution of the hydrogen economy. There are currently three principle methods available for hydrogen storage: as a pressurized gas, a cryogenic liquid or a metal hydride. The traditional storage of hydrogen in cylinders as liquid and high pressure gas is conceptually simple and commonplace in industrial facilities. These options are viable for bulk storage and the stationary consumption of hydrogen in large plants that are not restricted by weight and size limitations. These methods may be adequate for current uses of hydrogen but for its use in transportation and small and large scale power generation, more efficient means of hydrogen storage will be required. A principle reason for this is that although hydrogen has one of the highest energy densities based on unit weight, it has one of the lowest energy storage densities based on unit volume at ambient temperature and 100 bar pressure; the hydrogen gas density is only approximately 7.5 kg m^{-3}.

Hydrogen storage requires the reduction in the gas volume and thus to pack hydrogen as close as possible, that is to reach the highest volumetric density, using as little additional material as possible (Zuttel, 2004). To increase the density of hydrogen, either work must be applied to compress the gas, the temperature must be decreased below the critical temperature, or the molecular repulsion reduced through 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 (71 kg m^{-3}).

Hydrogen occurs in many forms; as an anion (H^-) or cation (H^+) in ionic compounds, covalently bonded to other elements, for example with carbon, and behaving like a metal to form alloys or inter-metallic compounds (Zuttel, 2003). Storage of hydrogen chemically with other elements can be achieved with reasonable volumetric energy densities but an important issue for a hydrogen storage system is the reversibility of uptake and release. This aspect is particularly important for transportation application where rapid supply of hydrogen fuel is required. The reversibility criterion excludes all covalent hydrogen–carbon compounds, as hydrogen release requires heating to temperatures

above 800 °C or if the carbon is oxidized. The methods for reversible hydrogen storage which provide a high volumetric and gravimetric density known today are: conventional high pressure gas cylinders and liquid hydrogen, physisorption of hydrogen on materials with a high specific surface area; for example many forms of nanoporous carbon (nanotubes, nanofibres, fullerenes, activated charcoals, etc.); other inorganic nanoporous materials, hydrogen intercalation in metals and complex hydrides and storage of hydrogen based on metals, and 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 and volume to store the gas. Recently 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 volumetric density of 36 kg m^{-3}, which is approximately half that as its liquid form, at the normal boiling point. These types of tank have a storage 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. Of course the issue of compression of hydrogen to these pressures should not be forgotten, that is the energy costs and the need for specialized 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 the pressure applied such that at such high pressures it approaches a maximum in volumetric storage capability (Figure 1.5)

As a fuel hydrogen has high energy storage capabilities (Figure 1.6) with high gravimetric storage capability as a liquid of 38 kWh kg^{-1}. But hydrogen has a relatively low volumetric energy storage capability which is one of the major challenges in its use.

For transportation and other applications where weight and volume are at a premium the storage of hydrogen is a greater challenge. Sufficient fuel must be stored to make it practical to drive distances comparable with petrol powered cars. For example the energy content of 1 kg hydrogen is approximately equal to 3 kg petrol (~4 l). Thus an average tank of some 60 l requires an equivalent storage for 15 kg hydrogen. An 800 bar storage tank (40 kg m^{-3}) would thus need to have a volume for hydrogen of 375 l; that is six times that of a petrol tank (Committee on Alternatives and Strategies for Future Hydrogen Production and Use, 2004).

On a positive note, an attraction 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

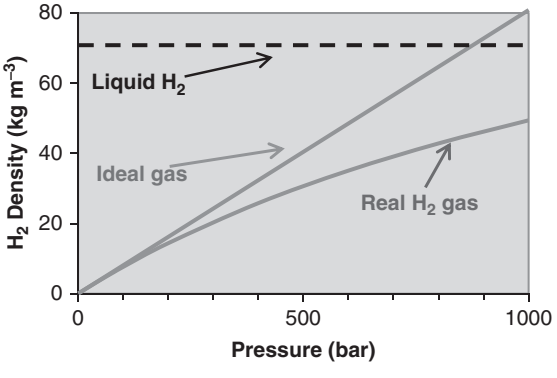

Figure 1.5 Hydrogen density storage.

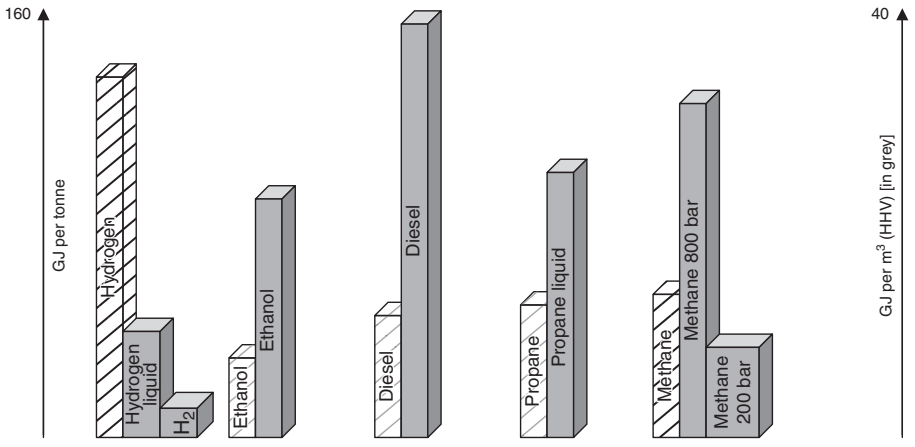

Figure 1.6 Comparison of energy storage of hydrogen with other fuels. Gravimetric and volumetric [in grey] energy storage of hydrogen and typical fuels.

combustion engines. Hence for cars, the hydrogen container is only required to store around half the energy required from petrol. Even so, the energy density of petrol is much greater than hydrogen, in either liquid, hydride or gaseous form. For hydrogen, that added weight of the container is a major fraction of the total weight and significantly affects its ability to compete with petrol.

Cryogenic Hydrogen Storage Storage of hydrogen as liquid can in principle help to meet the requirement for transportation. However, there are significant cost and operational efficiency loss issues with this method. The low critical temperature of hydrogen (33 K), means that the liquid form can only be stored in open systems (21.2 K), as there exists no liquid phase above the critical temperature. The simplest liquefaction cycle is the Joule–Thompson cycle (Linde cycle). The gas is first compressed and then cooled in a heat exchanger, before it passes through a throttle valve where it undergoes an isenthalpic Joule–Thomson expansion, producing some liquid (Gupta, 2008). For hydrogen to cool upon expansion, its temperature must be below its inversion temperature of 202 K. Hydrogen is therefore usually pre-cooled using liquid nitrogen (78 K), before the first expansion step occurs. The cooled gas is separated from the liquid and returned to the compressor via the heat exchanger. The free enthalpy change between gaseous hydrogen at 300 K and liquid hydrogen at 21 K is 11640 kJ kg^{-1}, that is the theoretical energy (work) to liquefy hydrogen from NTP conditions is 3.23 kWh kg^{-1} which is around 10% of the energy content of the stored hydrogen. In practice, a much higher energy consumption is required to liquefy hydrogen; the technical work to liquefy hydrogen is around 15.2 kWh kg^{-1}, nearly 40% of the lower heating value of hydrogen combustion. In addition there are evaporation losses that can occur when the low-pressure tanks are filled and when it is stored. The loss of cryogenic hydrogen by evaporation is caused by heat transfer between the tank and the environment. A standard vehicle carrying a conventional, low-pressure (5 bar) cryogenic hydrogen fuel tank would lose around 1% of the hydrogen fuel per day due to evaporation.

The problems with storing pure hydrogen has increased interest in alternative methods using adsorption, absorption and metal complexes.

Physisorption of Hydrogen Hydrogen absorption on surfaces is a potential method for high hydrogen storage densities and also for fast adsorption and desorption cycling (Klebanoff, 2012). Hydrogen can be adsorbed in molecular or atomic form on suitable surfaces, using pressure and temperature (and electrochemical potential) to control its surface structure and bonding strength. Adsorption has been explored mainly for carbon substrates. In general, a major challenge is controlling the bonding and kinetics of multiple layers of hydrogen. Materials with a large specific surface area, for example activated or nano-structured carbon and carbon nanotubes (CNTs), are possible substrates for physical adsorption. The main difference between CNTs and high surface area graphite as absorbents lies in the curvature of the graphene sheets compared with the cavity inside the tube. In microporous solids with capillaries with widths less than a few molecular diameters, the potential fields from opposite walls overlap. Hence the attractive force acting upon adsorbate molecules increases in comparison with that on a flat carbon surface which contributes to increasing adsorption capabilities (Jopek *et al*., 2012). Other nanoporous materials than carbons have been investigated for hydrogen absorption such as microporous metal–organic framework and zeolites, of different pore architecture and composition, in the temperature range 20–300 °C and at pressures of 25–100 bar.

The main advantages of hydrogen storage by physisorption are the low operating pressure, the relatively low material costs involved and potential simple storage system design. The disadvantages include the currently relatively small gravimetric and volumetric hydrogen density on carbon, coupled with the low temperatures needed. The experience to date with carbon suggests that multiple layers are needed for effective storage capacity.

Metal Hydrides Hydrogen can be stored in the form of metal hydride (Klebanoff, 2012). Metal hydrides are formed by the reaction of metals or metal alloys with hydrogen but can differ by the nature of the bond between the metal (or alloy) and hydrogen. The nature of that bond can be metallic, ionic, covalent or complex (e.g. mixed covalent–ionic). Because hydrogen is chemically bonded to the alloys, heat is required to release it. In general, the materials should have the following characteristics:

- High mass absorption capacity (ratio of hydrogen mass to mass of metal).
- Fast absorption and desorption kinetics.
- Low equilibrium pressure at atmospheric temperature. This is to avoid leaks and to secure containment.
- Insensitivity to impurities in the hydrogen stored. Impurities can irreversibly react with the hydrides.
- Low manufacturing cost. Simple to make and use and a small amount of energy in production.
- Safe to handle.

To achieve high gravimetric storage capacity requires strong chemical bonds between hydrogen and light host materials thus creating stable compounds, such as lithium borohydride ($LiBH_4$). The hydrogen atoms occupy close and usually ordered spaces (often interstitial sites) in the atomic lattice of the metal atoms. The result is extremely compact packing of hydrogen atoms, usually giving volumetric hydrogen densities much higher than is contained in an equivalent volume of liquid hydrogen. However, to achieve fast

cycling for everyday use requires weak chemical bonds, fast kinetic, and short diffusion lengths, as potentially found in surface adsorption. Thus, the high capacity and fast recycling requirements result in a compromise in material choice. In addition, the problem is that hydrides are usually burdened with relatively heavy atoms, so that gravimetric hydrogen density is not so impressive.

Hydrides can be alloys of rare earth, transition metals and magnesium. The families of metal hydrides are shown in Figure 1.7. The metal hydrides can be broadly defined as simple, complex or hydrogen absorbers. A versatile set of metallic hydrides is those formed with inter-metallic compounds; in the simplest case the ternary system AB_xH_n. Several families of inter-metallic compounds (Figure 1.7) are interesting for hydrogen storage and consist of an element, A, with a high affinity to hydrogen, and element B with a low affinity to hydrogen. Element A is usually a rare earth or an alkaline earth metal and tends to form a stable hydride. Element B is often a transition metal and forms only unstable hydrides. They often include Ni as it is an excellent catalyst for hydrogen dissociation. Some well-defined ratios of B:A ($x = 0.5, 1, 2, 5$), form hydrides with a hydrogen to metal ratio of up to two.

The AB_5 alloys form the basis of commercial NiMH batteries (see Chapter 7). The AB_2 alloys use typically Ti, Zr and Hf for the A component and V, Cr, Mn, Fe for the B component. The AB_5 and AB_2 alloys, decrepitate (self pulverize) into powder. The AB alloys are based on TiFe with substitution of Mn and Ni for part of the Fe. The AB range of metal hydrides can absorb large amounts of hydrogen at a constant pressure, that is the pressure does not increase with the amount of hydrogen absorbed. The characteristics of hydrogen absorption and desorption can be tailored by partial substitution of the constituent elements in the host lattice which can result in some of these metal hydrides being capable of absorption and desorption of hydrogen around ambient temperature and atmospheric pressure.

One of the most interesting features of metallic hydrides is the extremely high volumetric density of hydrogen atoms present in the host lattice. Complex hydrides involve mixtures of ionic species and covalently bonded complexes of hydrogen and

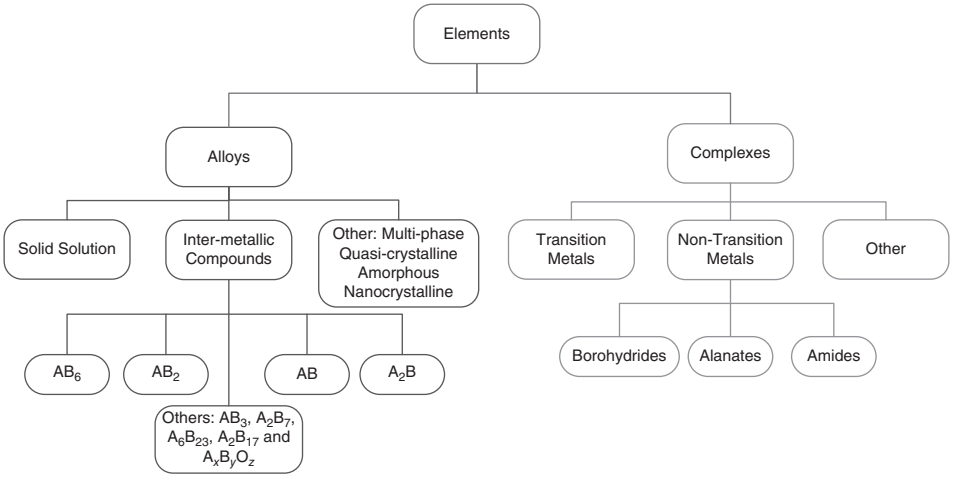

Figure 1.7 The family of metal hydrides.

non-transition or transition metals. A complex hydride such as $TiFeH_2$ has a hydrogen energy storage capability of 102 kg m^{-3}, and Mg_2FeH_6 and $Al(BH_4)_3$ of 150 kg m^{-3}. Metallic hydrides, for example $LaNi_5$ can reach a volumetric hydrogen density of 115 kg m^{-3}. Most metallic hydrides absorb hydrogen up to a hydrogen to metal ratio of H/M = 2. Greater ratios up to H/M = 4.5, for example for $BaReH_9$, have been found, although hydrides with a hydrogen to metal ratio >2, are ionic or covalent compounds and belong to the complex hydride group.

Although metal hydrides store large amounts of hydrogen very effectively, in a safe and compact way, all the reversible hydrides, working around ambient temperature and atmospheric pressure, consist of transition metals and their gravimetric hydrogen densities are limited to less than 3.0 mass%.

A family of non-transition metal complexes under consideration as hydrogen storage media are called the alanates, for example catalysed $NaAlH_4$, composed of a tetrahedral, methane like AlH_4^- or BH_4^- anion and a metal cation. By doping with selected titanium compounds, the dehydriding of anionic aluminium hydrides can be kinetically enhanced and rendered reversible under moderate conditions in the solid state. Recent catalytically enhanced hydride materials, based on the aluminium hydride complex (AlH_4), and alkali and non-alkali metals (e.g. Na, Li, K, Mg, Zr), have shown the potential to store 5 wt% hydrogen and greater, and release hydrogen below 200 °C; thereby overcoming the limitations of many metallic (interstitial) hydrides. $Mg(AlH_4)_2$ has a storage capacity of 7 wt% hydrogen. Although alanates represent promising storage candidates, they involve high cost in manufacturing.

Table 1.2 shows the volume density of hydrogen stored in several compounds and liquid hydrocarbons (Schlapbach and Zuttel, 2001). The volumetric energy densities of those compounds (except the graphite monolayer) 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. Hydrocarbon based compounds, for example methanol and octane, are both high volume density hydrogen storage compounds and high energy

Table 1.2 Comparison of energy density storage characteristics for hydrogen.

Method	Storage capacity (wt% hydrogen)	Volumetric capacity (kg H_2 l^{-1})
Metal hydrides $FeTiH_2$ and $LaNi_5H_6$, Mg_2NiH_4	~2	0.115–0.145
Pressurized H_2 gas (330 bar)	5	0.05
Cryogenic liquid H_2 (20 K)	100	0.066
Solid hydrogen	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

density fuels. An alternative to 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 $LiBH_4$ (18 wt%) which makes it an ideal hydrogen storage material for mobile applications. $LiBH_4$ desorbs three of its four hydrogens upon melting at 280 °C and decomposes into LiH and boron.

$$LiBH_4 \leftrightarrow LiH + B + 1.5\,H_2$$

The desorption of hydrogen on these compounds can be catalysed by adding SiO_2 and significant thermal desorption has been observed, starting at 100 °C.

Prospects of Hydride Storage The advantage of metal hydrides for fuel storage is their compactness relative to the use of gas cylinders. The hydride can store in the order of 2 or more kg of hydrogen per unit volume of storage space. For example, hydrides can hold 5 kg of hydrogen in one-half to one-third the volume of a gaseous hydrogen tank at 330 bar. In addition, metal hydrides are also inherently safe as hydrogen is chemically bonded to the hydrides, in a solid state, and is held at a low pressure and will thus not readily discharge on impact. The biggest drawback of metal hydrides is that they are heavy. A metal hydride storage system that can hold 5 kg of hydrogen, including the alloy, container, and heat exchangers, would weigh approximately 300 kg. This mass storage density is much lower than most chemical compounds and liquid or high pressure stored hydrogen. However, the volumetric hydrogen storage capabilities are as good as or better than most chemical compounds, for example methanol. In transportation applications this would lower the fuel efficiency of the vehicle. Table 1.2 compares the energy density characteristics of hydrogen stored as hydride and under pressure or as a cryogenic liquid.

Although the metal hydride fuel has attractive hydrogen storage capacities, when introduced into a complete system, which includes tanks and heat exchangers for use of heat to release the gas, the storage capabilities are less than that of cryogenic storage. This factor is a more important issue for transportation applications than for stationary applications. The challenges for on-vehicle hydrogen storage and use is overcoming the conflict between the necessary high capacity and fast cycling performance under on-board conditions of (0–100 °C, 1–10 bar). Many bulk hydrogen storage compounds, such as metallic magnesium nitrogen hydride, have high volumetric hydrogen densities but require temperatures of >300 °C at 1 bar to release their hydrogen.

A major issue for most metal hydrides, the enthalpy and entropy of formation are negative, which leads to a significant heat evolution during hydrogen absorption. The same heat has to be provided to the metal hydride to desorb the hydrogen (endothermic reaction). For a stable hydride, such as MgH_2, the heat necessary for the desorption of hydrogen, at 300 °C and 1 bar is approximately 25% of the higher heating value of hydrogen. For fuel cell applications it is envisaged that the heat can be provided by the 'waste' heat produced by the fuel cell.

The stability of metal hydrides is usually presented in the form of Van't Hoff plots of desorption pressure against inverse temperature (Figure 1.8). The slope of the plot gives the heat of adsorption. The most stable binary hydrides have enthalpies of formation of around −226 kJ mol^{-1} H_2 (e.g. HoH_2). The least stable hydrides have positive enthalpies of formation (e.g. $FeH_{0.5}$, ~+20 kJ mol^{-1} H_2). Unfortunately, most metal hydrides do not exhibit good adsorption/desorption characteristics. Most lie outside the practical range for fuel cells of 1– 10 bar pressure and 0–100 °C, as indicated in Figure 1.8.

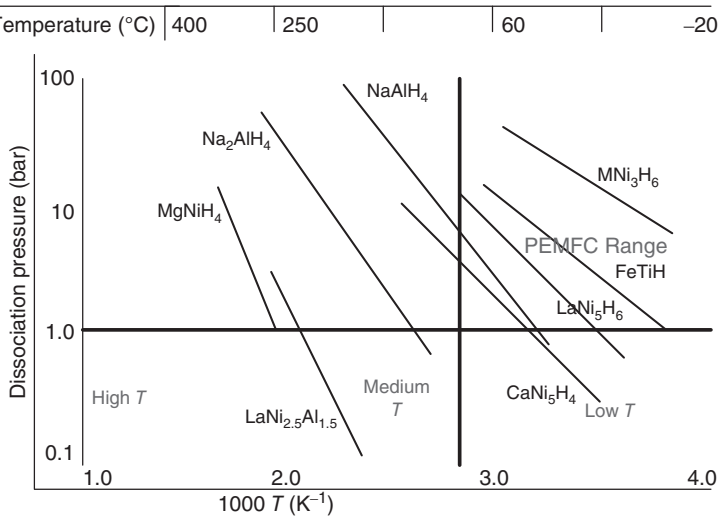

Figure 1.8 Pressure–temperature relationship (Van't Hoff) for metal hydrides. PEMFC, polymer electrolyte membrane fuel cell.

1.5.1.1.2 Generation of Hydrogen

Hydrogen can be produced by several methods which include chemical, electrochemical, catalytic, thermal and biological processes (Backus, 2006). Hydrogen production routes can be put into four general categories:

- Fossil fuel and chemical reforming
- Renewable energy
- Biological
- Nuclear fission/fusion

Hydrogen has historically mainly been produced from coal, gasoline, natural gas and other fossil fuels. Some fossil fuels have high hydrogen to oxygen ratios, making them suitable for reforming processes. The fossil fuel with the highest hydrogen to carbon ratio is natural gas (mainly CH_4). 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 sulfur (mainly as H_2S); 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 sulfur. For transmission of natural gas, odour compounds such as mercaptans, thiophenes and diethyl sulfide are added for safety. Such additives have implications in the processing of natural gas to hydrogen and its potential use in fuel cells, that is catalyst poisoning in gas processing and in fuel cells, and thus must be removed before use.

Gasification and pyrolysis of biomass presents a route to more sustainable hydrogen production than the use of fossil fuels. Using biological waste materials as feedstock for hydrogen production offers a possible renewable, sustainable method of hydrogen generation. Thermal processing techniques for plant derived material (biomass) and fossil fuels are similar in many respects, including the downstream unit operations

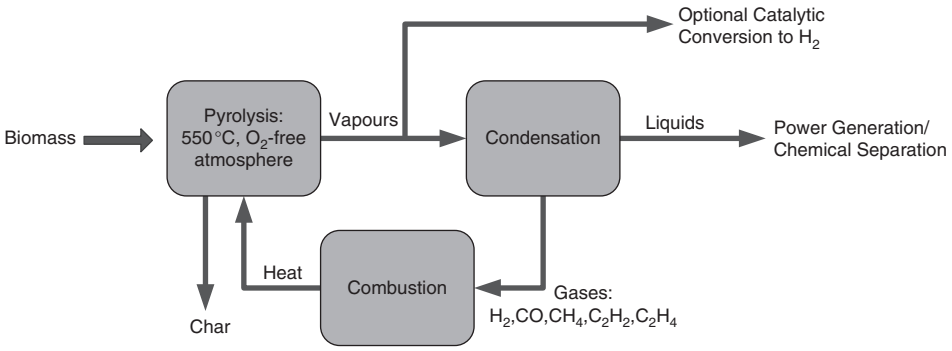

Figure 1.9 Process for biomass liquefaction by pyrolysis. *Source:* Adapted from Briens *et al.*, 2008.

for hydrogen separation and purification. Hydrogen can be produced via pyrolysis (Figure 1.9) or gasification of agricultural residues, agricultural and municipal wastes, and so on or biomass ideally grown for energy use (Briens *et al.*, 2008). Pyrolysis and gasification are related processes which use heating with limited oxygen.

Currently around 95% of the hydrogen produced worldwide is from hydrocarbons using typically reaction with steam, with the remainder from the electrolysis of water. The hydrogen economy will need to rely on inexpensive and efficient routes to create hydrogen in sufficiently large quantities from non-fossil natural resources. Only around 5% of hydrogen is produced from renewable energy sources using electrolysis of water. Estimates of hydrogen requirements vary from country to country, but the quantities are massive and orders of magnitude greater than current production. A 50 million kg per year hydrogen production (approximately the current worldwide production) would be sufficient to fuel around 225 million cars (at 50 miles per kg of hydrogen and 10 000 miles per year); only around 25% of the worldwide numbers of cars. 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 and natural carrier of hydrogen, with a volumetric 'hydrogen energy density' of approximately 110 kg m^{-3}. 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 use of hydrogen, at point of use, in relatively small quantities, as it does not demand a substantial requirement for storage. Compared with steam reforming, electrolysis is expensive: the electricity required can account for around 80% of the cost of hydrogen generation. Notably, electrolysis, when coupled with a renewable electrical energy source, can provide a clean and renewable source of hydrogen. In other circumstances, off-peak electricity can reduce the cost of electrolysis.

The conversion of sunlight to hydrogen is potentially an important development in water splitting (Kahn *et al.*, 2002). Established technology splits water in two steps: photovoltaic cells convert solar radiation to electricity which then powers separate electrolysis cells to electrolyse water to hydrogen. Photovoltaic conversion occurs with varying efficiency depending upon the semiconductor material used. High efficiency up to 32% has been achieved with expensive single crystal semiconductors, used in multi-junction

stacks, while only around 3% is achieved with much cheaper organic semiconductors. The cost of delivered electricity is similar in both cases. The solar conversion to electricity and water splitting can also 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 chemically and physically robust semiconductor materials that satisfy the competing requirements of efficient photon absorption and water splitting.

The use of biological processes to produce methane by anaerobic fermentation is established technology worldwide. Using the methane containing biogas to produce hydrogen by a reforming process is seen as one method to use the 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. An approach to hydrogen production which is potentially sustainable is through bioprocesses, which can be achieved by several approaches (Gloaguen *et al*., 2002):

- biophotolysis
- indirect biophotolysis
- photofermentations
- dark fermentations

Photosynthesis is a process in which plants convert carbon dioxide, water and sunlight producing hydrogen and oxygen and use the hydrogen to manufacture carbohydrates in their leaves and stalks and emit oxygen. The natural mechanisms for producing hydrogen involve elaborate protein structures in plants: for instance, a catalyst based on manganese–oxygen clusters to split water. Similarly, single cell organisms, such as algae and bacteria, produce hydrogen at ambient temperatures by molecular level processes. For example, bacteria use iron and nickel clusters as the active elements to combine protons and electrons into hydrogen. Bacteria can also split hydrogen into protons and electrons.

Dark fermentation, using anaerobic bacteria grown in the dark, can produce hydrogen from carbohydrate substrates. The dark fermentations produce a mixed biogas containing primarily hydrogen and carbon dioxide and smaller amounts of methane, carbon monoxide and hydrogen sulfide. The fermentations can operate in different temperature ranges: mesophilic (25–40 °C), thermophilic (40–60 °C), extreme thermophilic (65–80 °C) and hyperthermophilic (>80 °C). Several bacteria and algae, for example *Escherichia coli*, *Enterobacter* aero-genes, *Clostridium butyricum*, *Clostridium acetobutylicum* and *Clostridium perfringens*, are active for hydrogen production under anaerobic condition. The most effective hydrogen-producing microorganism is *C. butyricum*. *Escherichia coli* and *Enterobacter* aero-genes are facultative anaerobes and ferment glucose and lactose to produce hydrogen. The amount of hydrogen produced depends upon the substrate, fermentation pathway and end product. In practice for high hydrogen yields the end products should be acetates and butyrates and not reduced end products such as alcohols (propionate) and lactic acid.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_2CH_2CH_2COOH + 2H_2 + 2CO_2$$

These latter species still contain large amounts of hydrogen that has not been liberated. Hydrogen production is very sensitive to process conditions and in particular hydrogen

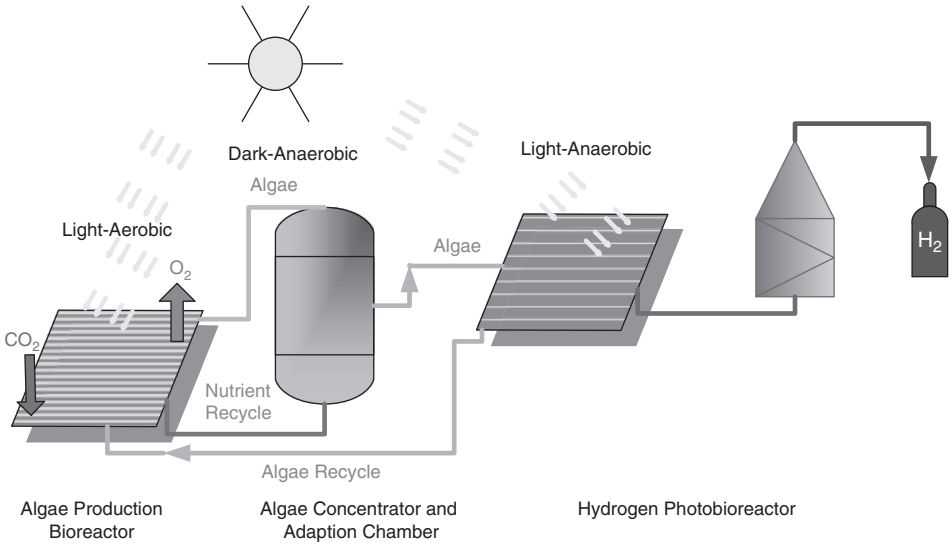

Figure 1.10 Hydrogen generation based on an indirect photobiological process. *Source:* Adapted from Luzzi *et al*., 2004.

concentration. As hydrogen concentrations increase the metabolic pathway shifts to the production of more reduced substrates and thus lower hydrogen yields. Continuous hydrogen production requires hydrogen partial pressures of <50 kPa at 60 °C.

The above approaches are not used commercially and thus a large amount of research and development is required in the future. One system for hydrogen generation based on an indirect photobiological process is shown in Figure 1.10 (Luzzi *et al.*, 2004). In this system sunlight and CO_2 are used to produce algae (aerobically). The produced algae are then concentrated and used to from H_2, anaerobically. The projected cost of hydrogen generation would be ~US$10 per GJ hydrogen based on a solar to hydrogen conversion efficiency of 10%. The photobioreactor costs are on the order of US$100 m^{-2} and amount to 50% of the total cost.

1.5.1.1.3 Solar Hydrogen

Hydrogen can be produced in many ways from solar energy using only water as the chemical source. An example is the coupling of high-temperature thermochemical processes with concentrated solar power. Thermochemical cycles operating at elevated temperatures facilitate fast reaction kinetics (Grochala and Edwards, 2004). Heat sources include solar collectors operating up to 3000 °C or nuclear reactors designed to operate between 500 °C and 900 °C. Many chemical cycles have been proposed, including systems based on sulfur–iodine operating at 850 °C, calcium–bromine at 750 °C, and copper–chlorine at 550 °C. These processes in principle offer a sustainable energy source and the potential to be more cost-effective and more energy-efficient than the solar electric power generation options coupled with conventional electrolysis. However, there are many challenges to their development including operation at the required high temperatures, a high intensity of radiation, dealing with the complication of integrating the chemical processing into a concentrating solar plant, and sufficient land space to collect and concentrate the radiation.

Table 1.3 Methods for converting solar energy into hydrogen.

Solar energy						
Thermal energy			Electrical energy		Photons	
Thermolysis	Thermochemical cycles	Hybrid processes	Electrolysis	Hybrid processes	Photocatalysis	Biophotolysis
		Thermochemical and electrolysis		Photoelectrolysis		
		Heat and electrolysis in steam electrolysis				

In addition to using the heat from the sun in thermochemical cycle processes the energy can be used in other ways to produce hydrogen, as illustrated in Table 1.3. One example is a high temperature solar driven thermochemical process based on the use of metal oxides (e.g. ZnO). Zinc oxide can be reduced to zinc in an exothermic reaction and the zinc is then used to reduce water to generate hydrogen:

$$2ZnO + \text{solar energy} \rightarrow 2Zn + O_2 \ (\Delta H_{1700\,^\circ C} = 557 \text{ kJ mol}^{-1}) \text{ endothermic}$$

$$Zn + H_2O \rightarrow ZnO + H_2 \ (\Delta H_{450\,^\circ C} = -107 \text{ kJ mol}^{-1}) \text{ exothermic}$$

Decomposition of zinc oxide takes place at around 1700 °C using solar energy. Zinc is then reacted with water at around 450 °C to produce hydrogen and zinc oxide which is then recycled.

Another example is the use of highly concentrated sunlight to generate the high temperatures (1600–2000 °C) needed to split methane into hydrogen and carbon. The process achieves extremely high reaction rates at these temperatures:

$$CH_4 \ (-76 \text{ kJ mol}^{-1}) + \text{heat} \ (-890 \text{ kJ mol}^{-1}) \rightarrow C \ (-394 \text{ kJ mol}^{-1}) + 2H_2 \ (-286 \text{ kJ mol}^{-1})$$

The process is inherently simple and both hydrogen and carbon could be used to generate electricity in fuel cells. The electricity generated from the direct carbon fuel cell could also be used to generate hydrogen by electrolysis. The process offers reductions in the fossil fuel use per kilo of hydrogen produced, in comparison with steam reforming and a reduction in the carbon dioxide emissions (but not eliminations of such), from the combined use of the sun's thermal energy and the efficient fuel cell systems.

1.5.2 Fuel Cells

Hydrogen is an ideal fuel for use in fuel cells which can be used to power a broad base of electrical technology and transport systems (cars, buses, ships), consumer electronics, and generate community heat and light. The higher efficiency of fuel cells, currently >60% compared with approximately 22% for gasoline or 45% for diesel internal combustion engines, will dramatically improve the efficiency of future energy use.

A basic fuel cell operates like a battery and is based on two electrochemical reactions separated by a thin electrolyte to form an electrochemical cell. Unlike a battery, a fuel cell

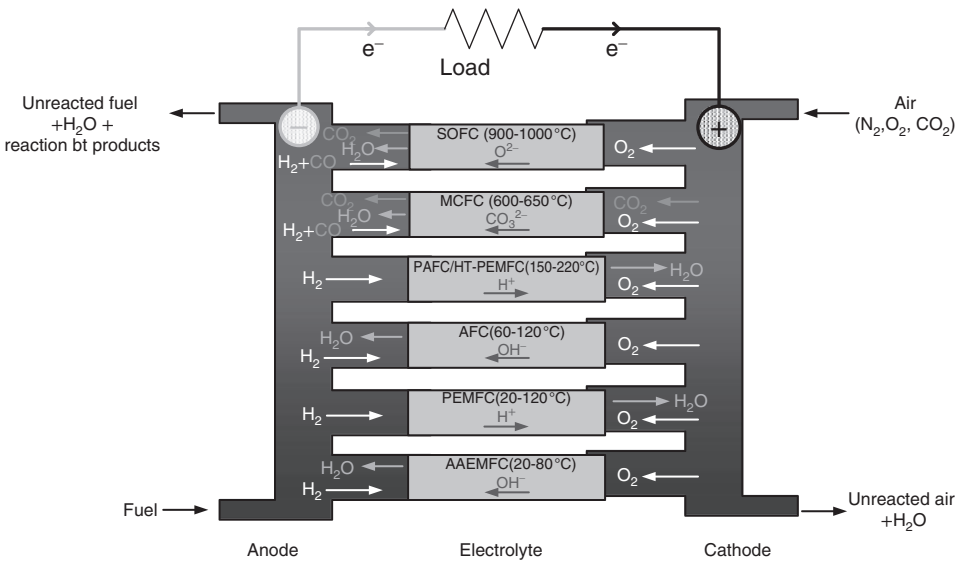

Figure 1.11 Fuel cell operations and types.

does not need to be electrically recharged; it will continue to produce energy in the form of electricity (and heat) as long as fuel is supplied. The fuel cell converts the chemical energy of a fuel directly into electrical energy to produce power (Figure 1.11) (Larmanie and Dicks, 2003). In one type of a typical fuel cell, hydrogen gas reacts electrochemically at one electrode (anode) and is converted into protons (hydrogen ions) and electrons. The protons move through the electrolyte to the other electrode (cathode), where they combine with oxygen (typically in air) and the electrons to form water, as liquid, vapour (or steam).

Because the intermediate steps of producing heat and mechanical work typical of most conventional power generation methods are avoided, fuel cells, unlike heat engines, are not thermodynamically limited by the Carnot efficiency, and offer power generation with high efficiency and low environmental impact. To date there have been 5 fuel cell types developed as viable systems for a range of power applications. These fuel cells, are classified in terms of the electrolyte and operate at very different temperature ranges. High temperature cells operate at temperatures between 600 °C and 1000 °C, as in the case of the molten carbonate and the solid oxide cells. Low temperature cells include the phosphoric acid, alkaline and the solid polymer electrolyte cells which operate at temperatures of 200 °C and below. Other types of fuel cells continue to be developed to operate with different electrolytes and different fuels, such as carbon as mentioned above.

Growth in fuel cell research and technology is due to its potential to provide a continuous supply of clean and efficient power from hydrogen. However, this research and development does not directly tackle the growing needs for sustainable energy generation. Fuel cells can use other chemical fuels based on carbon, such as alcohols and methane but systems are less efficient and more expensive and complex, than those using hydrogen. If these carbon based fuels are produced from sustainable sources, then fuel cells can make a real contribution to their more efficient use in energy generation.

Research is underway to indirectly use fuel cells to capitalize on some of these potential fuel sources, for example through purification (and reforming) of biogas. The world has an abundant resource of sustainable carbon based 'fuels' which are produced 'naturally' or via industrial processes in the form of wastes or by-products. Most of these carbon materials are currently not immediately viable fuels for current chemical fuel cell technology. Development of a technology which could directly use such carbon sources would provide an opportunity to make a major contribution to energy requirements. Biological fuel cells (BioFCs) have the potential to directly convert a wide range of carbon sources (e.g. urea, waste, sludge, etc.) into electrical energy. BioFCs utilize the properties of whole organisms or isolated biomolecules for direct production of electrical energy from bioelectrochemical reaction of the carbonaceous fuel (in an anaerobic anode compartment) with oxygen (in air) at the cathode. They fall into two broad classes, microbial fuel cells (MFCs) and enzyme based fuel cells. Their development could also provide a means of simultaneously reducing waste treatment costs associated with many waste carbon sources, and remove much of the cost of storage and distribution of the fuel substrate, unlike conventional hydrogen fuel cells. MFCs are an emerging technology which holds promise towards sustainable power generation and wastewater treatment along with broad applications in areas of the life sciences. The MFC has potential applications in several areas including wastewater treatment and energy recovery, renewable energy generation from biomass, onsite power generation in remote areas and bioremediation of petroleum contaminants in the groundwater.

Although fuel cells are generally more efficient than internal combustion engines, there can be good reasons for simply burning hydrogen in heat engines for transportation. Jet engines and internal combustion engines can be modified relatively easily to operate with hydrogen instead of hydrocarbon fuels. Internal combustion engines are up to 25% more efficient using hydrogen compared with gasoline and they produce no carbon emissions. Commercial airliners with jet engines modified to burn hydrogen (Hoffmann, 2001) and cars powered by hydrogen internal combustion engines, that achieve a range of 300 km, have been tested. Networks of hydrogen filling stations are being implemented in areas of the US, Europe and Japan giving some access to hydrogen fuel for internal combustion powered vehicles, although much greater networks will need to be in place to meet the requirements of fuel cell based power systems.

The versatility of fuel cells makes them workable in nearly any application where electricity is useful. Stationary plants already provide power capabilities greater than 200 kW of neighbourhood electrical power with efficient operation. Such plants can connect to the electrical grid to share power but are independent of the grid, and provide back-up power, in case of grid failure. Smaller scale residential uses of fuel cells to generate electricity and heat are developing rapidly.

1.6 Conclusions

Sustainability in chemicals and energy supply is essential for the expanding world population. Electrochemistry plays a significant role in providing chemicals and energy to meet this expansion. The demand worldwide for energy is growing rapidly, with an increasing emphasis being placed on providing sustainable sources of energy. Major efforts are thus being put into technologies based on renewables which use wind or solar

power to produce electricity and transform biomass of various forms. The electricity thus generated is the driving force behind electrochemical technologies which support chemical synthesis, power generation and energy storage. For a hydrogen based energy system to become a competitive option and for fuel cells to become the preferred power sources, significant developments in technology and basic research in materials and design are still required, particularly regarding economic cost targets. Fuel cells are seen as an ideal partner to hydrogen to link into electrical supply chains/grids and not a replacement of such.

Using biomass, fermentation, photobiological methods and algae offer alternative ways of producing hydrogen (or methane) from plant or waste materials. As yet none of these technologies can compete economically with the generation of hydrogen from fossil fuels using thermal based processes such as reforming. Many of the processes based on renewables or sustainable materials have limitations in efficiency, and involve high process plant costs. Fuel cells are seen as one means of efficiently converting the chemical energy inherent in such fuels into electrical energy.

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