Pathways to hydrogen as an energy carrier

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When hydrogen is used as an alternative energy carrier, it is very important to understand the pathway from the primary energy source to the final use of the carrier. This involves, for example, the understanding of greenhouse gas emissions associated with the production of hydrogen and throughout the lifecycle of a given utilization pathway as well as various energy or exergy1 efficiencies and aspects involved. This paper which is based on a talk given at the Royal Society in London assesses and reviews the various production pathways for hydrogen with emphasis on emissions, energy use and energy efficiency. The paper also views some aspects of the breaking of the water molecule and examines some new emerging physical evidence which could pave the way to a new and more feasible pathway.

A special attention will be given to the use of the renewable energy pathway. As an example of a hydrogen society that could be based on renewable primary energy, the paper describes the hydrogen society experiments in Iceland as well as unconventional hydrogen obtained from geothermal gases. In the light of our experience, attempts will be made to shed light upon drivers as well as obstacles in the development of a hydrogen society.

Keywords: hydrogen; production; raw materials; utilization; emission; life cycle

1. Introduction

The realization that humankind is at a crucial crossroads regarding future energy policy (Smil 2003) has rekindled interest in hydrogen as an energy carrier. Hydrogen, the most common element of the universe, is bound in huge deposits of various chemical compounds on Earth. A variety of routes are possible in order to derive hydrogen from a diverse range of primary feedstock. These include fossil fuels with emphasis on natural gas, but also oil and coal, in addition to biomass and water which plays an important role in most processes in one way or another (table 1). The primary energy resources also vary greatly, not least as regards their resources on Earth. The main criteria for production are capital and maintenance costs, efficiency, flexibility in design and operation, safety and hazard risk management—all including the condition that waste minimization is always kept in mind. To meet this last requirement, a so-called life cycle analysis (LCA) is done on every pathway studied. LCA is a technique for quantifying and assessing the inputs and outputs affecting environmental

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1 More commonly known to physicists as ‘availability’.

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Table 1. Hydrogen production divided into three primary methods with different processes and feedstocks. Notice the role of water and the vastly dominating proportion of the water resource on Earth. The quantities of the resources are roughly estimated. The mass proportion of hydrogen in water is approximately 11% but 25% in natural gas. In the utilization of hydrogen in fuel cells, internal combustion engines or turbines, the water is returned to the atmosphere and re-enters the hydrological cycle. In the last column, comments are made of major life cycle aspects and emissions associated with each pathway.

<table>
<thead>
<tr>
<th>primary method</th>
<th>process</th>
<th>primary feedstock</th>
<th>other feedstock</th>
<th>energy</th>
<th>quantity on earth (gigaton level)</th>
<th>carbon footprint or emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermal</td>
<td>steam reforming</td>
<td>natural gas</td>
<td>water</td>
<td>heat</td>
<td>345 USGS (2000)</td>
<td>carbon sequestration needed</td>
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<td></td>
<td>gasification</td>
<td>coal</td>
<td>water, oxygen</td>
<td>steam at high T and P</td>
<td>400 Smil (1987) and Laherrère (2000)</td>
<td>carbon sequestration needed essentially renewable</td>
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<td></td>
<td>pyrolysis</td>
<td>biomass</td>
<td>oxygen</td>
<td>moderately high temp steam</td>
<td>6200 Rogner (1997)</td>
<td>carbon sequestration needed essentially renewable</td>
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<tr>
<td></td>
<td>thermochemical</td>
<td>water</td>
<td></td>
<td>nuclear</td>
<td>1.400 000 000 (USGS incl. oceans)</td>
<td>nuclear waste disposal problems emissions mostly related to life cycle minor emissions</td>
</tr>
<tr>
<td>electro</td>
<td>electrolysis</td>
<td>water</td>
<td>renewables incl. solar wind, hydroelectric</td>
<td>1.400 000 000 (USGS incl. oceans)</td>
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<tr>
<td>chemical</td>
<td>photoelectro-</td>
<td>water</td>
<td>direct sunlight</td>
<td>1.400 000 000 (USGS incl. oceans)</td>
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<td>biological</td>
<td>photobiological</td>
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<td>direct sunlight</td>
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<td>high temperature steam</td>
<td>LCA related minor</td>
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<td>microorganisms</td>
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<td>high temperature steam</td>
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</tbody>
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performance associated with a product throughout its life cycle from production, to use, and finally to disposal. LCA can assist in identifying opportunities to improve environmental performance.

When observing different fuels throughout history, it is easy to note a tendency towards a lower ratio (Nakicenovic et al. 1993) of carbon to hydrogen C/H which is maximum in wood, yet smaller in coal and oil, goes towards a small number in the case of natural gas and finally converges to zero in pure hydrogen.

Hydrogen production routes can be divided into a number of categories: they can be categorized by division into thermal processes, electrolytic and photochemical. Or they can be categorized by division by main supply: fossil fuel and chemical; renewable energies and electrolytic processes; biological systems; and nuclear fission or fusion incorporating electrolytic production or chemical methods. In the following, these routes will be analysed further.

The world production of hydrogen is approximately 50 million tonnes annually and most of this amount results from reforming of natural gas. Most of the hydrogen produced is used in refineries and is, as such, a crucial ingredient in the oil industry. The hydrogen is produced mostly by a process called steam reforming. The basics of this process involve the mixture of natural gas with water steam where molecular H2 is freed from both components. In fact, half of the hydrogen from this process originates from the water steam (Nitsch & Winter 1988). In the USA, approximately 95% of all hydrogen is produced by steam reforming of natural gas.

The technical hurdles in the steam reforming process of natural gas, or for that matter other hydrocarbon streams, often involve getting rid of naturally occurring sulphur-containing compounds which stem from the ancient origins of the fossil fuels. The catalytic processes used to convert most of the sulphur-containing compounds to hydrogen sulphide (H2S). The H2S is then absorbed in a zinc oxide (ZnO) bed and converted to zinc sulphide (ZnS). Further refinement is done by a copper-based purification catalysis.

After the purification, steam is added to the feed in an expanding mixture which consists of various molecular components, mostly hydrogen and carbon monoxide. Pressures can be high, of the order of 20–40 atmospheres, and temperatures in the range up to 950°C. The products from the reformer include CO, CO2 and CH4. The so-called water–gas shift reaction which converts CO and water to CO2 and H2 is used for eliminating carbon monoxide and increasing the hydrogen content, and finally the so-called ‘chemical scrubbing’ is employed in order to clean the mixture and isolate the hydrogen.

Yet another method is partial oxidation. It is mostly used for heavy feeds. A third method is the auto-thermal reforming (ATR) process which is a mixture of reforming and partial oxidation. In general, the partial oxidation and ATR are the least demanding in terms of hardware space of the reforming technologies.

The US Department of Energy has set a target for 2010 for the cost of producing hydrogen to 1.06 USD per kilogram of H2, at a primary energy efficiency of 75%.

It is important to keep in mind that all these methods of converting fossil fuels into hydrogen suffer from one fundamental problem, each and every one emits CO2 to the atmosphere and are not different from the burning of fossil fuels in power plants, automobiles, etc., which are all notorious greenhouse gas emitters. The vicious cycle which is created in this way is not halted unless there is a way...
to trap the CO\(_2\) early in the process, by sequestering the carbon dioxide. When discussing hydrogen as an energy carrier today, it is usually expected that possible carbon sequestration pathways to the production will be incorporated.

In the following, the basic chemical equations for hydrogen processes mentioned above are shown.

Hydrogen from hydrocarbons.

Steam reforming: \[ C_nH_m + 2nH_2O \Rightarrow nCO_2 + (2n + m/2)H_2. \]

Partial oxidation: \[ C_nH_m + nO_2 \Rightarrow nCO_2 + m/2H_2. \]

Pyrolytic cracking: \[ C_nH_m \Rightarrow nC + m/2H_2. \]

Hydrogen from coal.

Coal gasification: \[ C + 2H_2O \Rightarrow 2H_2 + CO_2. \]

Steam–iron process.

\[ \begin{align*}
C + H_2O & \Rightarrow H_2 + CO \\
H_2 + Fe_3O_4 & \Rightarrow 3FeO + H_2O \\
CO + Fe_3O_4 & \Rightarrow 3FeO + CO_2 \\
6FeO + 2H_2O & \Rightarrow 2Fe_3O_4 + H_2
\end{align*} \]

The advantage of the steam–iron process is that step 4 can be separated from the previous three steps, thus giving pure hydrogen.

2. Fuel reforming

Common hydrocarbon fuels like natural gas or propane, gasoline, methanol and ethanol, have carbon and hydrogen bound in a molecular structure. It is possible to provide relatively pure hydrogen from most of these primary fuels by steam reforming in the corresponding system, the reformer.

A simple steam reforming of, for example, natural gas involves letting CH\(_4\) react with water vapour to form carbon monoxide and hydrogen gas. The chemical equation for the case \( n=1, m=4 \), CH\(_4\) is

\[ \text{CH}_4 + \text{H}_2\text{O} \Rightarrow \text{CO} + 3\text{H}_2. \]

Then the oxygen combines with CO to form CO\(_2\) according to

\[ \text{H}_2\text{O} + \text{CO} \Rightarrow \text{CO}_2 + \text{H}_2. \]

The reactions are not complete as they are written, and some natural gas and carbon monoxide goes through without reacting. At this point, a catalyst is used for burning the product in the presence of oxygen from air. This burns most of the CO to CO\(_2\). Sophisticated engineering is used to further purify other unwanted compounds from the original feedstock, such as sulphur. It is very important to eliminate CO completely, since this is a poison when used in a fuel cell and will gradually reduce its lifetime.
Methanol has the formula CH$_3$OH. A methanol reformer combines methanol and water vapour in the presence of a catalyst which splits the methanol into CO and H$_2$. Again here, the water vapour reacts with the CO to form CO$_2$ and H$_2$.

Fuel reforming as well as all the production pathways involving fossil raw materials suffers from the same problem: emission of CO$_2$ and the subsequent need for carbon sequestration.

### 3. Thermochemical cycles

Where heat is available, hydrogen can be obtained from various thermochemical cycles with water as a raw material. A very common process sometimes referred to as Mark 9 is

$\begin{align*}
6\text{FeCl}_2 + 8\text{H}_2\text{O} & \Rightarrow 2\text{Fe}_3\text{O}_4 + 12\text{HCl} + 2\text{H}_2 & (650^\circ\text{C}) \\
2\text{Fe}_3\text{O}_4 + 3\text{Cl}_2 + 12\text{HCl} & \Rightarrow 6\text{FeCl}_3 + 6\text{H}_2\text{O} + \text{O}_2 & (<200^\circ\text{C}) \\
6\text{FeCl}_3 & \Rightarrow 6\text{FeCl}_2 + 3\text{Cl}_2 & (350^\circ\text{C}).
\end{align*}$

$2\text{H}_2\text{O} \Rightarrow 2\text{H}_2 + \text{O}_2.$

Another process is the so-called hybrid process often referred to as Mark 13:

$\begin{align*}
\text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O} & \Rightarrow \text{H}_2\text{SO}_4 + 2\text{HBr} & (50–100^\circ\text{C}) \\
2\text{HBr} & \Rightarrow \text{H}_2 + \text{Br}_2 & \text{(electrolysis)} \\
\text{H}_2\text{SO}_4 & \Rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 & (730–830^\circ\text{C}).
\end{align*}$

$\text{H}_2\text{O} \Rightarrow \text{H}_2 + 1/2\text{O}_2.$

When examining general thermochemical hydrogen production which could be an option for producing hydrogen fuel from nuclear heat we finally mention the so-called sulphur–iodine process as an example. This process was originally developed by General Atomics in the 1970s. It involves iodine and sulphur dioxide; it emits oxygen but remains a closed cycle. Many of these processes are what we could call ‘a plumber’s nightmare’ and demand a lot of detailed knowledge about materials degradation and strength. Another important method is the bromine/calcium/iron process, sometimes called UT-3. It consists of reduction of water by bromide and a resulting hydrogen release.

The iodine–sulphur process is based on the decomposition of two acids at high temperature, sulphuric acid which yields oxygen and SO$_2$ and hydrogen iodide (HI) which yields hydrogen and iodine. Iodine and SO$_2$ react at low temperature in the presence of water to reconstitute these two acids (Bunsen reaction):

$\begin{align*}
\text{H}_2\text{SO}_4 & \Rightarrow \text{H}_2\text{O} + \text{SO}_3 & (400–600^\circ\text{C}) \\
\text{SO}_3 & \Rightarrow \text{SO}_2 + 1/2 \text{O}_2 & (800–900^\circ\text{C}) \\
2\text{HI} & \Rightarrow \text{H}_2 + \text{I}_2 \\
\text{SO}_2 + 2\text{H}_2\text{O} + \text{I}_2 & \Rightarrow \text{H}_2\text{SO}_4 \text{ (aqueous)} + 2\text{HI} \text{ (aqueous)} & (20–120^\circ\text{C}).
\end{align*}$
The Westinghouse hybrid cycle is

$$\text{SO}_2 + 2\text{H}_2\text{O} \Rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \ (20–110^\circ \text{C}),$$

which requires only sulphur.

The UT-3 cycle is

$$\text{CaO} + \text{Br}_2 \Rightarrow \text{CaBr}_2 + 1/2\text{O}_2 \ (550^\circ \text{C})$$
$$\text{CaBr}_2 + \text{H}_2\text{O} \Rightarrow \text{CaO} + 2\text{HBr} \ (725^\circ \text{C})$$
$$\text{Fe}_3\text{O}_4 + 8\text{HBr} \Rightarrow 3\text{FeBr}_2 + 4\text{H}_2\text{O} + \text{Br}_2 \ (250^\circ \text{C})$$
$$3\text{FeBr}_2 + 4\text{H}_2\text{O} \Rightarrow \text{Fe}_3\text{O}_4 + 6\text{HBr} + \text{H}_2 \ (575^\circ \text{C}).$$

When discussing the life cycle of the thermochemical cycles, it is important to note the fact that, whereas the process is free for carbon emissions, the primary energy resource, being nuclear, has problems associated with nuclear waste. However, this issue is addressed in the article by Ion (2007).

4. Gasification of biomass

Biomass is constantly being produced as a result of plants and living organisms using the energy of the rays of the Sun. Carbon dioxide and water are the main raw materials for the C–H binding of biomass. It is important to note that the proportion of hydrogen in the biomass is very different for each feedstock. As an example, wood contains cellulose which has approximately 6% hydrogen. When wood is converted, there is a need to get rid of volatile components in the wood. These dominant ingredients (all up to four-fifths of the mass) are vaporized at temperatures of 500–600°C. There exist various sophisticated pyrolysis methods and technologies for use in gasification of wood-like biomass. Many people believe that such conversion will be a major technology for a future hydrogen economy and it is currently enjoying considerable research interest. The University of Vaexjö in Sweden, in a cooperation with a number of partners has, for example, installed a gasification testing facility with 18 MW thermal energy involved, corresponding to some 4 tonnes of biomass per hour. The project called CHRISGAS aims to produce hydrogen-rich gases from biomass, including residues. This gas can then be upgraded to commercial quality hydrogen or to synthesis gas for further upgrading. This EU funded project takes place at the Vaexjö Varnamo Biomass Gasification Centre.

Thermal gasification initially converts biomass into a synthesis gas. With pyrolysis, it is possible to vaporize the dissociated and volatile components of the biomass at a temperature around 600°C. In some cases, this process has been assisted by solar energy as well as using supercritical conditions of an aqueous biomass.

As regards commercialization of hydrogen from biomass, a progressive company in Brazil, RAUDI, is basing its work on gasification of sugarcane. Their work aims at developing turnkey plants ready for the market within a few years. In Brazil, some 215 million tonnes of dry biomass would be available for this process, leading to approximately 7 million tonnes of H₂. RAUDI quotes the target cost of 1.87 USD per kg H₂.
In the gasification process, an outlet can be made at various points in the material flow in order to use the product already as fuel. It is possible to produce a dimethylether (DME) which has, e.g. in Sweden, been used successfully as a liquid transport fuel for diesel engines. In Japan, a 100 tonnes per day demonstration facility has been operating through the Ministry of Energy, Trade and Industry.

Another possibility is to convert the biomass to Hythane (registered trademark) where hydrogen is mixed with methane. By a mixture of up to 20% H₂ in CNG (compressed natural gas), the internal combustion will be accelerated and will reduce emission of methane. This has been demonstrated in Sweden and Canada in CNG vehicles from original equipment manufacturers.

In the paper and pulp industry, there is an interesting source of hydrocarbons, the so-called black liquor which can be used in a gasification process or pyrolysis, but is also used by combustion. The input energy exceeding 500 MW for a typical paper and pulp plant can yield considerable energy in the form of black liquor.

The combination of gasification with modern membrane technology is a worthy research subject. The US Gas Technology Institute has been testing proton conducting membrane materials developed for optimum hydrogen flux, e.g. barium cerate perovskites, the basic crystal structures of which are quite common in minerals. They have found that by doping the material with Zr an increased CO₂ resistance is obtained.

### 5. Hydrogen from micro-organisms and biomass

Biomass is termed renewable because the carbon dioxide released to the atmosphere by the biomass gasification was previously absorbed from the atmosphere and converted to hydrocarbons by photosynthesis of the plants involved.

The feasibility of producing hydrogen from biomass is very much dependent upon local conditions in the various areas of Earth. Most of the world outside the polar regions has ample sources of biomass to serve as a feedstock for such production. They range from wood, to agricultural crops, agro-industrial waste, animal manure, sewage sludge and household waste.

The methods available for the hydrogen production from biomass can be divided into two major routes: thermochemical and biological (fermentation) processes. An exciting future development is the road involving photobiological processes such as photosynthesis in cyanobacteria or algae. Biological electrolysis (splitting water into hydrogen and oxygen) is the first step in photosynthesis.

Photosynthesis occurs when chlorophyll in cells absorbs sunlight. Enzymes use this energy to break water down into hydrogen and oxygen. The hydrogen is subsequently combined with carbon dioxide to form carbohydrate. Certain micro-organisms release hydrogen instead of carbohydrate during photosynthesis.

Fermentation can also take place in the dark involving, for example, cyanobacteria. Nature has a way to speed these processes with the aid of hydrogen-producing enzymes, of which Fe-hydrogenase, nitrogenase and NiFe-hydrogenase are the most common ones. These enzymes exist in a number of micro-organisms. The hydrogen produced originates in the water. The use of thermophilic bacteria and hydrogenases for hydrogen production enjoys much interest in the research community.
The main hurdle in adopting these natural processes is the relatively low energy conversion efficiencies. In other words, a small proportion, perhaps as low as 1% of the power of the incident light is effectively converted into the hydrogen. Furthermore, the presence of oxygen slows down the process, even at oxygen concentrations as low as 0.1%, and so their hydrogenase production is severely hampered. Light saturation effects have also been observed as well as efficiency losses when the micro-organisms start converting a part of the light directly into heat.

There exist enormous challenges for research in this exiting area of nature imitation. This part of the science is called biomimetic hydrogen production. Nature uses chlorophyll as a central molecule for the process of using light for photosynthesis. The Nobel prize in 1988 was given to Deisenhofer, Huber and Michel for the discovery of photosynthesis reaction centres in purple bacteria.

Green algae and cyanobacteria are the main categories of micro-organisms that can produce hydrogen. They operate at different wavelengths and the photosynthesis of cyanobacteria can use light in the infrared, whereas algae can use light from the ultraviolet part of the light spectrum.

At first the organisms are kept incubated in darkness and deprived of oxygen (anaerobic conditions). Once they are exposed to light after their prolonged adaptation to life in the dark, they initially emit significant amounts of hydrogen and oxygen (at very high efficiencies) until they revert to performing normal photosynthetic carbon dioxide reduction. The challenge facing the researchers is that the algae saturate at low solar irradiances and thereby lose their ability to produce hydrogen in commercially useable quantities.

Fermentation, both light assisted as well as dark fermentation, enjoys considerable attention currently. With the use of genetic engineering, there seems to be no end to the possibilities of this ‘in principle’ old technology. The fermenting micro-organisms have an inherent weakness to oxygen, and indeed oxygen is poison in their primitive life. Hence, research is aimed at increasing the enzyme’s tolerance to oxygen. Perhaps, there is a revolutionary ground-breaking advanced species of micro-organisms, anthropogenic—designed by genetic engineering—or natural, lurking out there awaiting to be put into action. Such a species still remains to be found.

6. Electrolysis of water

When Jules Verne wrote his famous novel on the Mysterious Island which was published in Paris in parts between 1874 and 1875 (Lile mystéruse), and prophesized ‘water replacing coal’, he was well aware of the technology of electrolysis, which was discovered by William Nicholson in 1800.

The water molecule is held together through strong molecular forces. These ties can be ‘broken’ by the use of electric energy. Electrolysis is a word from Greek with ‘lysis’ standing for ‘cutting’ or separating. Breaking the bonds requires separating water into its elemental constituents, hydrogen and oxygen. The energy amounts to approximately 33 kWh per kilogram of water and is easily verified when the caloric value of burning hydrogen is measured. Compared to fuels such as gasoline and diesel, a given mass of hydrogen contains about three times more energy.
Industrial electrolysis is well known in many countries and territories where available electricity is ample. These are countries like Brazil, Canada, Egypt, Iceland, New Zealand, Norway, Tasmania and Democratic Republic of Congo. In countries like France, Belgium and Switzerland where nuclear energy is an important part of the energy mix, electrolysis is also a potentially important method. It needs to be kept in mind, however, that the amount of hydrogen produced by electrolysis in the world is very small compared with fossil fuel-based hydrogen, that is, about one part in a thousand. The most common single electrolysis producing process for hydrogen is the so-called chlor-alkali process where hydrogen is a by-product.

When water is split by electrolysis, the water itself is the electrolyte separating two electrodes that carry the current from the electric source needed to break the intra-molecular bonds. The water has been mixed with an alkaline compound to make it more conductive. The direct current voltage, theoretically 1.481 V at 298 K, gives each of the two electrons needed per water molecule enough energy to split the molecule. In industrial facilities, the voltage is typically 1.7–2.1 V. The amount of water needed for electrolysis is approximately 0.8 l per cubic metre of hydrogen at standard pressure. The hydrogen is released at the negative electrode (cathode) and oxygen at the positive electrode (anode). The ions of the electrolyte, the hydroxide, are enhanced by the alkali compounds, and hydrogen ions adjust the charge balance of the bath. The anode and the cathode are separated by a microporous diaphragm to prevent the mixing of the product gases. The current research into classical alkaline electrolysis addresses the use of high pressures and more economical materials. One of the consequences of going to higher pressures is to avoid gas bubble formation. Usually, the gas formed at the electrode has a tendency to form gas bubbles which act as insulators regarding the passage of electric current. In the case of higher pressure, bubbles are less of an obstacle. Bubble formation can also be prevented by proper electrolyte circulation. The main advantage of going to higher pressures is that the internal electrical resistance of the electrolyser is lower so that the overall energy efficiency is increased.

Considerable research is ongoing in this field. For example, tests have been made by using slightly elevated temperatures up to 300–600°C and electrolysis of the water vapour using a hydroxide salt melt electrolyte. Another important environmental demand is to replace asbestos in alkaline electrolysis with materials like Ryton. The research challenges include, for example, the reduction of resistive losses during electrolysis. Such losses will, in general, increase the voltage across the electrolysis path proportionally to the electrolysis current and resistance developed. These are most often called IR losses. They can be reduced if the temperature is raised but only up to 150°C when working with the most common electrolytes NaOH and KOH.

A so-called PEM electrolyser, where the electrolyte is a solid substance, has a proton exchange membrane similar to that of fuel cell technology (Larminie & Dicks 2002), presents a promising new development in electrolysis technology.

A number of companies around the world produce electrolysers and are constantly improving their quality and durability. One of the new developments, besides the PEM electrolyser, is the high-pressure electrolysers that can go up to pressures around 120 bar. By going to higher pressure, the producer gains on two levels: increased efficiency is obtained (as discussed above) and, no less importantly,
the need for a special compression unit for storage is reduced or eliminated. This can lead to large savings in energy for producing hydrogen gas.

In fact, the electric energy needed for electrolysis is reduced if the temperature of the bath is increased. There have been some promising experiments with high-temperature electrolysis (HTE) since the last decades of the twentieth century.

Energy changes for splitting water (figure 1), either in liquid or gaseous phase, are given by the following thermodynamic equation:

\[ \Delta H = \Delta G + T \Delta S, \]

where \( \Delta H \) is the enthalpy change or total energy demand, \( \Delta G \) denotes the Gibbs free energy or the minimum work, \( T \) is the absolute temperature and \( \Delta S \) the entropy change.

The term \( T \Delta S \) can be considered as the total amount of thermal energy needed to split water. The contribution of this term lowers the need for electric energy in the water-splitting process.

High-temperature electrolysis has been tested since the early 1980s in Germany by Dönitz and his co-workers (e.g. Dönitz et al. 1990). At that time, the process which was nicknamed HOT ELLY was deemed not sufficiently economical to be pursued further. In the range 800–1000°C, the required electrical energy for electrolysis is reduced by roughly 25\% compared to conventional electrolysis. In addition, HTE allows for more compactness and the use of higher current densities. One can think of the HTE electrolyser as the exact opposite of a solid oxide fuel cell, SOFC, sometimes called the SOEC (Jensen & Mogensen 2004).

The atomic energy establishment CEA of France has done very interesting work on HTE. The French CEA combines HTE with their new generation of

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Figure 1. The thermodynamics of hydrogen electrolysis showing how the demand for electrical energy decreases with increasing temperature.

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high-temperature nuclear reactor. Supplying the heat for HTE from outside has coined the name *allothermal* for this process. Another route, devised by CEA, assumes heat provided by, for example, geothermal heat sources and electricity from a hydroelectric origin. Steam will, in this case, enter the electrolyser and be heated by simple Joule heating provided by the electric current in the electrolyser and its ohmic resistance. This is called the *autothermal* route. CEA, the University of Iceland and more partners have been looking at this possibility under in the so-called Jules Verne Project using geothermal heat before finally converting to nuclear heat.

Before leaving the subject of hydrogen production from water by electrolysis, another method deserves to be mentioned. This is the use of oxygen-ion conducting membranes operating between chambers of different oxygen pressure. By introducing water vapour on the high oxygen pressure side, it is possible to exchange oxygen through the membrane and produce hydrogen on the water rich side. There are reports of significant amounts of hydrogen being produced even at moderate temperatures by removing hydrogen molecules from the water to oxygen/hydrogen chemical equilibrium. This technology is worth watching in the near future (Balachandran *et al.* 2004).

Breaking water is one of the most important challenges of modern hydrogen production. Greater understanding of the underlying physics is believed by many to be the core to the ultimate solution to this problem. There is, in this context, one final physical mechanism which should be mentioned here. Electrical energy can, in principle, interact with the molecule through microwave excitation. In a microwave cavity it should, in principle, be possible to excite water molecules as was shown in the early work of the Kurchatov Institute in Moscow. This has now been confirmed by the NFRC Institute in Korea where a patent has been filed for a method of a low pressure and low temperature microwave-assisted water splitting resulting in up to 84% efficiency in hydrogen production (BongJu Lee 2006, personal communication; figure 2). The Korean team uses only approximately 0.1 atm pressure and transverse electromagnetic waves guided by a waveguide. Dissociation energy (5.099 eV) of the water molecule is considerably lower than the ionization energy (12.621 eV). The dissociation performed in the system is believed to be of the Auger type. More detailed work is needed to determine the feasibility of microwave-assisted water splitting.

7. Hydrogen from wind energy

One of the derivatives of the solar heating of Earth is wind. Harnessing wind energy is increasing around the world. Stability of wind energy is of course limited due to the nature of the wind as a source. In a large grid-connected system, the grid can always absorb extra energy and provide electricity in conditions of no wind. Wind–hydrogen as a production pathway enjoys much attention. One possible use of hydrogen is to store wind power to even out the fluctuations in production due to natural variation of the wind.

On the island of Utsira in the Atlantic Ocean, just outside the magnificent fjords of Norway close to Haugesund and the ancient Viking heritage, Norsk Hydro and its partners have been running a wind generator-based hydrogen system since 2004. Two wind generators of 600 kW each deliver electric energy to
a small electrolyser which stores its hydrogen under pressure. The hydrogen is used for powering a number of houses on this small island. There is a 12 kW fuel cell from a Danish producer, IRD, delivering the power in addition to some 50 kW of electric energy stemming from an internal combustion-based generation unit. The combustion generator has an appreciably longer start up time than the fuel cell and the interplay of the two has proven a development challenge. The system also uses a flywheel for stabilization. This first proper wind–hydrogen system in the world, has proven a valuable experience for the coming generations of wind hydrogen systems.

In Denmark which has more than 20% of its electricity production from wind energy—and a world-leading knowledge position—wind-based hydrogen enjoys considerable research interest. The main problem of wind-based energy shows up during days of calm weather where ideally hydrogen storage would be needed. The islands like Utsira are not particularly known for still winds but such periods do occur.

Costs of wind-based hydrogen are rather difficult to assess accurately. The US Department of Energy has set a target for hydrogen from electrolysis, based on grid power, of 2.85 USD per kilogram of hydrogen.

### 8. Solar hydrogen

The use of solar energy to produce hydrogen is by many seen as the holy grail and the ultimate goal of renewable energy use. Solar-to-hydrogen conversion efficiencies can vary from as low as 1% in the case of a natural photosynthesis conversion to biomass—up to 67% for tandem, multi-photon and multi-bandgap photoelectrolysis devices which are being tested experimentally.

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The solar-thermal electric power technologies that are used to operate advanced alkaline water electrolysis are the most efficient and commercially available methods today. Solar-to-hydrogen net efficiencies up to 20% have been reported, using either Stirling engines or steam turbine systems based on the solar heating provided through a paraboloid dish. Another and quite different variant is the integration of a photovoltaic (PV) cell into monolithic devices with electrolysis. In such a system, a PV cell operates with alkaline water electrolysis and is capable of reaching up to 16% efficiency.

The sulphur–iodine or bromine/calcium/iron processes, as we discussed in §3, can also be solar powered and as such are also possible and promising ways of using solar energy for hydrogen.

An exciting, relatively new development is taking place in the area of photochemical hydrogen production which was first introduced by Fujishima & Honda (1972). In a photoelectrochemical (PEC) system, a semiconductor material which is photoactive is arranged to form a junction in contact with a liquid (or sometimes solid) electrolyte. When such a junction is illuminated by sunlight, electron–hole pairs are formed at the junction. These light-induced electron–hole pairs in turn drive a chemical reduction and an oxidation in the electrolyte of PEC systems.

Appreciable research work has gone into characterizing various materials for use in the PEC system. Various photoanode materials like tungsten trioxide, titanium dioxide, iron oxide, gallium arsenide, silver chloride and many more have been experimented with. The art of using these materials is to introduce controlled impurities for energy level bridging for a jumping electron or hole inside the material.

The various projects with PEC which are run all around the world concentrate mainly on two kinds of systems studied: (i) consisting of one photoelectrode and one metal electrode and (ii) a more sophisticated system comprised one n-doped in addition to one p-doped photoelectrode. Technical challenges for such systems include photochemical stability, efficiency and general energetics since the energy levels of oxygen and hydrogen reactions need to lie between the valence and the conduction band edges.

Photobiological hydrogen research has evolved considerably during the past decades. Initially, this work was based on screening and characterizing hydrogen-producing micro-organisms. The main constituents here are green algae and cyanobacteria. Genetic manipulation of the ability of these micro-organism to produce hydrogen is regarded as a promising way forward as discussed earlier under bioprocesses.

If we go from lower to higher temperature processes using sunlight, we come to high-temperature solar thermochemical production processes of hydrogen. They can involve five possible pathways: thermolysis, thermochemical cycles, reforming, cracking and gasification. In four of these cycles, water is the main raw material to be used with the solar heat in a process called thermal dissociation; in cracking, however, fossil fuels are a major primary resource.

In thermal dissociation, zinc oxide is used for breaking up into zinc and oxygen. The zinc oxide consequently can split water.

In cracking which, in fact, is a thermal splitting of long-chain hydrocarbons into shorter ones, the carbon from the fossil resource is diverted into CO and CO₂, leaving hydrogen as a product.
A European project, HYDROSOL, has concentrated its effort on making a catalytic monolith reactor based on solar heat for producing hydrogen at a very high efficiency of up to 80% at 800°C. The basic idea is to combine a support structure capable of achieving high temperatures when heated by concentrated solar radiation, with a catalyst system suitable for the performance of water dissociation and at the same time suitable for regeneration at these temperatures, so that the water splitting and catalyst regeneration can be achieved by a single solar energy converter.

The overall solar-to-hydrogen efficiency is approximately 7–8%. This project was awarded the Global 100 Eco-Tech award at the Expo in Japan 2005 as an outstanding project paving the way for a sustainable future. The project was recently a recipient of the IPHE Technical Achievement award in recognition of ‘its significant potential to advance the production of renewable based hydrogen’ (IPHE 2006).

9. Hydrogen from geothermal vents

Molecular hydrogen is difficult to find in a free form on Earth. Geothermal energy in association with groundwater can lead to natural hydrogen production. The heat from the Earth’s mantle continuously flows outward. It conducts to the surrounding layer of rock, the crust. When temperatures and pressures become high enough, some mantle or crustal rock melts, becoming magma. Then, owing to its relative lightness when compared with the surroundings, the magma rises, moving slowly up through the Earth’s crust, carrying the heat from below. Sometimes this creates lava flows. But most often the magma leads to heating the rock and groundwater. Some of the hot geothermal water and gases travel up through faults and cracks and they reach the Earth’s surface as hot springs or geysers, but most stay deep underground, trapped in cracks and porous rock thus forming natural geothermal reservoirs. The geothermal gases can contain a number of compounds, carbon oxides, sulphides, methane and hydrogen, to name a few. In a few cases, the amount of molecular hydrogen is probably sufficient for economically feasible production.

Hydrogen sulphide is a common compound in many areas of the world, bound in water/sea or in geological form. In the geothermal areas of Iceland considerable amounts of H₂S, for example, are emitted to the atmosphere. In the already harnessed parts of the Icelandic high-temperature areas, well over a thousand metric tonnes of hydrogen could be recovered annually, thus turning a polluting effluent into renewable fuel. In geothermal boreholes in the Krafla area in northern Iceland where the whole area is very close to a magma chamber and hydrogen is probably produced by some sort of a steam–iron-like process (the old method of developing hydrogen by flushing a glowing hot iron surface with steam), there are boreholes emitting up to 50 metric tonnes of molecular hydrogen annually. The borehole gas consists of hydrogen mixed with hydrogen sulphide, H₂S, carbon dioxide, CO₂, nitrogen, N₂, and of course steam.

In a project undertaken at the University of Iceland, hydrogen was recovered from the borehole gas using a closed cycle of acidic ferric chloride solution which the geothermal gas is bubbled through. The ferric ions are reduced to ferrous ions and the sulphide ions become oxidized to solid sulphur that can be separated from the solution. When the remaining ferrous and hydrochloric acid solution is subjected to
electrolysis, the ferrous ions are oxidized back to ferric ions at the anode and hydrogen ions reduced to recoverable hydrogen gas at the cathode. The electric energy needed to split hydrogen sulphide into its components has proven to be two-thirds of the energy needed for splitting water by electrolysis. The electric energy for the electrolysis is obtained at the power plant by flash turbine generators. Solid sulphur is the main by-product of the total process (Sigfusson et al. 2005).

Geothermal vents are, indeed, an interesting field of utilization but there is another even more important domain awaiting possible larger scale production. An example area enormously rich in hydrogen sulphide is the Black Sea, which really is a living tribute to an ancient fossil producing seabed like the one which fostered the fossil deposits on Earth in the dawn of oil formation. The Black Sea is literally infested with H_2S (Oslund & Alexander 1963). Below a depth of approximately 170 m, its waters contain no oxygen and very limited life in a vast hydrogen sulphide dominated world. The maximum depth is over 2200 m. A concentration of 7 mg l^{-1} undissociated hydrogen sulphide has been reported from an anoxic region of the Black Sea at depths of around 200 m—making it the largest anoxic basin of the global ocean. Approximately 4.6 billion tonnes of H_2S are estimated to be contained in the Black Sea. When categorizing this hydrogen, it should be classified as more fossil than renewable.

The name of the sea, given by seafarers, is believed to originate from the inhospitable environment sometimes caused by storms rather than its murky abyss.

10. A society based on renewable hydrogen is emerging

In Iceland, the proportion of renewable energy amounts to approximately 71% of the total energy portfolio (figure 3). The two main renewables are hydroelectric and geothermal. Approximately 20% of all electricity in Iceland is derived from geothermal, the rest from hydroelectric (Sigfusson 2005a,b,c).

At the turn of the millennium, Iceland was importing approximately 29% of its energy in the form of fossil fuels, mostly oil and gasoline for the transport and fishing sectors. In 1998, the government declared its intention to aim for a hydrogen economy in Iceland within the next half a century (Arnason & Sigfu´sson 2000; Sigfusson 2005a,b,c). One of the keys to the competitive advantage of hydrogen in Iceland is that it would be produced in a CO₂ neutral pathway based on renewables and owing to increased energy efficiency by the use of fuel cells (e.g. Larminie & Dicks 2002) when compared with internal combustion engines (ICE).

In order to carry out this aim, a public private company was established, Icelandic New Energy Ltd (INE) owned by an Icelandic consortium of companies as well as the international companies Shell Hydrogen, DaimlerChrysler and Norsk Hydro. In 2003, INE started a hydrogen fuelling station in Iceland, the first hydrogen station in the world placed within an existing gasoline/oil commercial fuelling station. This was a part of an EC-supported project ECTOS, Ecological City TranspOrt System, where three fuel cell powered hydrogen buses (figure 4) by DaimlerChrysler and Ballard have been running in Reykjavik and completed approximately a hundred thousand kilometres of driving. In 2006, the project was extended along with other sister projects from Europe into the so-called HYFLEET-CUTE project.
Figure 3. Proportional use of primary energy in Iceland from 1930 to the end of the millennium. The primary energy sources are depicted as a three phase diagram: coal, oil/gas and renewables (Sigfusson 2005).

Figure 4. One of the fuel cell powered buses in the ECTOS project. Powered by hydrogen obtained from electrolysis of water using renewable energy. Onboard storage of gaseous hydrogen at around 350 atm. Testing fuel cell performance in the, at times, harsh weather in Reykjavik has led to considerable learning and resulted in improvements of fuel cell systems.

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The aim of Icelandic New Energy is to gradually increase the use of hydrogen cars in Iceland and finally examine the possibility of using hydrogen aboard fishing vessels. The company has been examining the socio-economic hurdles faced when attempting to change a fuel base (Joergensen et al. 2004; Maack & Skulason 2005). INE has enjoyed a very good back-up from the government of Iceland and opinion polls reveal that the general public is very positive towards the anticipated transition.

In fact, Iceland has faced two transitions of its primary energy sources in the past century. In the 1920s, a transition to hydroelectric energy was initiated and then in the post-World War II period, geothermal energy displaced coal as a source of heat for municipal central heating systems as can be seen in figure 1. The relatively inexpensive electricity in Iceland makes hydrogen from electrolysis of water a feasible option. When geothermal electricity is produced as a part of a combined heat and power process the exergy (available energy) of the method is much higher. The price of hydrogen thus obtained is expected to have the potential to be comparable to imported oil and gasoline in a large scale production scenario. The cost of infrastructure has been calculated for Iceland in a first approximation. In the calculations, two scenarios are considered: (i) all hydrogen produced by electrolysis and delivered as compressed gas to automobiles and (ii) in the form of liquefied cryogenic for seaborne applications. In a full-fledged hydrogen scenario, Iceland will need approximately 80 000 tonnes of hydrogen annually to replace all oil and gasoline imports to the transport and fishing sector. This would call for approximately 5 TWh of electricity used, or an increase of just over 50% in the electric production above the present level.

Iceland is actively participating in the international movement towards a hydrogen economy. It is taking part in the IEA implementation agreement on hydrogen and currently Iceland serves as one of the chairs in the Implementation and Liaison Committee of the International Partnership for the Hydrogen Economy (IPHE).

It is to be expected that renewable hydrogen will be an option in many regions and societies around the world in the coming decade. But hydrogen will continue to originate from various different sources, through different pathways (Sperling & Cannon 2004; IEA 2006). This, in turn, will call for innovative and tailor-made solutions that will keep on requiring a great range of production pathways all around the globe.

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