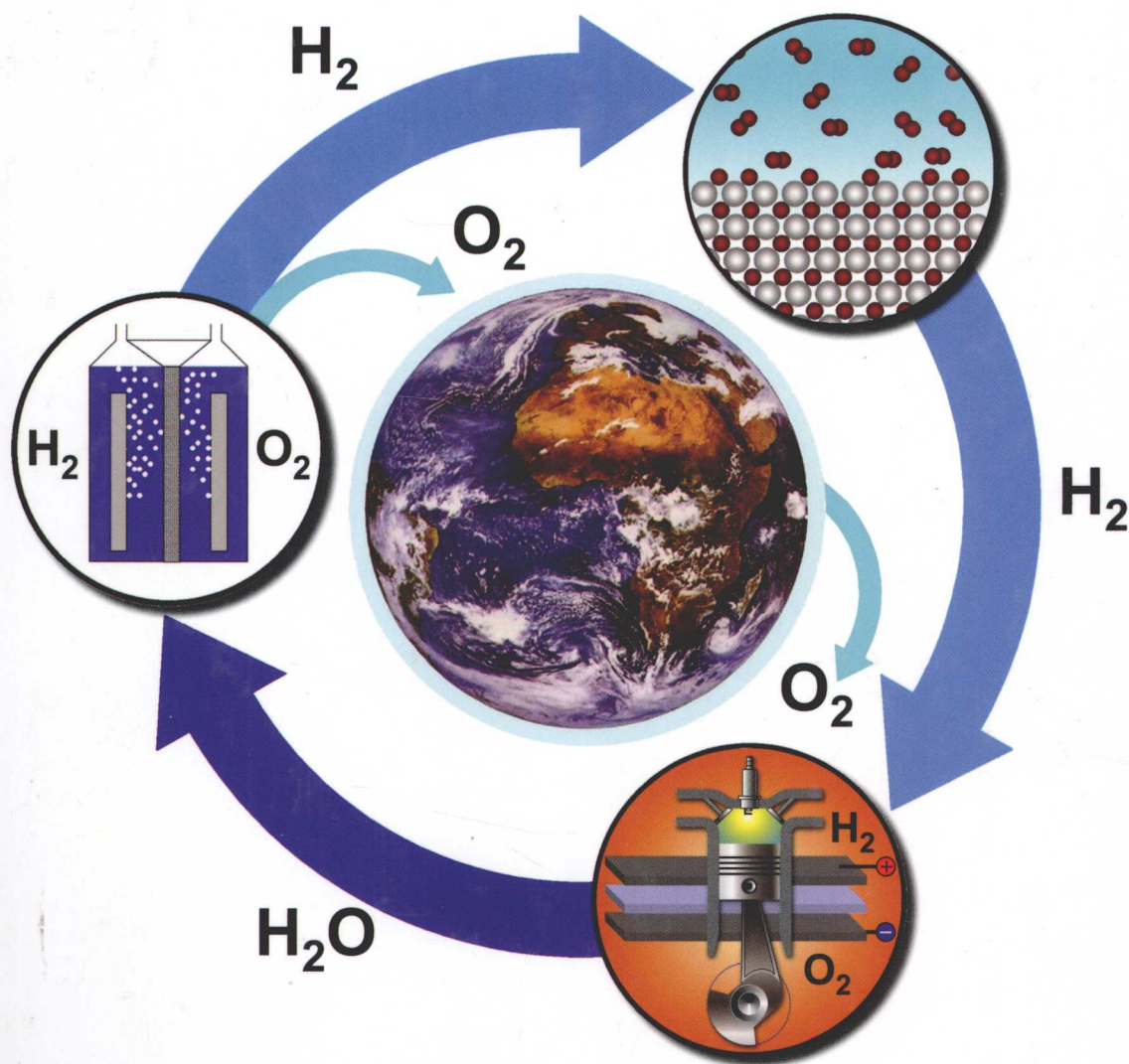


Edited by Andreas Züttel,  
Andreas Borgschulte, and Louis Schlapbach

WILEY-VCH

# Hydrogen as a Future Energy Carrier





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*Edited by*  
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*and Louis Schlapbach*



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## Preface

Thermodynamically speaking a human being, like any animal, is an engine combusting an energy carrier like food into work. In other words, the difference between living matter and dead matter is the ability to convert energy. Therefore, energy is essential for our existence and development. Natural processes led to a spontaneous accumulation of carbon- and hydrogen-based energy carriers – the so-called fossil fuels. A large amount of fossil fuels was given by nature, which allowed us to start the industrial age and to develop enormously over the last century. However, we are now starting to realize that these reserves of stored solar energy are finite and that the combustion of fossil fuels leads to climate change. No matter how much fossil fuel is left and who consumes most of it we have to develop a world sustainable energy economy for the future. Today most of our energy demand is covered by energy carriers; however, all renewable energy sources deliver energy fluxes. Therefore, a synthetic energy carrier is needed. At present, the only energy carrier that can be synthesized efficiently without materials limitations and in real-time is hydrogen. Furthermore, the combustion of hydrogen leads to the release of water to the atmosphere and the cycle is closed naturally.

Thus, this book starts with a short description of the history of the energy cycle from biomass to the fossil fuels and finally the outlook to the future hydrogen-based energy cycle. The provision of energy by depletion of natural carbon sources should be abandoned, because the burning of carbon results in a massive release of the greenhouse gas CO<sub>2</sub> into the atmosphere. Therefore, carbon has to be avoided in future energy carriers. Hydrogen is a renewable energy carrier, produced from water and a renewable energy source, e.g. solar energy. Furthermore, if a future society is able to operate fusion reactors and produce heat and electricity from this nearly unlimited energy source an energy carrier like hydrogen will be needed in order to store and transport the energy.

This book is a comprehensive overview of the basic knowledge about hydrogen and the opinions about the potential and future development of hydrogen science and technology. The primary focus of the book is the description of the technology and science of the hydrogen cycle, including hydrogen production, hydrogen storage and hydrogen conversion. In addition, it contains chapters on new applications using hydrogen, e.g. in functionalized materials. The oldest

hydrogen-based application is nearly 200 years old and thus the book contains an interesting survey of the history of hydrogen.

The publication of the assessment report of the intergovernmental panel on climate change in 2006 triggered awareness of the need for a change in the current energy policy. Accordingly, the recent progress in research is enormous, and can hardly be summarized in one book. Still, this book can serve as a basis for future research, and is a short introduction to the most important challenge of the 21st century. We thank the authors for their valuable contributions which have allowed the realization of this book.

Dübendorf, January 2008

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## 1

**Introduction***Andreas Züttel*

## 1.1

**Introduction**

Human beings developed on Earth on the basis of plants, that is biomass, as the only energy carrier. The average power consumed by a human body at rest is 0.1 kW and approximately 0.4 kW for a hard working body, delivering about 0.1 kW of work. The consumption of plants by humans and animals did not change the atmosphere because the carbon dioxide liberated by humans and animals was reabsorbed by the plants in the photosynthesis process. The only mechanical work available from nonliving systems were the windmills and the waterwheels, where solar energy was converted into mechanical power.

With the discovery of the steam engine in 1712 by Thomas Newcomen [1] humanity had for the first time a nonliving machine available, consuming carbon or hydrocarbons and delivering mechanical power on demand. This initialized the industrialization process and thereby changed society completely, in particular the demand for more and more energy. The energy for the steam engine was found in the form of mineral coal, solar energy stored in the Earth's crust over millions of years.

Coal as a solid energy carrier was later complemented by liquid crude oil and natural gas. Not only did the state of the energy carrier change with time, from solid to liquid and finally gas, but also the amount of hydrogen in the fuel increased from zero to four hydrogen atoms per carbon atom.

The world energy consumption increased from  $5 \times 10^{12}$  kWh/year in 1860 to  $1.2 \times 10^{14}$  kWh/year today. More than 80 % is based on fossil fuels, such as coal, oil and gas [2].

The population of human beings has increased in the last century by a factor of 4 and the energy demand by a factor of 24. The world wide average continuous power demand is 2 kW/capita. In the USA the power consumption is on average 10 kW/capita and in Europe about 5 kW/capita [3], while two billion people on Earth do not yet consume any fossil fuels at all. However, the reserves of, for example crude oil on Earth are limited and predictions based on extrapolation of the energy consumption show that the demand will soon exceed the supply [4]. The reserves

of other fossil fuels, for example coal, are larger [3]. Still, no matter how long the fossil fuels will last their amount is finite. The demand of fossil fuels has also a strong impact on social, political and economic interactions between the various countries. For example two thirds of the crude oil reserves are located in the Near East region, but most of the petrol is consumed in the USA, Europe and Japan. The transportation over long distances by, for example pipelines or tank ships, causes significant damage to the environment [4]. The imbalance of the distribution of resources is one of the driving forces of political instability leading to war and terrorism. This is the first important fact forcing the world to search for an energy solution not depending on fossil fuels but on unlimited renewable energy.

The consumption of fossil fuels together with deforestation leads to the liberation of  $7 \times 10^{12}$  kgC/year in the form of  $\text{CO}_2$ . The plants are able to absorb  $2 \times 10^{12}$  kg/year by means of the photosynthesis process and the same amount is dissolved in the ocean (see Fig. 1.1). Therefore the net increase in  $\text{CO}_2$  in the atmosphere due to human activities is approximately  $3 \times 10^{12}$  kg/year [5]. This corresponds to an annual increase of 0.4% of the  $\text{CO}_2$  concentration in the atmosphere. The  $\text{CO}_2$  concentration in the atmosphere is continuously measured at the Mauna Loa observatory in Hawaii. Due to the seasonal variation of the solar intensity the  $\text{CO}_2$  concentration shows oscillations. The plants absorb more  $\text{CO}_2$  in the growth period, the summer time, than during the winter. However, plants are not able to absorb all the additionally liberated  $\text{CO}_2$  in real time. Carbon dioxide is a greenhouse gas and causes an increase in the average temperature on Earth. A careful investigation of the climate and atmospheric history of the past 420 000 years from the Vostok ice core in Antarctica has shown that the variations in the temperature on Earth correlates with the variations in the concentration of greenhouse gases in the atmosphere. This correlation, together with the uniquely elevated

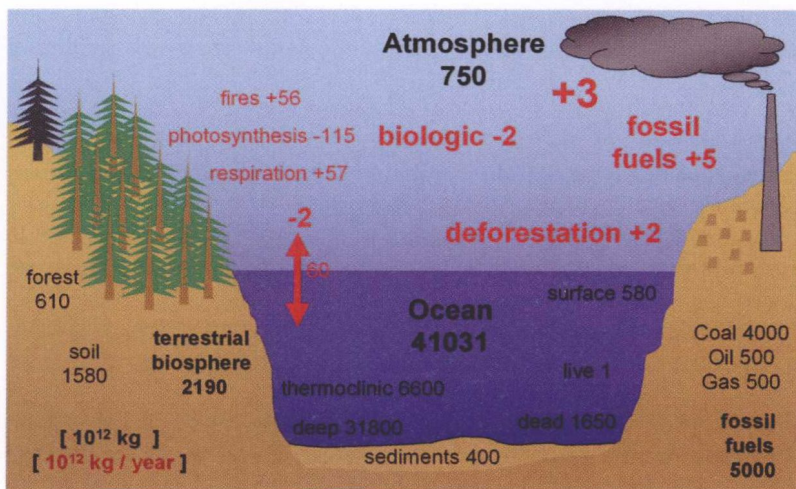


Fig. 1.1 Carbon reservoirs and rates of exchange. From (Climate Change (2001), Ref. [5]).

concentrations of CO<sub>2</sub> today, is of great relevance with respect to the continuing debate on the future of the Earth's climate.

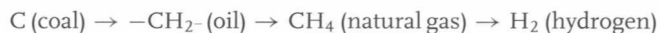
Currently we are in a period of decreasing solar activity and therefore the average surface temperature on Earth should decrease. However, for 100 years the temperature on Earth has been increasing. Furthermore, for the last 10 years an unusually steep increase in the average temperature versus time has been observed. This is the second important reason for the necessity to develop a new energy carrier which is free of carbon.

Fossil energy has a very strong influence on the development of a society and the standard of living. A dependence of the gross national product on the average amount of energy consumed per person can be found. Countries with low energy consumption per person have a low gross national product and vice versa. This led to the conclusion, that today the economic gain of the industrialized world is to a significant part due to the energy from fossil fuels.

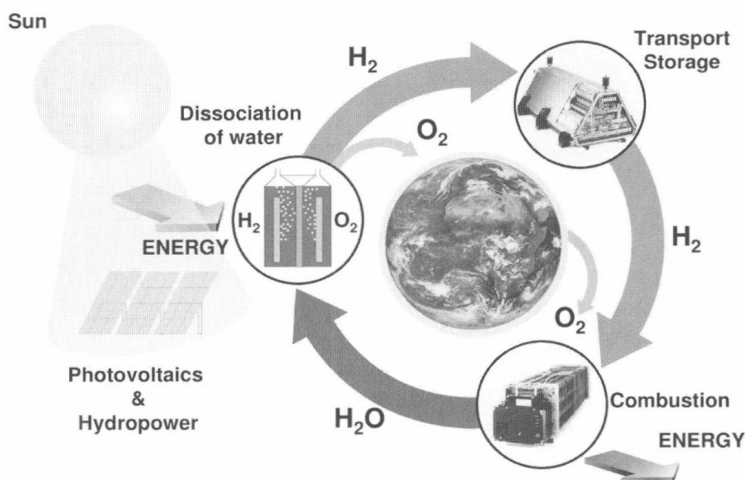
Fossil fuels are energy carriers given to human beings by nature. Basically we know two types of energy carriers. The first is a reversible system which can be charged with energy in the form of mechanical or electrical work and delivers the energy again on demand. Examples of such a system are capacitors, batteries and flywheels. We can define a charge and discharge efficiency and the overall efficiency of the system is the product of all partial efficiencies. The energy density in such systems is given by the physical properties of the active material and is, in general, limited to 1 to 2 eV per atom. The second system stores energy by means of the reduction of a compound, liberating oxygen to the atmosphere and producing a semi-stable product, for example photosynthesis ( $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ ) or ( $2\text{ZnO} \rightarrow \text{Zn} + \text{O}_2$ ). The product can be reacted with oxygen again, liberating energy and leading to volatile or nonvolatile compounds. If the compound is volatile a natural process in the atmosphere should transport it. The advantage of the second system over the first is the natural transport and the storage of the oxygen and the volatile products in the atmosphere. Therefore, rather high-energy storage densities are possible and can, in many cases, exceed the storage densities of the first system. But more processes are involved and this limits the overall energy efficiency of the system.

The natural cycles in the atmosphere are able to transport only a few compounds namely oxygen, nitrogen, water and carbon dioxide. Many more gases could of course be transported; however, they would significantly affect life on Earth.

Considering the historical development of energy carriers towards more hydrogen rich fuels and the necessity to avoid the carbon dioxide emission that causes the greenhouse effect, one concludes that hydrogen should be the energy carrier of the future (see Fig. 1.2)



This series also shows a development from a solid to a liquid and then finally to a gaseous state energy carrier. Hydrogen occurs on Earth chemically bound as H<sub>2</sub>O in water and some is bound to liquid or gaseous hydrocarbons. The production of hydrogen by means of electrolysis consumes electricity, which is physical



**Fig. 1.2** In the hydrogen cycle, solar energy and process of water electrolysis are used to generate, store and combust hydrogen with oxygen, thus returning it to water.

work. Therefore, a primary energy source is necessary to produce hydrogen. In contrast to the biomass produced by all plants using sunlight, there are only a few natural processes leading directly to hydrogen gas. The fundamental question to be answered is: what are the possible sources of energy for a hydrogen-based society.

The answer today is nuclear fission or nuclear fusion. Human controlled nuclear fission is limited by the mining of the materials used in nuclear reactors and the handling of the products of the fission reaction. Furthermore, the reserves of highly concentrated fission materials in the Earth's crust are finite and would not allow production of the world energy demand for more than a century. Natural fission in the Earth leads to a reasonable amount of heat. This heat is the source of geothermal power used in suitable regions, like Iceland, as a primary energy source. However, estimates of the potential amount of energy from geothermal sources show that they cover only a small percentage of the actual worldwide energy demand [6].

On a geological timescale the only source of primary energy is the nuclear fusion of hydrogen. The two options are terrestrial fusion or extraterrestrial fusion on the sun. The terrestrial fusion is human controlled and could deliver the energy in a centralized and concentrated form at a high temperature. While the principle of the release of an enormous amount of energy is realized in nuclear H-bombs, the peaceful use of fusion as a primary energy source has not been achieved yet due to massive technical problems. The Sun on the other hand delivers fusion energy over the whole surface of the Earth in a continuously oscillating way with a frequency of 24 h on a base frequency of one year. The energy arrives on Earth with a rather low average intensity of  $165 \text{ W m}^{-2}$ . The challenge is to convert and concentrate the energy by means of hydropower, windpower, solar-thermal, photovoltaics or even biomass. The conversion via photovoltaics, for example can be estimated as



follows: The solar constant is  $1.369 \text{ kW m}^{-2}$  and approximately 50 % of the solar radiation reaches the surface of the Earth. Photovoltaic systems have an efficiency of approximately 10 %. In the best case, half of the time is night and, therefore, under ideal conditions about  $473\,000 \text{ km}^2$  ( $80 \text{ m}^2/\text{capita}$ ) covered with photovoltaic cells are necessary to produce the world energy demand of today. This number can be compared to the settlement area per capita in Switzerland, which is  $397 \text{ m}^2/\text{capita}$ . The total area corresponds to a square with a side of length 700 km located in northern Africa, for example.

Energy from sunlight is converted into electricity, for example by means of photovoltaic cells. Electricity from a renewable energy source is used for the electrolysis of water. The oxygen is released into the atmosphere and hydrogen is stored, transported and distributed. Finally, hydrogen, together with the oxygen, is combusted and the energy is released as heat and work leaving water or steam for release into the atmosphere. Therewith the hydrogen cycle is closed.

Electrolysis of water is an established technology and is used today to produce high purity hydrogen. Electrolysis at ambient temperature and pressure requires a minimum voltage of 1.481 V and therefore, a minimum energy of  $39.4 \text{ kWh kg}^{-1}$  hydrogen. Today electrolyser systems consume approximately  $47 \text{ kWh kg}^{-1}$  hydrogen, that is the efficiency is approximately 82 % [7]. The only impurities in the hydrogen gas from electrolysis are water and oxygen. The chemical energy per mass of hydrogen ( $39.4 \text{ kWh kg}^{-1}$ ) is three times larger than that of other chemical fuels, for example liquid hydrocarbons ( $13.1 \text{ kWh kg}^{-1}$ ). In other words, the energy content of 0.33 kg of hydrogen corresponds to the energy content of 1 kg of oil. There is, however, a technical and an economic challenge to overcome before the hydrogen energy economy becomes reality.

The technical challenge is real time production, the safe and convenient storage and the efficient combustion of hydrogen. In order to satisfy the world demand for fossil fuels, more than  $3 \times 10^{12} \text{ kg}$  hydrogen will have to be produced per year. This is roughly 100 times the current hydrogen production. The number of single processes (hydrogen production, conditioning, distribution, transportation, conversion) reduces the overall energy efficiency; and the installation of the corresponding devices requires an enormous amount of energy to be spent in advance, coupled to a large financial effort.

The economic challenge is the cost of the hydrogen production. The world economy today is based on free energy naturally stored over millions of years. The price we are used to paying for fossil fuels is only the mining costs. In order to adapt the world to a synthetic fuel like hydrogen the world economy has to be convinced to pay also for the conversion of solar energy into a fuel.

This book is a comprehensive review of the fundamentals of such a hydrogen economy. Chapter 2 is devoted to an outline of the history of hydrogen and relevant events which coined the overstated concerns about the safety of hydrogen. In order to underline the need for a new energy strategy, Chapter 3 is a precise analysis of the world's energy status and the currently used fossil fuels. The discussions reflect the various opinions on this subject, in particular how a sustainable future should be developed. Hydrogen is, apart from its use as an energy carrier, one of the most