

7 Hydrogen production

[S. Richter, U. Wagner]

7.1 Introduction

Hydrogen is seen by many experts as the energy carrier of the future. The use of hydrogen could be a way to store impermanent renewable energy and realize an emission free power generation for mobile, stationary or portable applications. One of the advantages of hydrogen as an energy carrier is that it can be produced from a wide variety of primary energy sources and different production technologies (see Fig. 7.1). Techniques based on fossil fuels like steam reforming of natural gas, gasification of coal or partial oxidation of heavy oil are state of the art technologies and are used for decades. Beside these mature processes there are some technologies, e.g. electrolysis, used only for special applications, and others, like photo-electrolysis or photobiological methods, which are object of current research activities and have to be developed for the industrial scale.

In contrast to this variety of different hydrogen production processes, nowadays more than 90% of the 500 billion m³ hydrogen (i.e. 5.4 EJ) produced per year is based on fossil fuels such as petroleum, natural gas or coal. The main applications for this hydrogen are by far the production of ammonia fertilizers and methanol synthesis. Further usages are welding, hydrochloric acid production and metallic ore reduction. Only a small amount is used for energetic purposes such as the propulsion of rockets or submarines.

For the future hydrogen energy economy huge amounts of cheap hydrogen have to be provided. Seen in an energy economic context, the amount of fossil hydrogen used for chemical processes today is only a small part of world's energy consumption of about 385 EJ per year [02OEC]. But in the future more and more sustainable energy sources have to be used and hydrogen is the best storage for impermanent renewable energies e.g. based on wind or solar power.

The production of hydrogen can be carried out either in large centralized facilities or in decentralized units, depending on the used primary energy source, the application and other factors like distribution costs. Target figures for the costs of hydrogen for transport purposes (including compression and delivery to a filling station) are about 1.50 € per kg (i.e. 0.05 €/kWh) as given by the U.S. Department of Energy [03USE]. For conventional techniques based on non-renewable resources this may be achievable in the short term, but for the new technologies today this is a challenging objective, and it has to be proven which of the processes can reach the target. Actually the price for gaseous hydrogen produced by natural gas in distributed plants is about 5.00 €/kg excluding taxes [03USE].

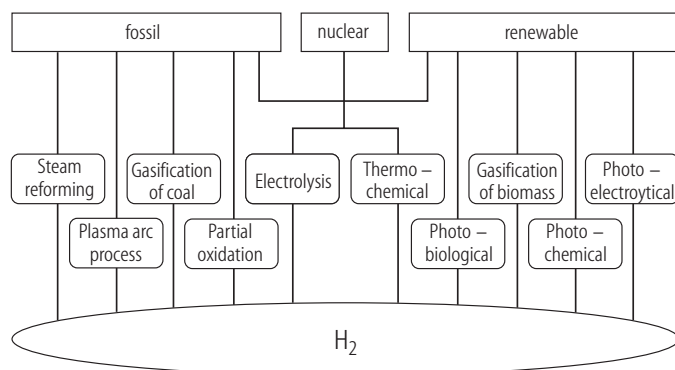


Fig. 7.1. Hydrogen production processes.

7.2 Hydrogen generation by electrolysis

Hydrogen production by electrolysis was the most common way until the mid of the last century. Currently only a small percentage of the hydrogen is produced by electrolysis, mainly for applications requiring small quantities of high purity. Driven by electricity from renewable power sources, e.g. wind or solar-power, electrolysis could be a technology for a sustainable hydrogen supply. Especially large solar thermal power units in the world's sunbelt combined with electrolyzers may produce a high amount of CO₂-free hydrogen in the future.

In electrolysis (see Fig. 7.2) an ion conducting electrolyte which separates the cathode (hydrogen generation) and the anode (oxygen generation) may be made of potash lye in a porous diaphragm (alkaline electrolysis), a proton conducting membrane (membrane electrolysis) or an oxygen ion conducting solid oxide (solid oxide electrolysis).

In alkaline electrolyzers two electrodes coated with a catalyst material (e.g. nickel) are immersed in potash lye. At the cathode side water is fed and separated into protons and hydroxide ions by a voltage impressed to the electrodes (1.4 to 2.1 V for a single cell). The protons combine to hydrogen and the hydroxide ions pass a diaphragm to the anode side where four of them form oxygen and two water molecules and emit four electrons which flow to the cathode via the external electric conductor (see Table 7.1).

Contrary to the process in the alkaline electrolyzer, in solid oxide electrolyzer oxygen ions are the product of the cathode reaction and pass the diaphragm to combine at the anode side. In a membrane electrolyzer protons are transferred through between the two electrodes, so that the water has to be fed to the anode side.

Table 7.1. Chemical reactions in electrolyzers.

	Cathode reaction	Anode reaction
Alkaline electrolyzer:	$4 H_2O + 4 e^- \rightarrow 2 H_2 + 4 OH^-$	$4 OH^- \rightarrow O_2 + 2 H_2O + 4 e^-$
Membrane electrolyzer:	$4 H^+ + 4 e^- \rightarrow 2 H_2$	$2 H_2O \rightarrow O_2 + 4 H^+ + 4 e^-$
Solid Oxide electrolyzer:	$2 H_2O + 4 e^- \rightarrow 2 H_2 + 2 O^{2-}$	$2 O^{2-} \rightarrow O_2 + 4 e^-$
Overall reaction:	$2 H_2O \rightarrow 2 H_2 + O_2$	

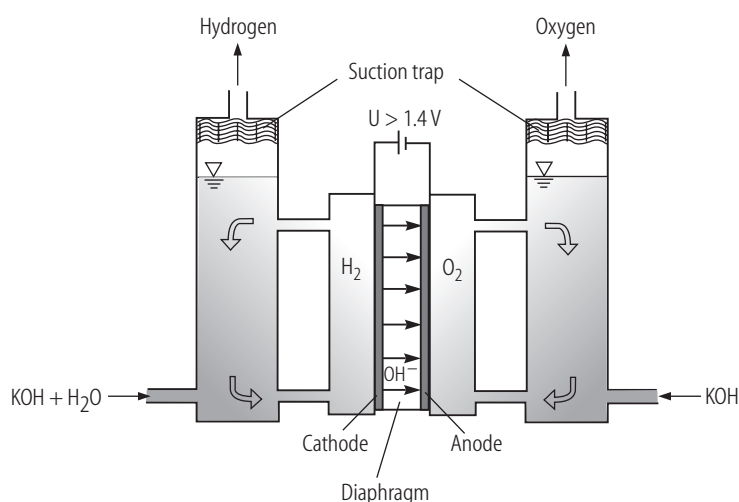


Fig. 7.2. Alkaline Electrolyzer with internal electrolyte circulation.

So far only the membrane and the alkaline electrolyzers (see Fig. 7.3) are commercially available. They are offered from a hydrogen output smaller than 1 m³/h up to 500 m³/h and with an efficiency factor higher than 70% (based on the lower heating value of hydrogen). For centralized hydrogen production by electrolysis in a future hydrogen economy a scale up of two orders of magnitude would be necessary to allow low costs.

Reducing the costs of investment and operation is the main objective in research and development of electrolyzers. Elimination of exotic material on the electrodes (e.g. precious metal catalysts in membrane electrolyzers) and extending the lifetime by using electrodes with higher electrochemical stability are two approaches for lower capital costs. Since about two thirds of hydrogen production costs are caused by electricity [01Kru], improving the system efficiency has an outstanding relevance for electrolysis. Alkaline electrolyzers benefit for example from activation of the electrodes by a plasma arc process, and membrane electrolyzers profit from improved catalysts, especially for the oxygen electrode [00DLR]. Operation cost could also be lowered by substituting electricity by heat energy. As less electricity is needed for the electrolysis of steam, the thermal energy of solar concentrator plants, nuclear reactors or geothermal heat could be used in high-temperature electrolyzers with solid oxide cells (“Hot Elly”) to produce hydrogen with high efficiency. Even though there has been a strong development of this technology years ago, it is not yet commercially available due to technical problems and a lack of market demand.

Another approach to raise the overall efficiency of hydrogen supply is the pressurized electrolysis. Membrane electrolyzers are normally operated at a pressure of about 0.5 MPa. To reduce the energy demand for compression of hydrogen, the fed water could be compressed before high pressure electrolysis at 3 MPa or, in the future, at 10 MPa. Primarily for mobile applications where storage systems with a pressure level of 35 or 70 MPa are used, the total efficiency could be highly improved in this way.

Hydrogen production costs by electrolysis strongly depend on the electricity costs. Today an electricity price of about 0.07 €/kWh results in costs of 4.00 € per kg of hydrogen [04Ivy]. But the economic efficiency of (PEM-) electrolyzers could also be raised if new materials for the electrodes and cheaper membranes were available. Further basic research is necessary, especially in the fields of high-temperature electrolysis. Improvements of electrolyte materials and system components would allow large solid oxide electrolyzers for central hydrogen production with high efficiency.

As electricity is transportable more easily than hydrogen, the hydrogen production by electrolysis is only expedient when there is a local or temporal oversupply of renewable energy. Otherwise the integration of renewable electricity into the public grid should be privileged. Nevertheless water electrolysis is capable for a decentralized supply of small amounts of hydrogen, e.g. at fuelling stations for vehicle fleets, especially at the beginning of a hydrogen energy economy.



Fig. 7.3. Industrial alkaline electrolyzer with a production rate of 485 Nm³ hydrogen per hour [02NHE].

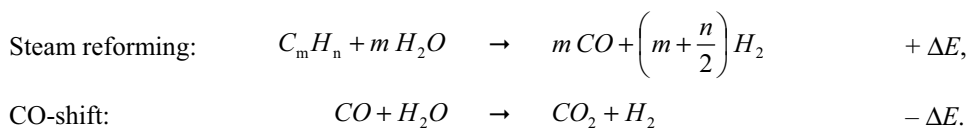
7.3 Hydrogen from fossil energy carriers

Today the production of hydrogen from fossil fuels is the most common way. Either hydrogen is needed as a basic material for the chemical industry or it accrues as a by-product of crude oil refining. Hydrogen for energetic purposes could be produced with high efficiency and low costs using natural gas, oil or coal. But the applied techniques are not sustainable because they cause CO₂-emissions and are based on non renewable energy sources. Nevertheless during a transition period towards a hydrogen energy economy it will be necessary to revert to these established methods for an ongoing market and to supply hydrogen at competitive costs and in a large quantity ab initio.

7.3.1 Steam reforming

Steam reforming of natural gas is one of the most effective methods of hydrogen production. There are large steam reformers with a capacity of 100000 m³ of hydrogen per hour and an overall efficiency of 70 to 80%. Nowadays the major part of hydrogen, about 50%, is produced from natural gas by steam reforming. The costs are about 0.80 €/kg H₂ [00Ang].

At the first step of the steam reforming process, light hydrocarbons (e.g. natural gas) react with steam to a mixture of carbon monoxide and hydrogen. This endothermic catalytic process requires temperatures of 800 to 950°C and a pressure of 3 to 4.5 MPa. The necessary heat is produced by combustion of off-gas and additional natural gas. In the subsequent exothermic shift reaction (CO-shift), carbon monoxide is oxidized by dint of catalysts and supplementary steam to carbon dioxide and additional hydrogen is gained (with $m = 1$, $n = 4$ for natural gas):



The catalysts used in these processes are usually non-precious metals such as nickel or copper/zinc. Nevertheless organic sulphur contained in natural gas has to be removed (to a content < 1 ppm) to avoid the blocking of the catalytic surface. With an upstream feedstock purification, a downstream CO₂-washing and a purification of the hydrogen by PSA (Pressure Swing Adsorber), there are in total five process steps for the reforming of natural gas to hydrogen (see Fig 7.4).

Steam reforming of natural gas in large scale is a mature technology. Anyway, there is a potential for optimization such as incorporating a CO₂-adsorbent in a combined reformer/shift-reactor to remove carbon dioxide from the product stream and driving the reaction to produce additional hydrogen at lower temperatures. By this and by improved catalysts with higher reactivity, the production costs for hydrogen may be reduced by 25 to 30% [03Rei], [04USE].

There are two types of steam reformers for small scale hydrogen production: conventional, down-sized reformers for the use at hydrogen filling stations and specially adapted reformers for combined heat and power plants with small stationary proton exchange membrane fuel cells. The latter operate under lower pressure and temperature than a conventional reformer and are more compact. Improving the overall performance by minimizing and simplifying the system are the main approaches here.

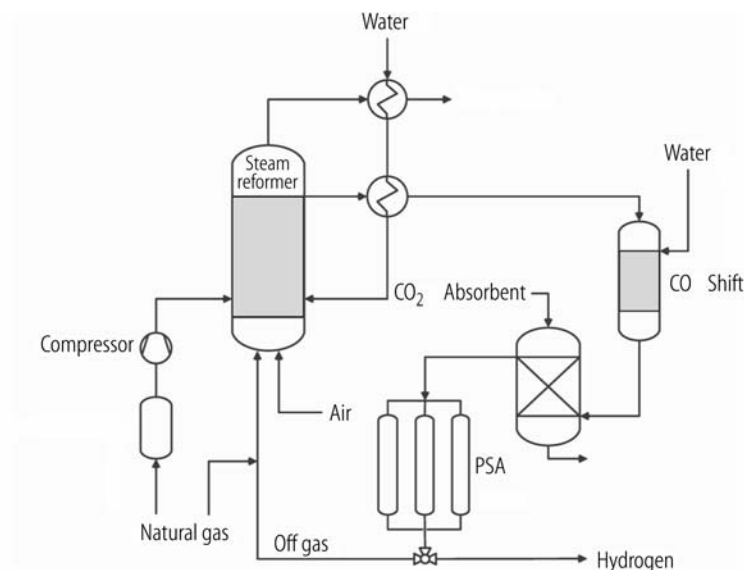
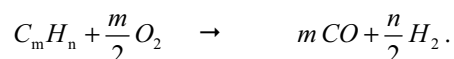


Fig. 7.4. Hydrogen production by steam reforming of natural gas.

7.3.2 Partial oxidation

Heavy hydrocarbons cannot be broken down catalytically by means of steam reforming because solid carbon separates out above 800°C and, within a short time, it would block the catalyst and the gas flow. Therefore, derivation of hydrogen from heavy, less pure liquid or solid hydrocarbons is accomplished by partial oxidation with oxygen or air. Unlike steam reforming this process is carried out without the use of catalysts at higher temperatures between 1300 and 1500°C and at a pressure of 3 to 10 MPa:



After the partial oxidation process, a desulphurization and a CO-shift are necessary before the hydrogen can be separated from carbon dioxide. Partial oxidation of heavy fuel oil has been realized in industrial-scale processes by Texaco and Shell. The achievable total efficiency is about 73 % and costs are about 0.80 €/kg H₂. The low costs are mainly due to the cheap basic material. However, high specific CO₂-emissions are caused by this process. In the future, the use of ceramic membrane reactors, where a simultaneous separation of oxygen from air and the partial oxidation of methane for hydrogen production is possible, promises an improvement in efficiency and costs. Even optimized systems integration may raise the overall performance of partial oxidation by some percentage points [00Ang].

7.3.3 Gasification of coal

Coal is still an important pillar of our present-day power supply. The anticipated lifetime of worldwide coal deposits surpasses that of petroleum and natural gas by far. Compared to natural gas which is used for many chemical processes, coals are quite inflexible energy carriers and their main application is the production of electricity and heat. In the context of final consumption of fossil fuels, hydrogen production of anthracite or lignite combined with a CO₂-sequestration may be a way to apply these energy sources even for applications in the transporting sector.

At coal gasification a thermal decomposition of the fuel into a combustible gas takes place. For this process air, oxygen, hydrogen, steam or a mixture of these fluids is supplied. There are two types of processes: in allothermic gasification heat is supplied from outside the system; in autothermic gasification the process itself generates the necessary temperature by open flame combustion of part of the fuel.

Several different techniques could be used for the gasification of anthracite and lignite. All of them have in common that, due to their complexity, the efficiency is low (about 60%) and the specific carbon dioxide emissions and costs (about 1.30 €/kg H₂) are quite high [00Ang].

7.3.4 Plasma arc process (Kvaerner process)

Another technology to generate hydrogen from fossil fuels is the so called “Kvaerner Process”. In a plasma arc at temperatures of 1600°C light hydrocarbons are converted to hydrogen and ultra pure carbon by electricity. Due to the specific process conditions, there are practically no CO₂-emissions. A pilot plant utilizing this technology produces 500 kg/h of carbon and 2000 m³/h of hydrogen from 1000 m³/h of natural gas and 2100 kWh of electricity, which leads to an overall performance near 50% [03TUE]. Even though the carbon could be used for technical purposes, the economic efficiency of this process for hydrogen production has not yet been reached.

7.4 Hydrogen from renewable energy sources

On the account of sustainability, in the long term hydrogen must be produced from renewable energy sources. There are quite a number of techniques for the production of hydrogen without harmful emissions, especially devoid CO₂-emissions. But today, nearly all of them cause quite high costs and most of them still have to be developed for the use in a technical or large-scale manner.

Electrolysis (see Sect. 7.2) driven by electricity from renewable energies may be an option for a sustainable hydrogen production whenever the integration of fluctuating energy, e.g. wind or solar power, into the public grid cannot be realized due to excess supply or high costs. Additionally, there are quite a few more processes which may be used for a sustainable hydrogen generation.

7.4.1 Hydrogen generation through photoelectrolysis

A newly developed type of electrolysis is the so called photoelectrolysis. By special photovoltaic cells a sufficient voltage (higher than 1.23 V) is generated to split water directly by the UV-content of sunlight or by visible light. As the photovoltaic cells work directly in the de-ionized water, this technique eliminates the costs of the conventional electrolyzers and may increase the overall efficiency of solar hydrogen generation. Theoretically the efficiency for tandem junction systems is 42%. Actual research results show a practical solar-to-hydrogen efficiency up to 12.4% [04USE].

In tandem junction cells (see Fig. 7.5) a transparent photo-anode absorbs light of the blue spectrum of sunlight and oxidizes the oxygen of water. Photons of the green and red spectrum are absorbed in a second system and thereby, a photo-voltage is generated that is sufficient to reduce the protons of water to hydrogen at the photo-cathode (i.e. the counter electrode of the photo-anode) [99Rel].

State of the art multi-junction cells made of amorphous silicon (a-Si), copper-indium-gallium-diselenide (CIGS) or advanced semiconductor materials like dye-sensitized titanium dioxide (TiO₂) or tungsten trioxide (WO₃) can either realize low costs or high efficiency. The main challenge is to find stable materials that split water, have a high light absorption and do not suffer from photo-corrosion or

have energetically unfavorable band-edge positions. So the objectives of further development are more stable and cheaper cells with a high solar-to-hydrogen efficiency. First good results were achieved with nano-crystalline iron oxide (FeO), a low-cost semiconductor with a favorable small band gap and low environmental impact, for the photo-anode. But the production of transparent layers made of FeO has to be improved [99Rel].

7.4.2 Hydrogen from biomass

Biomass resources such as consumer waste, agriculture residues or biomass specially grown for energy use, could be – similarly to coal – used for hydrogen production by gasification or by pyrolysis. Due to the low energy content of biomass, long transportation distances have to be avoided and the generation of hydrogen has to take place in small, decentralized plants. Thus the economy scale could only be utilized in a small range. The amount of CO₂ emitted by biomass processes has been absorbed by the plants in their period of growth, thus the hydrogen made of biomass is nearly CO₂-free. Only the expenditures of fossil fuels within the biomass-to-hydrogen path cause some additional greenhouse gas emissions.

In gasification of biomass at temperatures of about 1400°C, carbon hydrates and carbon are partially oxidized to carbon monoxide and hydrogen. A following shift-reaction totally oxidizes CO with water towards carbon dioxide and further hydrogen. There are some pilot projects of hydrogen production via gasification around the world (e.g. “Blauer Turm” in Herthen, Germany), but further developments in the field of preconditioning the biomass, ash-removal and synthesis gas cleaning (reducing the chlorine and sulphur content) are necessary for an economic operation. Even production of a uniform output utilizing inhomogeneous biomass input has to be implemented.

Biomass pyrolysis produces a liquid product (bio-oil) that contains a wide spectrum of components that can be separated into valuable chemicals and fuels, including hydrogen. Researchers are currently focusing on hydrogen production by catalytic reforming of biomass pyrolysis products. Specific research areas include reforming of pyrolysis streams and development and testing of fluidized catalysts.

Another technology is the hydrogen production by fermentation of biomass by microorganisms. Here organic materials rich of carbon hydrate are decomposed in aerobic biological processes, either on mesophilic conditions (temperatures of about 30°C) or on thermophilic conditions (about 60°C). The theoretical maximum hydrogen yield is four molecules hydrogen per mole of hexose sugar (e.g. glucose), i.e. approximately 0.5 m³ hydrogen gas per kilogram glucose [03Mad].

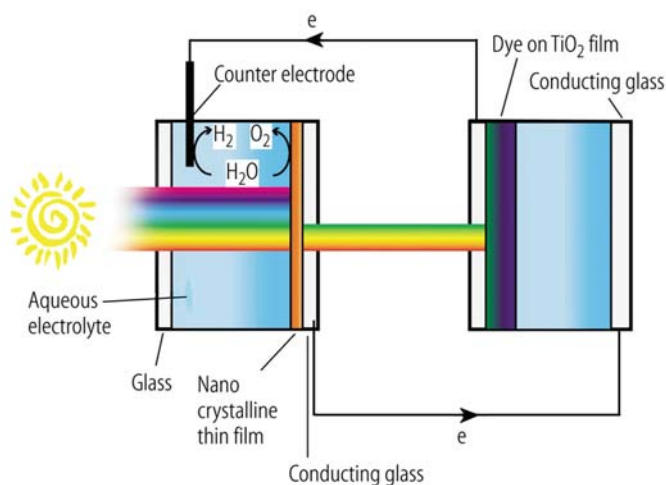


Fig. 7.5. Photo electrolysis by a tandem photo cell [04Gra].

7.4.3 Photobiological hydrogen generation

Some photosynthetic microbes produce hydrogen in their metabolic activities while using light as energy source. Cyanobacteria or algae (e.g. *Chlamydomonas reinhardtii*, see Fig. 7.6) can split water molecules into hydrogen and oxygen by enzymes. This sub-process of the photosynthesis is normally used to work up carbon dioxide and produce biomass, but on special conditions pure hydrogen is released. By use of metabolic switchers (e.g. sulphur deprivation), an alternation between photosynthetic growth phase and hydrogen production phase can be enforced. For hydrogen production in a technical scale these algae cultures can be cultivated in low-cost plastic tanks. No special light conditions are necessary; in fact the microbes prefer not too intensive sunlight radiation of the temperate climate zones [04Mue].

Another promising approach is the use of a separated enzyme (hydrogenase) of the algae. Theoretically a single enzyme molecule can produce up to 9000 molecules of hydrogen per second. Only about 60 mg of hydrogenase would be necessary to generate one cubic meter of hydrogen in one hour [04Mue].

In contrast to cyanobacteria, photosynthetic bacteria need an organic nutrient solution to produce hydrogen. A research goal is to optimize the process due to the oxygen sensitivity of the enzyme systems. Therefore scientists screen natural micro-organisms and design new genetic forms which are more tolerant to oxygen. Today, 150 liters of hydrogen can be produced per kilogram biomass by purple bacteria, at a total efficiency of about 70% [00Ang]. Not optimized algae systems have a production rate of about 30 m³ hydrogen per square meter and year (at twelve hours of radiation per day). Screening of different species, adaptation by genetic mutation and optimization of flow fields in the bioreactors will improve the system efficiency. But even research on detailed cellular processes is necessary to understand and improve hydrogen generation by photobiological systems.

7.4.4 Photochemical and photocatalytical hydrogen production

In the direct photochemical reduction of water a sensitizer (a molecule or semiconductor) is excited by visible light and can thereafter affect the reduction of water by the delivery of electrons. Several different sensitizers with different absorption characteristics can be used simultaneously, leading to a higher hydrogen production rate. A catalyst, usually a heterogeneous noble metal catalyst (e.g. PtBi₂O₃RuO₂), is needed to speed up the reaction.

Photocatalytical processes, e.g. using Ag/AgCl layers, are another promising approach for hydrogen generation by sunlight. At the photo anode (Ag/AgCl) water is oxidized into oxygen; at the photo-cathode (platinized GaInP₂) water is reduced to hydrogen. The charge equalization is realized by a salt bridge.

The main problem of all techniques is the fast aging of the materials due to the electrochemical conditions. Other research challenges are the improvement of efficiency and optimization of gas separation equipment.

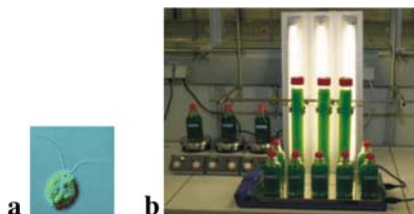


Fig. 7.6. (a) Picture of a *Chlamydomonas reinhardtii*. (b) Photobiological hydrogen production in laboratory scale [04Mue].

7.4.5 Thermochemical hydrogen production

Water separates at temperatures of about 3000 K into hydrogen and oxygen. Because it is nearly impossible to control or separate a mixture of the two gases at these high temperatures, several methods are developed to successively decompose the water in different steps at lower temperature levels.

In thermochemical water splitting processes like the sulfur-iodine cycle, the UT-3 cycle or the SybMet process, water is decomposed into hydrogen and oxygen through combinations of chemical reactions, and these reactions are carried out by utilising only heat to drive them. Suitable high temperature heat sources are solar thermal concentrator and central receiver systems or high temperature, gas-cooled nuclear reactors. The water splitting process takes place in different, separated process steps where water reacts in endothermic and exothermic chemical reactions, e.g. with sulphur dioxide or calcium bromide. The theoretical overall performance of these processes is reported in the range of 40 to 50%, but further improvements concerning the heat-transfer and the temperature control are required for commercial applications. Due to the complexity of these processes and problems in separating the products at high temperature, an economic operation could not be proven up to now.

7.5 Conclusion

The provision of cost competitive hydrogen in sufficient quantity and quality is the groundwork of a hydrogen energy economy. If there are no suitable technologies for economic processes without greenhouse gas emissions or other non-sustainable environmental impacts, hydrogen production will be the bottleneck of the future energy economy.

Today only procedures based on fossil fuels and electrolysis are commercially available. With improved efficiency, low costs and minimized carbon dioxide emissions, these technologies have to be used at the beginning of the hydrogen energy economy. Therefore research and development on materials and processes playing an important role within these mature systems have to be strengthened in the short term.

Nevertheless only hydrogen based on renewable energy sources conforms to all demands on a sustainable energy carrier. This means that research and development in all fields of hydrogen production have to be intensified in order to yield a wide variety of processes, based on different energy sources, to choose from depending on the varying basic conditions.

7.6 References for 7

- 99Rel Reller, A.: Solarchemie/Wasserstoff - Überblicksbericht zum Forschungsprogramm 1999, Bern: Schweizer Bundesamt für Energie, 1999.
- 00Ang Angloher, J., Dreier, Th.: Techniken und Systeme zur Wasserstoffbereitstellung - Perspektiven einer Wasserstoff-Energiewirtschaft Teil 1, Wasserstoff-Initiative Bayern, 2000.
- 00DLR Deutsches Zentrum für Luft- und Raumfahrt, Institut für Technische Thermodynamik (ed.): Elektroden für Hochleistungs-Elektrolyseure, Elektrolyse-Systemtechnik. Stuttgart, n.d.
- 01Kru Kruse, B., Grinna, S., Buch, C.: Hydrogen statu sog muligneter - Bellona rapport nr. 6. Oslo: Bellona Foundation, 2001.
- 02NHE Norsk Hydro Electrolyseurs AS (ed.): Hydro Electrolyseurs. Notodden (2002).
- 02OEC OECD, IEA (eds.): World Energy Outlook 2002 - Highlights, Paris, 2002.
- 03Mad Maddy, J., Cherryman, S., Hawkes, F.R., Hawkes, D.L., Dinsdale, R.M., Guwy, A.J., Premier, G.C., Cole, S.: Hydrogen 2003 - A sustainable energy supply for Wales: Towards the Hydrogen Economy, Mid Glamorgan: University of Glamorgan, 2003.
- 03Rei Reijers, H.T.J., Roskam-Bakker, D.F., Dijkstra, J.W., de Smidt, R.P., de Groot, A., van den Brink, R.W.: Hydrogen production through sorption enhanced reforming, Petten: Energy Research Centre of the Netherlands, 2003.
- 03TUE TÜV Süddeutschland (ed.): Hydrogen - a world of energy, Munich, June 2003.
- 03USE U.S. Department of Energy: Hydrogen, fuel cells and infrastructure technologies program - multi-year research, development and demonstration plan. Draft 06/03/2003.
- 04Gra Grätzel, M.: Laboratoire de Photonique et Interfaces, Institut des Sciences et Ingénierie Chimiques, Lausanne: École Polytechnique Fédéral de Lausanne, 2004.
- 04Ivy Ivy, J.: Summary of electrolytic hydrogen production - milestone completion report, Battelle: National Renewable Energy Laboratory, 2004.
- 04Mue Müller, K., Happer, Th.: Biokraftstoff aus Algen - Photobiologische Wasserstoffherzeugung und CO₂-Fixierung, Bochum: VDI-Expertenforum „Entwicklungslinien der Energietechnik“, 2004.
- 04USE U.S. Dep. of Energy: Hydrogen, fuel cells and infrastructure technologies - Hydrogen production and delivery, 04/10/2004; (www.eere.energy.gov/hydrogenandfuelcells/).