

Chapter 2

Hydrogen as Future Energy Carrier

In the view of a desirable and drastic reduction of both world-wide greenhouse gas emissions and not-renewable resource exploitation, the utilization of sustainable energy sources, such as solar, wind, hydro, or biomass are a mandatory option as well as the use of alternative fuels in the transportation field. In the context of new advanced energy conversion technologies, since 1990s a strong interest of international scientific and industrial community has been addressed towards the possible development of a global 'hydrogen economy' based on the hypothesis that hydrogen could play a basilar role as future energy carrier [1–3], in particular as innovative fuel in automotive field, where it could flank or, in a long-term scenario, replace the traditional oil-derived liquid mixtures in passenger cars. Hydrogen is the most common element in the universe, and its molecule (H_2) has the highest energy content per unit weight of any known fuel, but it never occurs by itself on earth, as it always combines with other elements such as oxygen (to form water as molecule) or carbon (to form hydrocarbons and coal). Thus, it needs to be produced and for this reason it is not a primary source, but only an energy carrier, which could be used in combination with electricity in an innovative overall energy system.

In this chapter, the state of art on the main technologies for hydrogen production, distribution and storage is detailed and analysed evidencing the technical potentialities of this fuel and the barriers which hinder its massive diffusion in automotive field. The key factor for a large utilization of hydrogen not only in transportation sector but also in all the other energy markets is represented by cost and efficiency of production technologies. In the first paragraph the technical issues of the main hydrogen production methods are discussed taking into account that hydrogen can be produced starting from a large variety of primary resources. Moreover, the application of hydrogen in the transportation sector introduces additional problems correlated to the creation of a large infrastructure network for fuel utilization, strictly related to the selected production technologies. The development of specific on-board storage technologies is necessary to match the

high energy densities typical of the traditional liquid fuels (gasoline, diesel, LPG) used to feed internal combustion engines in passenger cars. Hydrogen infrastructure scenarios are briefly reported in Sect. 2.2, while Sect. 2.3 analyses the potentialities of different on-board storage technologies.

2.1 Hydrogen Production

One of the advantages of using hydrogen as energy carrier is that all primary resources such as fossil fuels, renewable energy sources (solar, wind, hydro, geothermic, biomass) and nuclear power could be used for its production [4]. In particular, it can be extracted from any substance containing hydrogen atoms, such as hydrocarbons, water and even some organic matter. Thus, the different technologies utilize mainly these compounds as starting materials for the final H₂ molecule formation. In addition it can be readily produced from synthesised hydrogen carriers such as methanol, ammonia and synthetic fuels.

In Table 2.1, the contributions of the different sources to the current worldwide hydrogen production are summarized, together with the available technologies used for each raw material.

Almost half of the hydrogen used worldwide comes from steam reforming (SR) of natural gas (48%), as it is the most economical route from hydrocarbon feedstock. The other contributions to hydrogen production are based mainly on partial oxidation of refinery oil (about 30%) and coal gasification (18%), whereas only 4% of the produced hydrogen derives by water electrolysis. The hydrogen is mainly used to make ammonia for fertilizers, in refineries to make reformulated gasoline, and also in the chemical, food and metallurgical industries.

The pathways involving fossil fuels (natural gas, refinery oil and coal) that provide for almost 96% of the total production of hydrogen, release carbon dioxide in the atmosphere.

Innovative strategies able to capture and sequester carbon dioxide emissions, so-called Carbon Capture and Sequestration (CCS) technologies, are the object of several analysis and heated debate. CCS technologies should be applied for an environmental-friendly diffusion of fossil fuel-based H₂ production methods, but they are presently in the embryonic stage of development and certainly would involve a great growth of costs.

Table 2.1 World hydrogen production capacity from different sources

Raw material	Technology	%
Natural gas	Catalytic steam reforming	48
Refinery oil	Partial oxidation	30
Coal	Gasification	18
Water	Electrolysis	4

Adapted from [5]

On the other hand, water electrolysis, which is an intrinsic carbon-free method as it involves splitting water into its component parts, hydrogen (H_2) and oxygen (O_2), is strongly limited because of the present high costs of electricity generation. Thus, the costs will certainly represent one of the most important barriers to be overcome for a sustainable massive production of hydrogen.

An overview of the strategies for hydrogen manufacture is reported in Fig. 2.1, where all likely production technologies are related to the different resource options.

The different methods could be classified as: (i) thermal, (ii) electrolytic or (iii) photolytic processes, they will be all detailed in this Section.

The heart of the thermal processes consists of using the energy associated with chemical reactions to obtain directly hydrogen (see Sect. 2.1.1). Hydrocarbon reforming reactions as well as coal gasification are part of this type of processes. In natural gas SR the fuel reacts with steam at relatively high temperature, producing hydrogen and carbon dioxide [5]. In partial oxidation and gasification processes the fuels react with a controlled oxidant mixture (air or/and oxygen, and steam) producing similar product mixtures. A further method that should be considered as ‘thermal’ is the technology based on thermochemical cycles involving different

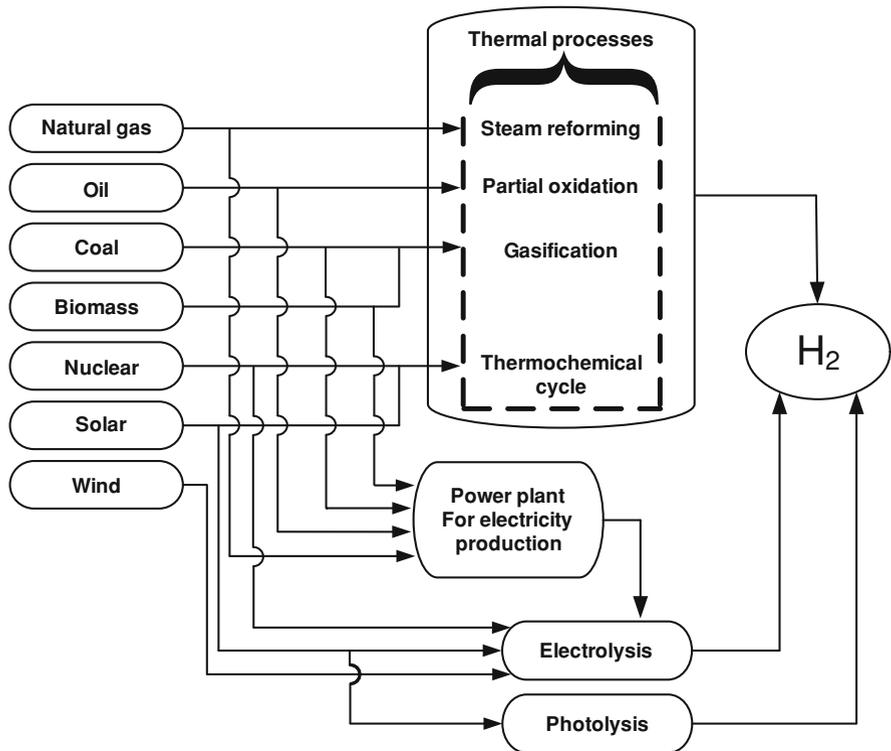


Fig. 2.1 Flowsheet of the main hydrogen production technologies

chemical reagents [4]. In these processes hydrogen is extracted from water thanks to heat combined with closed-chemical cycles, necessary to reduce the very high water decomposition temperatures ($>2500^{\circ}\text{C}$), difficult to be reached for heavy limitations due to materials and heat source.

Electrolysis uses electricity to split water into hydrogen and oxygen by means of an electrochemical approach (see Sect. 2.1.2). Hydrogen produced via electrolytic processes can result in zero greenhouse gas emissions, depending on the selected primary source of the electricity. In addition to renewable and nuclear power, fossil fuels or biomass could be also used in stationary power plants to produce electricity for water electrolysis (see Fig. 2.1).

The analysis of photolytic methods (see Sect. 2.1.3) completes the discussion about hydrogen production. They use sunlight energy to split water into hydrogen and oxygen by photo-electrochemical and photo-biological approaches. These *direct sunlight*-based processes are currently in the very early stages of research, but could offer long-term potential for sustainable hydrogen production with low environmental impact.

2.1.1 Thermal Processes

The thermal processes require the use of thermal energy to favour the advance of chemical reactions providing hydrogen as direct product. Thermal approaches involve, as reactants, various resources which contain hydrogen atoms as part of their molecular structure, such as hydrocarbons or water, and the conversion advance aimed at directly obtaining high hydrogen yield can be further improved by catalyst addition (hydrocarbon reforming) or should require chemical compound usage (water splitting by thermochemical cycles).

Natural gas SR, hydrocarbon partial oxidation or coal gasification are all examples of ‘thermal’ methods and they are described in Sects. 2.1.1.1, 2.1.1.2 and 2.1.1.4, respectively. The theoretical possibility to overcome the problem of carbon dioxide emissions without using the CCS technology is based on other possible ‘thermal’ methods, such as the hydrocarbon cracking (see Sect. 2.1.1.3), or gasification of biomass-derived fuels (see Sect. 2.1.1.5). Also the thermal production of hydrogen based on thermochemical cycles appears quite promising (see Sect. 2.1.1.6), being its overall reaction based on the decomposition of water aided by intervention of chemicals, anyway completely recycled.

2.1.1.1 Natural Gas SR

SR of hydrocarbons, in particular of Natural Gas (NG), is still today the major industrial process for the manufacture of hydrogen [6–8].

This process was introduced in Germany at the beginning of the twentieth century to produce hydrogen for ammonia synthesis, and it was further developed

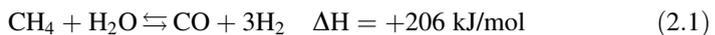
in the 1930s when NG and other hydrocarbon feedstocks such as naphtha became available on large scale. H_2 is currently produced from NG in large quantities in mixtures with nitrogen or carbon oxides for manufacture of ammonia, alcohols (mainly methanol) and for Gas to Liquid (GTL) processes [6]. In particular, SR produces a mixture of H_2 and CO (synthesis gas or syngas) that could be used directly for the synthesis of methanol or higher alcohols, and for Fischer–Tropsch synthesis.

Natural Gas feedstock is mainly constituted by methane molecule (CH_4), which represents the hydrocarbon with the highest H/C ratio. The composition of the NG could slightly change in dependence of the geographic region where it is extracted, but generally the mixture contains mainly small amounts of light hydrocarbons (C_2 – C_4). The compound present in the highest concentration is the ethane (C_2H_6) that can reach in some mixtures a volumetric concentration of 5%. Not negligible traces of sulphur are often detectable in the hydrocarbon mixture.

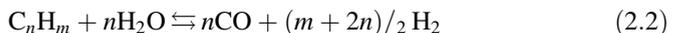
A simplified scheme of methane SR is shown in Fig. 2.2, which includes all main process steps involved in hydrogen production plants based on the SR reaction [8].

Two units remove the sulphur concentrations (ppm), added to natural gas as an odorant for safety detection, or present in higher hydrocarbon feedstocks, to protect downstream catalysts (sulphur is a poison for SR catalysts) and process equipment. In particular, the organo-sulphur species are converted to H_2S at pressures exceeding about 500 psig and temperatures higher than $350^\circ C$ by catalytic hydrodesulphurisation (HDS unit), and Co and Mo alumina-based particulates are used as catalysts. This step is not required for methanol but would be necessary for any sulphur-containing petroleum-based fuels. A second unit permits the H_2S produced in the first step to be removed by a particulate bed of ZnO. When necessary a further step for chloride removal should be included (not reported in Fig. 2.2).

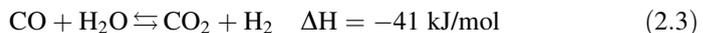
The third step is the heart of the process (steam reformer). Ni-based ($Ni-Al_2O_3$) catalysts, loaded in tubular reactors, favour the advancement of the following reactions:



or for higher hydrocarbons:



Simultaneously in high- and low-temperature shift reactors, the so-called water gas shift reaction produces further H_2 according to the exothermic equation:



Thus SR process is highly energy intensive as the Eqs. 2.1 or 2.2 are highly endothermic and requires high energy inputs, in dependence of the fuel. SR is normally carried out at 800 – $900^\circ C$ and about 0.1 – 0.3 MPa. Expensive alloy reaction tubes have to be used to withstand the severe operating conditions.

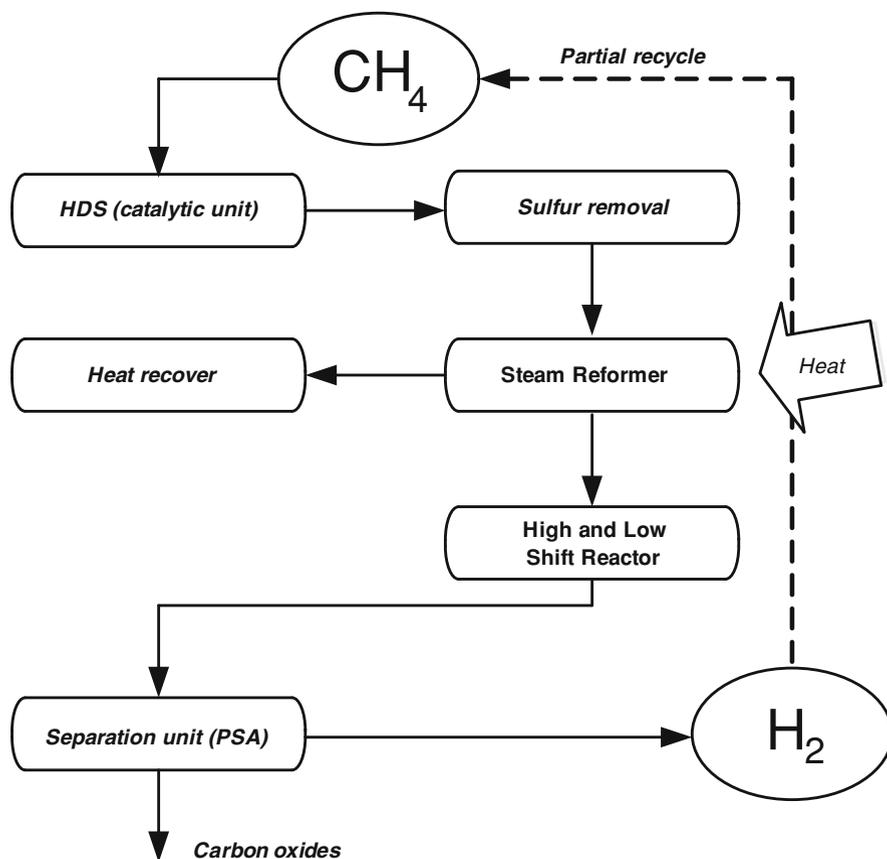
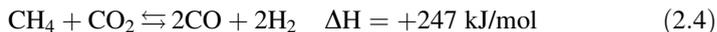


Fig. 2.2 Simplified scheme including all main process steps involved in hydrogen production plants based on methane SR

The array of tubes filled with the catalyst is suspended in a furnace that supplies heat for the highly endothermic reforming reactions.

In some cases carbon dioxide may replace steam to give a more favourable H_2/CO ratio for subsequent reactions of the products [8]:



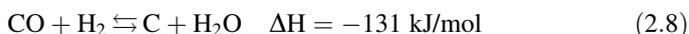
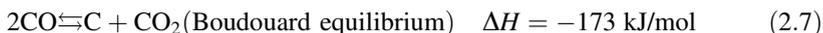
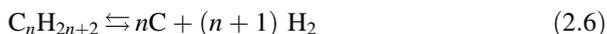
The product selectivity for all these reactions is controlled predominantly by thermodynamics, i.e. the final product composition can be foreseen by multi-component chemical equilibria calculations.

When other hydrocarbons (for example propane) are used as feedstocks, CH_4 is the favoured product at lower temperatures, while hydrogen is preferred at temperatures superior to 700–800°C [6], then the product gas leaves the tubular reactor at temperatures between 700 and 950°C, in dependence of the particular application. The necessity to operate at these temperatures introduces several

potential problems. In particular, the thermal stability of catalysts needs to be carefully verified [9], because steam tends to favour catalyst and support sintering [10]. However, the major problem lies in the formation of coke, according to the following thermodynamically possible reactions:



or for higher hydrocarbons:



The coke can affect the performance of active sites of SR catalysts [11, 12], determining their partial deactivation, with progressive loss of selectivity towards synthesis gas production, blockage of reformer tubes and increasing pressure drop.

The above reactions are in equilibrium and the formation of coke via reactions (2.7) and (2.8) becomes less favoured as the temperature increases. However, coke formation via reactions (2.5) or (2.6) becomes increasingly important at higher temperatures and, depending on the nature of the feed, can rapidly deactivate the SR catalyst and block the reactor [12].

Therefore, the minimization of coking is one of the major factors controlling the industrial application of SR. The thermodynamic of the process dictates reaction conditions that favour coke formation cannot be avoided, but operating conditions can be chosen to minimize coke. Temperature, pressure and feed composition must be carefully controlled to avoid catalysts deactivation due to coking. Perhaps, the most obvious way is to increase the steam to hydrocarbon ratio to favour the reverse of reaction (2.8). Rostrup-Nielsen et al. [13] have presented carbon limit diagrams which relate the propensity of the catalyst to coke formation as function of the H/C and O/C ratios in the gas phase.

The outlet from the secondary reformer contains about 10–14% CO (dry gas) which is fed to a high-temperature water gas shift (WGS) reactor (Fig. 2.2), typically loaded with Fe or Cr particulate catalyst at about 350°C. This further increase the H₂ content lowering CO content to about 2% as governed by the thermodynamic and kinetics of the Eq. 2.3, that is an exothermic reaction. Water gas shift reaction equilibrium is sensitive to temperature with the tendency to shift towards products when temperature decreases.

Then the product gas is fed to a low-temperature reactor where a Cu/Zn–Al₂O₃ particulate WGS catalyst works at about 200°C. Outlet CO concentration is decreased to <0.5%, while the remaining CO, which can poison downstream ammonia or methanol synthesis catalysts, is removed by pressure swing adsorption (PSA) unit. This method exploits the adsorption capacity of different molecular sieves or active carbon, which selectively permit the crossover of hydrogen but not of the other compounds present in the effluents. This technology has been

introduced relatively few years ago (the industrial application started in the 1970s) and results highly reliable and flexible.

Starting exclusively from Eqs. 2.1 and 2.3, considering a stoichiometric mixture of CH_4 and H_2O completely converted to H_2 and CO_2 , and taking into account the heat of reaction supplied by combustion of CH_4 , it is possible to calculate the theoretical energy associated with lower heating value (LHV) of methane to produce H_2 . The minimum energy consumption which can be reached by this process corresponds to 2.59 Gcal/1000 Nm^3 H_2 when starting from water vapour, and 2.81 Gcal/1000 Nm^3 H_2 when starting from liquid water, as the real process [6].

Hydrogen plants designed with conventional technology utilize reforming temperatures below 900°C and high steam to carbon ratios (>2.5), to limit coke formation problems. These plants are characterized by quite poor energy efficiency, as significant amounts of process steam have to be condensed by large air and water coolers. Moreover, investment costs are high, as large volumetric process flows have to be handled [6].

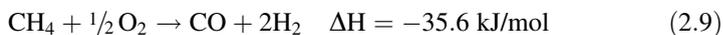
Modern hydrogen plants utilize the new developments in SR and shift technology, allowing apparatus to be designed with reforming temperatures above 900°C and steam to carbon ratios even lower than 2.0 [6]. These advanced SR plants have improved energy efficiency and reduced hydrogen production costs. Currently, the processes require about 2.98 Gcal/1000 Nm^3 H_2 implying that an advanced reforming technology consumes about 6% more energy than the theoretical minimum.

In recent years, new concepts to produce hydrogen by methane SR have been proposed to improve the performance in terms of capital costs reducing with respect to the conventional process. In particular, different forms of in situ hydrogen separation, coupled to reaction system, have been studied to improve reactant conversion and/or product selectivity by shifting of thermodynamic positions of reversible reactions towards a more favourable equilibrium of the overall reaction under conventional conditions, even at lower temperatures. Several membrane reactors have been investigated for methane SR in particular based on thin palladium membranes [14]. More recently, the sorption-enhanced steam methane reforming (Se-SMR) has been proposed as innovative method able to separate CO_2 in situ by addition of selective sorbents and simultaneously enhance the reforming reaction [15].

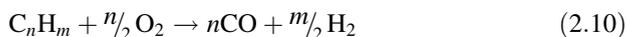
2.1.1.2 Hydrocarbon Partial Oxidation

An alternative route to produce synthesis gas starting from hydrocarbon feedstock is the partial oxidation reaction (POX) [16]. This reaction utilizes the oxygen in the air as oxidant and results moderately exothermic. The oxygen to carbon ratio is lower than that required by stoichiometric complete combustion.

The stoichiometric equation for methane conversion is:

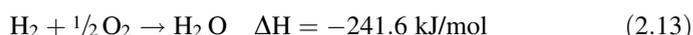
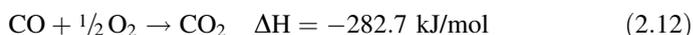


or for higher hydrocarbons:



The theoretical H_2 to CO ratio results lower than that of SR (about 2/3), as the main oxidant is O_2 instead H_2O . However, a small amount of water is often added to the reactor feed, to better control reaction temperature and coke formation [16].

The reactions (2.9) or (2.10) are not the exclusive routes of the process as other stoichiometric equations are thermodynamically compatible with the mixture composition fed to the reactor. Equations 2.1–2.8 involved in hydrocarbon SR might occur also in partial oxidation, i.e. they are possible reaction pathways in addition to (2.9) or (2.10). On the other hand, it is necessary to consider that further equations related to several oxidation reactions could occur during fuel conversion:



POX involves the combustion of hydrocarbon feedstock in a flame with less than stoichiometric oxygen required by complete combustion with production of carbon dioxide (CO_2) and water (H_2O), according to Eqs. 2.11–2.13, which in turn react with the unreacted hydrocarbon (Eqs. 2.1 and 2.4 in Sect. 2.1.1.1), to produce carbon monoxide and hydrogen. Usually a slight excess (20–30%) of oxygen with respect to the stoichiometric value required by equations (2.9) or (2.10) is fed to the system. The most recognized reaction mechanism hypothesis is that the highly exothermic total oxidation reaction consumes essentially all the available oxygen, and the large amount of thermal power produced by the combustion is exploited by endothermic reforming reactions. However, the POX process remains globally exothermic.

A non-catalytic partial oxidation process based on the above reactions has been largely used for the past five decades for a wide variety of feedstocks, in particular heavy fractions of refinery, such as naphtha, vacuum fuel oil, asphalt residual fuel oil, or even whole crude oil. The absence of catalysts implies that the operation of the production unit is simpler (decreased desulfurization requirement) but the working temperatures results higher than 1200°C . The high values of this parameter permit satisfactory yield to H_2 and CO to be obtained without using a selective catalyst.

A catalytic partial oxidation (CPO) reaction permits operation temperature to be lowered and meets the requirements of recently proposed decentralized applications based on small-scale reformer plants [17], better than the SR or the non-catalytic partial oxidation process. This evaluation is based on the dependence of costs associated with both SR and CPO manufacture and management plants by

power size. The potentialities of small-scale plants suggest a deeper discussion about hydrogen distribution network scenarios that is carried out in [Sect. 2.2](#).

The scientific community interest has been focused in recent years especially on H_2 catalytic production by partial oxidation of methane, due to the large diffusion of natural gas as primary feedstock. Coke formation and its deposition on catalyst active sites represent, as well as for SR process, the main barrier to be abated for a practical utilization of CPO in hydrogen production plants.

Methane CPO has been intensively studied to select new advanced catalysts able to maximize hydrocarbon conversion, hydrogen yield and especially to control catalytic deactivation phenomena, strictly connected to coke deposition problem, similar to SR process [18–23]. The role of transition metal-based catalysts in methane CPO reaction mechanism has been detailed [24], evidencing that fuel dissociation step is crucial for a viable overall process rate at reasonable temperatures, as expected taking into account the stability of methane molecule.

LPG could be another favourable feedstock for distributed hydrogen production since it is easy to store and transport. Furthermore, LPG and NG appear attractive because hydrocarbon mixtures with short aliphatic chains (C_1 – C_4) and no-sulphur or other electronegative atoms (Cl, P) could limit carbon deposition and catalyst poisoning. Commercial Ni catalysts used for SR plants have resulted very active also for CPO of methane and propane, but deactivation resistance due to coke is not yet acceptable [25–28]. Ni-based catalyst modification with rare-earth metal oxide La_2O_3 can reduce the Lewis acidity of the catalyst surface and enhance its ability to suppress carbon deposition [29], while among the various noble metal catalysts Rh has been reported as active and stable [30]. Bi-metallic Ni–Pt catalysts supported on Al_2O_3 result very promising if compared with monometallic catalytic solids [31]. Mixed oxides containing Ce seem useful to formulate a catalyst suitable for a durable hydrogen production, in particular CeO_2 is known to be an oxy-transporter, i.e. it is capable to oxidize deposited carbon particles and to actively participate in mechanism of redox catalytic reactions [32]. On the other hand, the incorporation of ZrO_2 into CeO_2 lattice promotes the CeO_2 redox properties, increasing the oxygen mobility within the solid solution formed [33].

If the water quantity added as feed increases up to a value corresponding to neutral energetic balance between exothermic and endothermic reaction steps, the overall process is denominated autothermal reformer (ATR). This approach combines both SR and POX catalytic processes and it has been recently proposed to optimize the performance in terms of compactness and efficiency of small-medium production plants. This technology could permit a compromise between the good efficiency of SR and the fast start up of POX. However, it needs a careful control of in going mass stream [6, 7].

2.1.1.3 Hydrocarbon Decomposition

The direct thermal decomposition of methane or higher hydrocarbons represents the unique approach for a theoretical direct decarbonization strategy [34, 35].

Equation 2.5, moderately endothermic, already involved in SR or partial oxidation processes as secondary undesired reaction, written for a general hydrocarbon



evidences that theoretically hydrogen produced by this route results carbon dioxide emission-free, with the additional potentiality of producing a valuable carbon material.

The non-catalytic route, as for the other fuel processing processes, requires a too high temperature (1300–1600°C) to obtain high reactant conversions, while a catalytic approach would permit the working temperature to be lowered to more practical values. Various Ni-supported catalysts [36–38], and more recently innovative systems doped with other transition metals such as Fe and Co [39, 40], greatly reduce the working temperature, but fast deactivation occurs, due to carbon deposition. The activity loss strongly limits both efficiency and environmental benefits, as catalyst regeneration is necessary, consuming additional energy and producing carbon dioxide emissions.

Carbon-based catalysts and in particular their kinetics have been intensively studied [41–43], because they should reduce the disadvantages related to metal-based catalysts. Carbon materials are more available, have the potential of cost reduction, do not require periodic regeneration because it is not necessary to separate the carbon-product from the catalyst. The fluidised bed reactor technology represents the optimal choice for this kind of hydrocarbon cracking process as it can withdraw the carbon particles evermore, permitting a reliable storage of produced carbon for further use [44–46]. A novel technological solution aimed to improve activity and stability of carbon catalysts has been recently proposed [47]. The presence of small amount of O₂ in an autothermal approach seems to be the best solution to minimize CO₂ emissions in the overall process.

Plasma technology has been proposed as alternative solution to be used in different fuel processing pathways [4, 35, 48, 49]. Similar to catalysis, the plasma approach could drastically increase the rate of the key reaction steps, mainly related to fuel molecule dissociation, abating the activation barrier for the advance of the overall decomposition reaction. The most common method utilizes a high electric discharge produced by two electrodes ('arc'), which determines intense heat, and breaks down organic molecules into their elemental atoms. However, this kind of processes suffers by many limitations, in particular the electricity cost impact on overall efficiency needs to be accurately verified for a transition to large-scale hydrogen production.

Recently, a laboratory atmospheric pressure microwave plasma reactor has demonstrated to be useful for a single-stage, non-catalytic dry methane thermolysis, resulting active and selective towards hydrogen production [50]. Similarly, another novel process proposed for thermo-catalytic decomposition, based on plasma generation of catalytically active carbon aerosol particles, has provided very high efficiency (higher than 80%) at working temperatures below 1000°C [51].

2.1.1.4 Coal Gasification

Another important thermal method is based on the gasification process, currently used on industrial scale essentially to generate electricity.

This technology is also the oldest method for hydrogen production and could convert any type of organic material, such as coal and other petroleum or biomass-derived mixtures. The interest towards this approach comes from the practical possibility of using coal as fuel that is the most world-wide available and relative cheap fossil fuel [52].

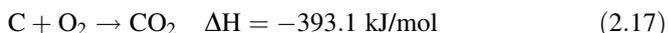
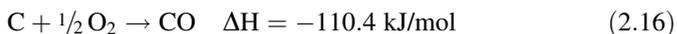
The gasification of coal or other carbonaceous substances was largely used in the past century especially for iron making. The process consists of a series of chemical reactions finally producing, similar to reforming reactions, carbon monoxide and hydrogen mixtures, also called ‘town gas’, which represented in the past century an important chemical feedstock in North America, Europe and China for domestic heating and lighting, public street lighting and domestic fertiliser industry. However, the popularity of town gas decreased significantly by the 1950s as natural gas became widely available. Gasification takes place at high pressure (up to 60 bar) and temperature superior to 700°C, with a controlled amount of oxygen and/or steam. Similar to hydrocarbon reforming-derived synthesis gas, the effluent mixture may be used to produce hydrogen or methanol, burned directly in internal combustion engines, or converted via the Fischer-Tropsch process into synthetic fuel [53].

Coal substances have complex chemical structures and their compositions are highly variable. For example a carbon/hydrogen composition in bituminous coal may be represented as about one atom of hydrogen per atom of carbon. For a generic gasification process based on the above coal feedstock, selected as reference carbonaceous fuel, the following (not balanced) overall chemical equation can be written as:



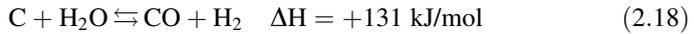
The carbonaceous particles are heated and volatilized at temperatures ranging from 1000 to 1500°C producing carbon oxides and hydrogen gaseous mixtures and simultaneously char (pyrolysis).

A limited amount of oxidant (oxygen or air) is introduced into the reactor and is mixed with crushed/pulverized coal feed (either dry or as slurry) to allow volatile products and some of the char reacts with oxygen to form carbon dioxide and carbon monoxide. The basic reactions for the CO and CO₂ formation are the partial and total combustion of C, respectively



The exothermicity of the above reactions provides heat for the subsequent gasification reactions. The char (or other resulting hydrocarbons) reacts with steam

(but also with carbon dioxide) to produce carbon monoxide and hydrogen, according to the following equation that is the reverse of Eq. 2.8



In addition, the reversible gas phase water gas shift reaction (2.3) reaches very fast equilibrium at temperatures typical of a gasifier. The above chemical equations balance all the product (CO, CO₂, H₂O, H₂) concentrations of the process.

Gasification process could be inserted in a Integrated Gasification Combined Cycle plant (IGCC) [54, 55] to improve the overall process efficiency. The syngas produced in the gasifier is used as fuel in the gas turbine generator of the integrated combined-cycle technology, which consists also of a heat recovery steam generator and a steam turbine/generator. A simplified scheme of a proposed gasification overall plant for generation of both electricity and hydrogen is reported in Fig. 2.3. The scheme evidences different steps to produce electricity and hydrogen. The heart of the overall process remains the gasifier. The coal fed to the reactor is

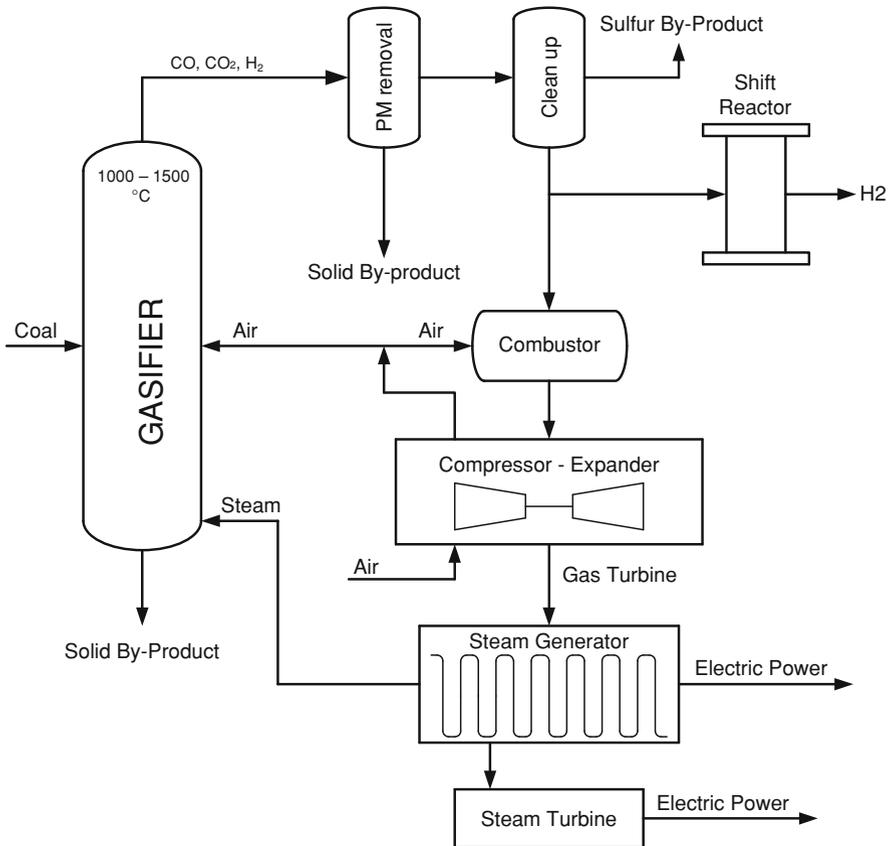


Fig. 2.3 Simplified scheme of an integrated gasification plant [54]

exposed to steam and carefully controlled amounts of air or oxygen under high temperatures and pressures. Sulphur is converted to hydrogen sulphide (clean-up reactor in Fig. 5.3) and can be captured by processes presently used in the chemical industry.

The exhaust heat from the combustion turbine is recovered in the heat recovery steam generator to produce steam. The waste heat is passed to a steam turbine system, while heat is recovered from both the gasification process and the gas turbine exhaust in advanced boilers producing steam. The steam is then used in steam turbines to produce additional electrical power, while the syngas mixture could also feed a fuel cell plant (IGFC).

A potential advantage of this technology is that carbon dioxide can be easily separated from the syngas and then captured, instead of being released into the atmosphere [56–58]. If oxygen is used in a coal gasifier instead of air, carbon dioxide is emitted as a concentrated gas stream in syngas at high pressure. In this form, it can be captured and sequestered more easily and at lower costs. Finally, plasma technology added to gasification plant has been recently proposed to improve energy performance and quality of product mixtures [59].

Hydrogen could be produced from coal gasification with near-zero greenhouse gas emissions only if CCS technology, in particular the crucial sequestration stage, will be successfully developed in the next decades. In this view, the coal gasification technology appears most appropriate for large-scale, centralized hydrogen production plants, where handling of large amounts of coal and CCS technologies could be more functionally managed. Significant technological efforts towards the development of an advanced apparatus capable to enhance efficiency, environmental performance and reliability appear necessary.

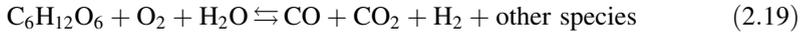
2.1.1.5 Biomass Gasification

The choice of a carbon neutral source class as feedstock for hydrogen production, such as biomass substances, could permit the problem of carbon dioxide emissions to be overcome.

In recent years, several methods for hydrogen production starting from biomass materials have been investigated [60–62], and great efforts have been addressed in particular in selecting advanced solutions for optimization of the previously analysed thermal processes, such as SR or gasification, by substituting the fossil fuel feedstocks (coal or petroleum-derived fuels) with different types of biomass-derived fuels.

In particular, biomass-derived materials could be converted in gasifiers, to obtain a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide and other compounds, by applying heat under pressure in the presence of steam and a controlled amount of oxygen, very similar to coal gasification process. On the other hand, the produced syngas could be reformed to maximize hydrogen production but it may also feed an electrical power plant coupled to an electrolysis unit [63].

Typically, a biomass-derived material contains substances constituted by carbon, hydrogen and oxygen atoms. As an example, the simplified not balanced chemical equation representative of the overall gasification process for a reference substance such as glucose is:



The exhaust gases contain CH_4 , N_2 , H_2O , tar, acidic and basic compounds (NH_3 , HCN , H_2S) considered as impurities. Tar conversion has to be controlled to maximize the reliability of mechanical equipments and to assure the operation of the successive clean-up catalytic steps for final hydrogen separation and purification [64]. This step involves the utilization of additional steam and selective catalysts, affecting the overall efficiency of the process [65]. The operation with oxygen instead of air may improve the efficiency of the process but it suffers the costs associated with air liquefaction process, necessary for O_2/N_2 separation.

The current industrial concept for biomass gasification is conditioned by several problems, i.e. heterogeneity of material availability, relatively high costs of collection and transporting the feedstock, and a relatively low thermal efficiency due to the vaporization cost of the moisture contained in the biomass. In order to lower capital costs many efforts are addressed towards the development of advanced membrane technologies able to separate oxygen from air (when the gasifier utilizes oxygen), replacing the cryogenic process of air liquefaction, and separate and purify hydrogen from the produced gas stream [66].

Similar to coal, biomass gasification technology seems to be more appropriate for large-scale, centralized hydrogen production, due to the nature of handling large amounts of biomass and the required economy of scale for this type of process, and it may be relevant in specific geographic zones where this feedstock is readily available. However, it will be also useful to explore the future possibilities to use biomass for improving economics of distributed and/or semicentral reforming processes. In this respect, heterogeneous waste and in particular municipal rubbish could represent an important feedstock, if thermally pretreated, in medium-sized power plants.

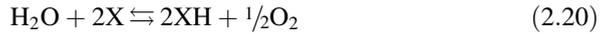
2.1.1.6 Thermochemical Methods

The possibility to transform directly a high-temperature thermal source to chemical energy makes quite attractive the water thermolysis process. This approach represents a direct route for conversion of heat associated with a primary source into hydrogen without intermediate steps; the constraint is that theoretically attractive efficiency can be obtained only if primary sources producing high-temperature energy are used.

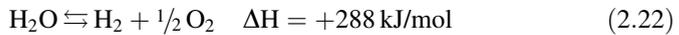
Severe engineering barriers are correlated to the very high temperatures necessary to split water exclusively by heat, together with the problems connected to heat extraction and thermal management. These problems require the practical

development of a more complex concept of water decomposition, based on multi-step thermochemical processes. This approach is founded on the characteristics of several chemical reagents, capable to lower the temperatures of water decomposition down to a commercially viable value, inferior to 1200°C.

A schematic overall process involves at least two steps:



where X represents the generic chemical agent. Obviously the net balance reaction is the reverse of Eq. 2.13:



where ΔH is calculated considering the water in liquid form. The nature and the role of intermediate compounds (XH) are the key point for a successful process, strictly related to the reaching of the following targets [4]:

1. Gibbs free energy variation of all individual reaction steps must approach zero.
2. The different steps should be minimal.
3. Direct and reverse reaction rates of the different steps need to be very fast.

A lot of thermochemical cycles have been proposed in literature [4, 67, 68], potentially able to exploit the high-temperature energy coming from nuclear or concentrating solar plants (CSP).

In particular iodine–sulphur reaction results quite attractive [68]. It consists of three steps at different operation temperatures, which involve the H_2SO_4 and HI dissociation and the re-production of both acids starting from I, SO_2 and H_2O . Particular interest is also focused on $\text{CeO}_2/\text{Ce}_2\text{O}_3$ cycle, cerium–chlorine cycle (Ce–Cl), Zinc–zinc-oxide cycle (Zn/ZnO), but also on a Cu–Cl cycle, which is a cycle with an electrochemical step [69].

This technology appears really promising for a massive efficient hydrogen production but it is still far to be practically realized in few years, basically because of engineering and material constraints associated with high operation temperature (not inferior to 900–1000°C).

2.1.2 Electrolytic Processes

The possibility to store the surplus of electric energy produced by the power plants into a hydrogen carrier represents an attractive potential solution to optimize the overall efficiency of energy production and utilization. This idea requires a technology able to transform the excess of produced electric energy into the chemical energy of hydrogen molecule.

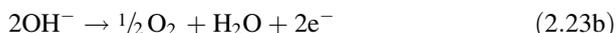
A well-known electro-chemical method to obtain hydrogen using electricity is the water electrolysis [70, 71], which permits the splitting of water molecule into H_2 and O_2 according to Eq. 2.22 reported in Sect. 2.1.1.6.

The galvanic cells produce electric energy via electro-chemical reactions, while electrolytic cells, such as those used in water electrolysis, are electrochemical cells in which a chemical reaction is forced by added electric energy.

The galvanic cells are based on a spontaneous overall reaction characterized by a negative value of the Gibbs free energy, which corresponds to the theoretical electric work (see details in Sect. 3.1). The electrolytic cells represent exactly the reverse of the galvanic process, then the overall reaction, characterized by a positive value of the Gibbs free energy, is not spontaneous, and needs an external energy resource to force the advance towards the products.

Different electrolysis technologies could be applied, from the commercially available method based on alkaline cells to the new advanced cells based on proton exchange membrane (PEM) and solid oxide mixtures as electrolytes. The basic schemes of these electrolyzers are shown in Fig. 2.4.

The alkaline device utilizes a solution of potassium hydroxide (KOH) as electrolyte (Fig. 2.4a). The two semi-reactions of reduction (cathode side) and oxidation (anode side) that occur in alkaline solution are, respectively



The sum of the two semi-reactions (2.23a) and (2.23b) gives the overall Eq. 2.22. Hydroxyl-ions represent the chemical species that close the electric circuit through the electrolyte. The alkaline solution contains about 30 wt% of potassium hydroxide and operates at about 80°C. Today, this technology gives

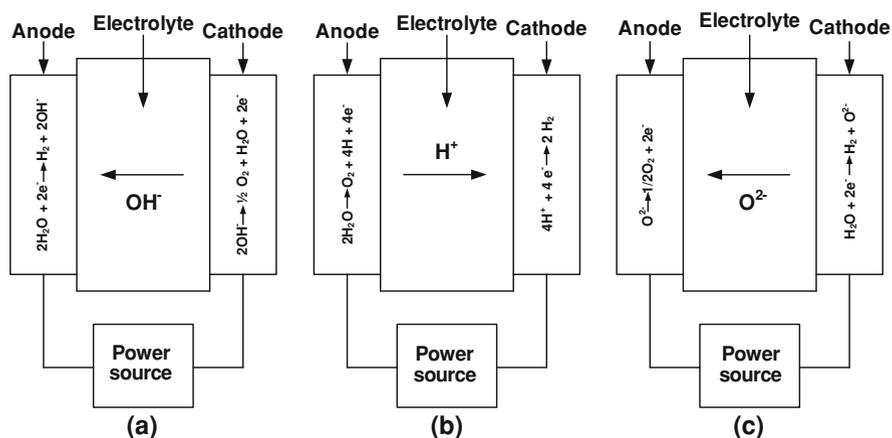


Fig. 2.4 Simplified principle scheme for alkaline (a), PEM (b) and solid oxide (c) cells for water electrolysis

a very low contribution to the worldwide hydrogen production (see Table 2.1), because of the high costs of electricity and the high but not complete conversion efficiency [72]. Furthermore, the KOH solution could limit the resistance of used materials because of corrosion phenomena. In the past years, many studies have been addressed towards a further improvement of catalysed electrodes to optimize the efficiency and reliability of the electrolytic process involving alkaline cells, but the results have not yet satisfactory [73–75].

New advances of the other two electrolytic cells reported in Fig. 2.4 have been recently encouraged to exploit the higher potentialities of PEM and solid oxide technologies, as electrolyser components to be integrated in plants based on wind and solar renewable sources [76, 77] or nuclear power [78], respectively.

As regarding electrolysis with PEM cells (scheme b of Fig. 2.4), which is just the reverse of fuel cell operation mode, the interest derives by greater energy efficiency, ecological cleanness, easy maintenance, smaller mass–volume characteristics and high degree of gases purity [79–81]. Furthermore, it is expected that future costs could be progressively reduced due to foreseeable technological advances of PEM devices working as electric power generation.

The two semi-reactions involved in the process are:



Equations 2.24a and 2.24b are the oxidation and reduction steps, occurring at anode and cathode side, respectively, while the protons represent the ion species passing through the solid polymer electrolyte. However, the overall electrochemical reaction is the same of alkaline electrolysers.

Recent studies have been devoted to the optimization of the already existent PEM electrolysers, first exploring the possibilities to increase the working pressure. The high pressure electrolysis (HPE) should reduce significantly the energy costs for the successive fuel compression step. Currently, the on board-storage of hydrogen in fuel cell cars (see details in Sect. 2.3) requires a compression stage before feeding the vehicle, while the need for an external hydrogen compressor could be avoided by pressurising the hydrogen in the electrolyser. The energy required to produce high pressure hydrogen by high pressure water electrolysis is estimated to be about 5% less than that required for devices working in atmospheric conditions [82]. However, high pressure operation could affect the performance of existent Nafion electrolytic membranes [83] and yield additional problems regarding efficiency loss due to cross-permeation phenomena [81] that implies also relevant safety issues. On the other hand, the application of this technology for electrolytic hydrogen production is mainly related to costs of noble metals used in membrane electrode assembly (MEA, see Sect. 3.2) materials, requiring the development of new high performance and low cost materials [84].

PEM electrolysis process has been proposed especially for wind turbines or solar photovoltaic (PV) panel utilizations. In this case, the electrolysis represents

only a step in the overall hydrogen production process. Efficiency, reliability and costs of overall integrated plants have to be carefully analysed, in particular taking into account the typical intermittent operation mode of each renewable source. Several configurations of PV arrays or wind turbines connected to an electrolyser, based on PEM technology, have been considered evidencing the potentialities of each solution [76, 77]. A possible optimal option is to select the PV panels so that their voltage–current output matches the polarization curves of the electrolyser. Solar PV energy has shown good potentialities as an electricity source for water electrolysis but recent analysis related to environmental and economical issues evidence that wind energy seems to be, at least for the existent technological level, a more promising option to produce electrolytic hydrogen [85, 86].

The operative temperature could play a crucial role for the development of a very efficient electrolyser plant. Solid oxide cells (scheme c in Fig. 2.4) have been proposed for high temperature electrolysis (HTE), because of the strong resistance at high temperatures of the related electrolytes. With respect to traditional room-temperature electrolysis HTE modules presents two main advantages [87]:

1. electrical energy requirement is reduced because of better recover of residual heat, which is cheaper than electricity
2. the power generating cycle, including also electrolysis reaction, is more efficient at higher temperatures.

Currently yttria-stabilized zirconia and doped LaGaO₃ systems seem the most promising materials for developing high temperature (about or higher than 800°C) and intermediate temperature (between 400 and 800°C) electrolysis technologies, respectively [88].

This method could be used for nuclear, concentrating solar or geothermal power plants without carbon dioxide emissions.

The process is based on the following two electrochemical semi-reactions:



where the ionic species are oxygen anions. As for alkaline and PEM electrolyser technologies the overall reaction is Eq. 2.22.

In Fig. 2.5, a simplified scheme of a high-temperature electrolysis plant based on nuclear power is reported [89].

Water is warmed up by outer heat in the boiler of the nuclear reactor, before entering as steam into cathode side, where it decomposes according to Eq. 2.25a, hydrogen molecule is removed as product, and oxygen anion moves to anode through a solid oxide electrolyte with high oxygen ion conductivity. Oxygen ion, losing electrons at the anode side, is the reactant of the oxidation semi-reaction, and is recovered as oxygen molecule, according to Eq. 2.25b.

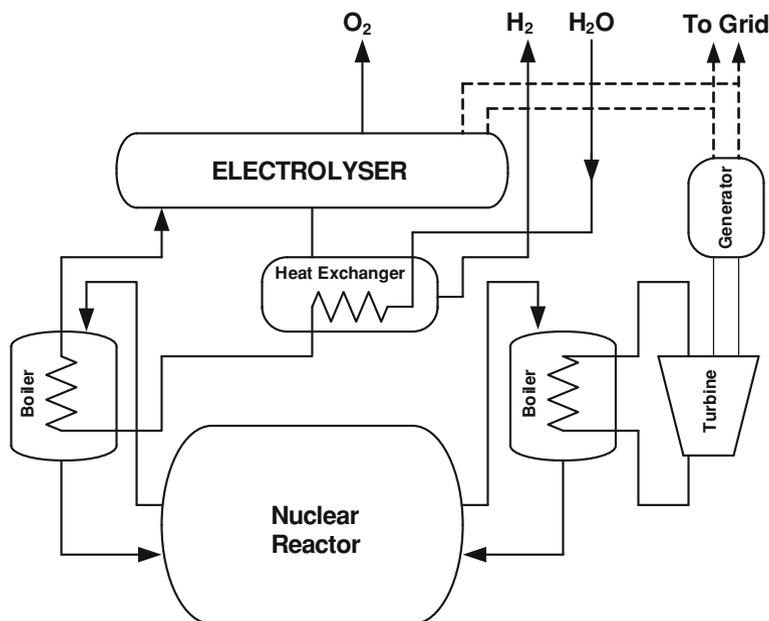
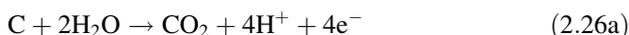


Fig. 2.5 Scheme of a HTE plant based on nuclear power [89]

The steam–hydrogen mixture exits from the electrolyser and the water/hydrogen gas mixture passes through a separator to obtain pure hydrogen, while a portion of the electricity produced by the reactor is used to feed the electrolyser.

Electrochemical oxidation of coal has been investigated at the beginning of 1980s [90] to evaluate the possibility to limit the high electric power required by H_2O electrolysis, simultaneously overcoming the limitations of the conventional hydrogen production starting from coal (see Sect. 2.1.1.4), related to the high costs due to working temperature and separation units. The electrolysis of coal takes place according to the following reactions:



Coal is oxidized at the anode, while protons are reduced to form hydrogen molecule at the cathode. The low current densities achieved in the reaction (about 2.5 mA/cm^2 at 1 V) have discouraged further studies in the successive two decades, but recent works on the development of noble metal carbon fibre electrodes have demonstrated the possibility to improve their activity [91] justifying further experimental tests aimed at fabricating a coal electrolytic cell (CEC) operating at intermediate temperatures ($40\text{--}108^\circ\text{C}$) [92]. Finally, another potential advantage of the coal electrochemical oxidation is that downstream separation of gases is not necessary as pure H_2 and CO_2 are generated in different compartments of the cell.

2.1.3 Photolytic Processes

The photolytic effect represents another technology able to directly exploit the sunlight, in addition to photovoltaic effect and concentrating solar technology. This process could be theoretically used to directly dissociate water molecules into hydrogen and oxygen [93]. The recent advances realized in this field [4, 94] encourage a wide research effort aimed at individuating technological pathways alternative to thermal, thermochemical and electrolytic approaches, for an useful contribution to medium–long term hydrogen production.

In particular, two kinds of processes are under investigation:

1. the photoelectrochemical (PEC) process that uses photoactive cells in which doped semiconductor electrodes are immersed in aqueous solutions or water;
2. the photobiological (PB) water splitting, related to the specific activity of specialized microorganisms.

In the PEC process, an electronic charge formed at the surface of the anode, radiated from solar energy, is able to generate an electron–hole pair. In the presence of an electric field, holes and electrons are forced to move in opposite directions determining the H_2O oxidation to oxygen at the anode side and the hydrogen ion reduction to molecular hydrogen at the cathode side. PEC research is mainly focused on finding reliable semiconductors able to split water in an energetically suitable way [95–97]. On the other hand, PB processes could exploit the potentialities of algae and bacteria in consuming water and produce hydrogen as a byproduct of their natural metabolic processes [98, 99]. This research is focused on the possibility of modifying or engineering them, addressing the solar energy selectively towards direct hydrogen production.

2.2 Hydrogen Distribution

The transition towards the so-called hydrogen economy requires the development of infrastructure plans. Currently, few limited networks for hydrogen utilization exist in the world, mostly concentrated in Europe (UK, Netherlands, Germany) and USA, and located close to refinery site for petrochemical or other industrial requirements.

A future massive network can be realized according to two possible scenarios:

1. a centralized management of the worldwide hydrogen production and distribution, corresponding to the existent energy production strategies
2. a distributed territorial production and utilization, for which H_2 is produced on-site at small–medium-scale filling station.

The analysis of the above strategies needs to include all the stages necessary to produce and distribute the fuel for a widespread use, and should benefit from the following two options for hydrogen transport and distribution:

1. delivery of compressed gas or liquid by tracks
2. gaseous pipelines.

The choice is strictly related to the above scenarios, and depends on the technologies and scale selected for hydrogen production [3, 100].

In Fig. 2.6, the most significant fuel supply options are represented, evidencing individual steps concurring to the realization of each production–distribution chain. The centralized manufacture of hydrogen requires means of transportation, as well as intermediate storage capabilities. In particular, the utilization of hydrogen produced as gas in centralized plants, located at sites quite far from the user points, would require a pipeline grid. Pipelines seem more indicated to transport large quantities of gaseous fuel, and to cover long distances. Road

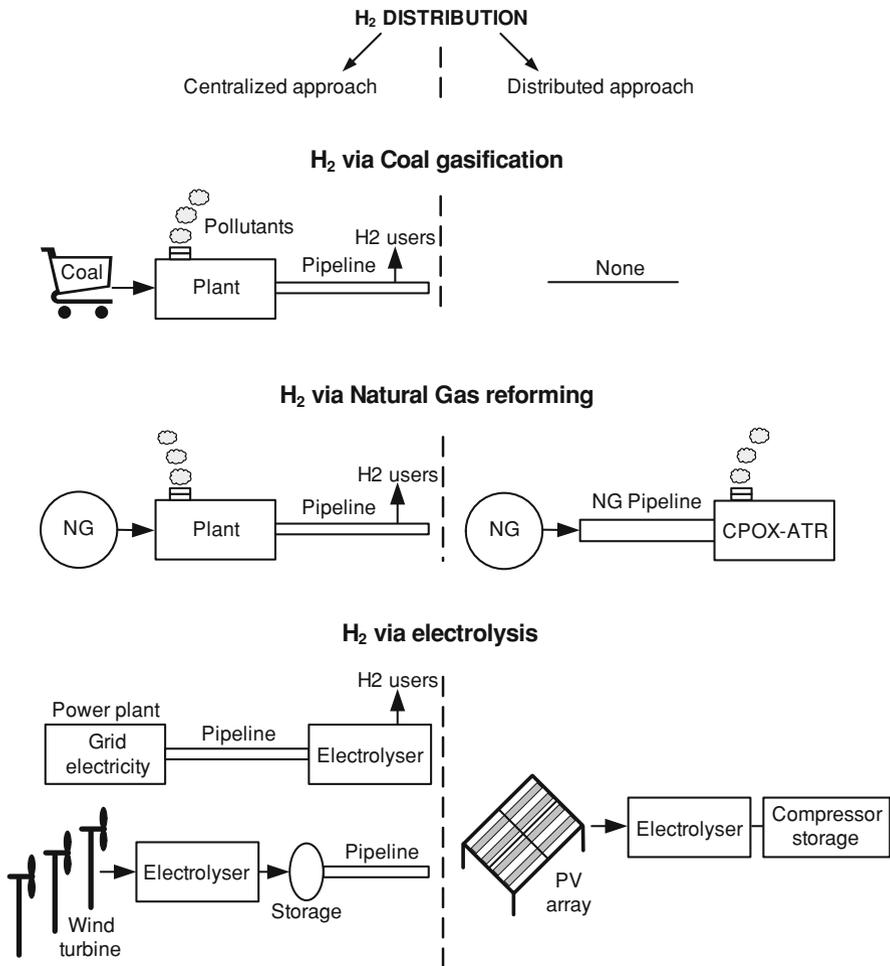


Fig. 2.6 H₂ supply options in centralized and distributed approaches

transportation by trucks, in both high-pressure gas and liquid, should become competitive to move only small quantities of hydrogen.

On the other hand, a distributed manufacture, based on either on-site small reforming plants or on small-size electrolyzers, would permit storage at the vehicle facility and strongly reduce the specific impact of fuel distribution and transport costs on a global techno-economic assessment.

Taking into account that hydrogen can be transported in pipelines similar to natural gas, it is interesting to verify if the existing pipeline infrastructure could be used, evaluating in particular the energetic limitations and the current performance of materials of construction and of shut techniques. This analysis first requires a comparison between the energy flows of hydrogen and methane. The volumetric flow rate through a pipeline can be calculated according to the following equation [101]:

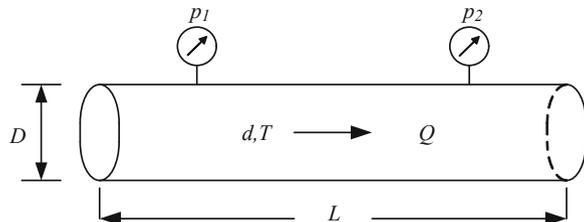
$$Q = CD^{2.5}\lambda\sqrt{\frac{(p_1 - p_2)^2}{dZTLf}} \quad (2.27)$$

where Q is the volumetric flow rate of the gaseous fuel (Nm^3/h), C is a proportionality constant (about 0.00013), D is the inner diameter (mm), λ is the pipeline efficiency, p_1 and p_2 are the inlet and outlet pressure, respectively (kPa), d is the relative density compared to air, Z is the compressibility factor, T is the absolute temperature, L the length (km) and f is the friction factor. In Fig. 2.7, a scheme of a section of pipeline is shown with the indication of main parameters affecting gas flow rate.

Considering the upper heating values of H_2 and CH_4 (12.8 and $40 \text{ MJ}/\text{Nm}^3$, respectively) as well as the wide difference in density values (0.09 for hydrogen and $0.68 \text{ kg}/\text{Nm}^3$ for methane, respectively), similar pressure drops have to be overcome to match the same energy demand. On the other hand, the accurate evaluation of compressibility and friction factor indicates that hydrogen is able to transport at least 80% of the energy carried by NG [102].

Also the aspects related to compression stage and pressure reduction stations need to be accurately considered. The performance of the centrifugal compressor, quite satisfactory for natural gas processing, becomes significantly limited when hydrogen is used, because of the need of higher rotational velocity, not compatible with material strength [101]. On the other hand, hydrogen fragileness [103] could represent a further problem for a sufficient reliability of the pipings and fixings

Fig. 2.7 Section of a pipeline with indication of the main parameters useful for volumetric flow rate calculation (Q)



during long-time operation, while hydrogen leakage, obviously higher with respect to methane, can be significantly limited, especially if polyethylene pipelines will be used for new hydrogen distribution infrastructures [101]. The transportation of hydrogen inside pipelines in liquid cryogenic forms theoretically should increase strongly the energy capacity, but it determines also a dramatic growth of capital costs and severe safety problems [101].

As regarding the transportation of hydrogen using the road, currently hydrogen travels mainly on trucks loaded inside high-pressure vessels (20 MPa). The overall transportation capacity utilizing liquid reservoirs should be higher than commercial vessels, in spite of much higher insulating and refrigeration costs that make them not yet satisfactory for a widespread transportation.

The above discussion suggests that the development of a hydrogen system concept based on distributed small-scale power plants should be easier. In this respect, the most appropriate hydrogen production technologies are based on PV-solar, natural gas reformer or wind-turbine resources, even if the last solution expects some infrastructure network to transport hydrogen from the production point to the user points.

The different pathways need to be environmental efficient and require a carefully evaluation of their impact not only on the costs but also on reliability, safety and social acceptance [104]. Since in a decentralized approach infrastructure cost related to hydrogen distribution is strongly reduced, a global economical evaluation related to both production and distribution has to accurately consider this perspective. On the other hand, the possibilities to lower the costs of centralized hydrogen production and to improve the technologies involved in the creation of a hydrogen transport and distribution infrastructure claim to be also carefully analysed. Optimization-based models capable to evaluate all these aspects for the development of a viable long-term plan has been recently presented, to aid the decision making process [105].

2.3 Hydrogen Storage

The storage capability of tanks is a crucial quality of fuels for road vehicles, because of the need to match the large driving range user demands. The mileage of conventional vehicles powered by liquid fuels reaches values clearly superior to those of battery powered electric vehicles. This is the main reason why the electric powertrain diffusion has been strongly limited up today. Hydrogen fuel cell powertrains could enter in a massive automotive market as potential competitor only overcoming successfully this important question.

The phase diagram for hydrogen is shown in Fig. 2.8, [106] while in Table 2.2 physical and thermodynamic data are reported for hydrogen in molecular form and for commercial liquid fuels, i.e. gasoline, diesel, LPG and liquid natural gas (LNG) that are high and low heating values, gravimetric density and volumetric energy

Fig. 2.8 Phase diagram for H₂

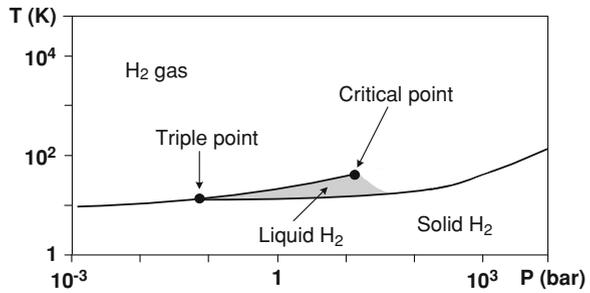


Table 2.2 Physical and thermodynamic data for automotive fuels

Property	Gasoline	Diesel	LPG	LNG	Hydrogen		
					Gas 350 bar	Gas 700 bar	Liquid
HHV (kJ/g)	47.5	44.8	50.3	55.5	141.9	141.9	141.9
LHV (kJ/g)	44.5	42.5	45.6	50.0	120.0	120.0	120.0
Gravimetric density (kg/m ³)	737	820–950	510	410–500	23.5	39.5	70.8
Energy density (MJ/L)	34.2	37.3	25.3	25.9	2.9	5.6	10.1

densities. The volumetric energy densities for hydrogen are calculated for liquid and gas form at pressure values varying from 350 to 700 bars.

The analysis of Fig. 2.8 evidences that hydrogen has very low boiling point. Liquid hydrogen exists only in a limited pressure–temperature region starting from the triple point and ending at the critical point. A narrow temperature range between 14 and 33 K is able to maintain the H₂ molecule in the liquid state in dependence of the pressure value (varying from 0.07 to 13 bar). The saturated liquid specific volume at atmospheric pressure is 0.014 m³/kg, while for H₂ gas in standard conditions (273 K and 1 atm) it results 11.1 m³/kg.

Table 2.2 evidences that hydrogen has very low gravimetric and volumetric energy densities. Hydrogen has the highest energy to weight ratio values (HHV and LHV), in particular it has nearly three times the energy content of gasoline and diesel fuels, but it contains less energy for a given volume when compared to the other fuels. Liquid hydrogen does not reach a density close to that of typical conventional liquid fuels, while hydrogen in gaseous form reaches a value of volumetric energy density lower than hydrogen in liquid form also at a pressure of 700 bar.

In the last years, the scientific community has investigated another interesting option regarding H₂ storage, based on the adsorption method [107–109]. The idea is that a strong reduction of volumes should be obtained by interaction of hydrogen with solid materials, in particular applying knowledge in gas–solid heterogeneous process and exploiting recent advances of the material science applied to physical and chemical adsorption.

The US Department of Energy (DOE) has established a series of targets which should be met by hydrogen storage tanks, including those related to overall system performance [110]. Both volumetric and gravimetric storage system performances are considered basically crucial; the relative target for the year 2010 is fixed in 1.5 kWh/l and 2 kWh/kg as regarding system volumetric and gravimetric capacity, respectively. These targets imply for the hydrogen storing material volumetric density values of at least 45 g/l and gravimetric density not lower than 6 wt%. The following sections contain an overview on hydrogen storage in molecular form (compressed gas and liquid) and some details about the main technological improvements related to the storage by absorption or adsorption processes.

2.3.1 Hydrogen Storage in High Compressed Gas Form

The compression in cylinders with a maximum pressure of 200 bar is a reliable well-established technology, today widely used for hydrogen and natural gas storage. Higher pressures permit the volumetric capability to be improved but not negligible power consumption has to be taken into account when high compression ratios are reached.

The ideal compression (in isothermal conditions) work can be calculated according to the following equation:

$$L = \Delta G = RTZ \ln \frac{p}{p^0} \quad (2.28)$$

where ΔG is the Gibbs free energy variation (corresponding to the ideal useful work L), R is the gas constant, T the Kelvin temperature, Z the compressibility factor and p/p^0 the ratio between the final and initial pressure value. Z factor is approximately 1 in the range 1–100 bar, when the hydrogen behaviour can be approximately assumed as ideal, while at high pressures the density of H_2 affects its compressibility and Z significantly increases in dependence of critical parameters of temperature and pressure.

It can be derived that for $p/p^0 = 700$ an energy loss due to ideal compression results about 2.2 kWh/kg, but in a real compression stage the energy losses are significantly higher because of the irreversibilities that also determine non-isothermal operation. Pressure increments could affect in a not negligible way the impact of the hydrogen compression step on the well-to-wheel efficiency evaluation for hydrogen fuel cell vehicles [111], the energy consumption at 700 bar is about 10% of the H_2 LHV [112]. Additionally, the heat produced during the compression stage gradually reduces the gas density, limiting the positive impact of compression on energy density of the tank.

Dynamic compressors, commercially used for natural gas compression, could be used in case of moderately high compression (p/p^0 up to 200–300), while alternative volumetric devices are necessary for higher pressure ratios. With respect to

methane the hydrogen compression introduces some specific difficulties, related to the different volumetric energy densities and to the choice of dedicated fixings [107]. On the other hand, at higher pressures the gravimetric density of the tank progressively decreases because of the increasing thickness of cylinder walls.

Austenitic stainless steel or aluminium alloys are widely used for 200 bar cylinders but recent advances in lightweight composite cylinders have permitted hydrogen storage systems reliable up to 700 bar to be developed. Composite materials are constituted by high-strength fibres, mainly carbon-based that are wrapped around the cylinders in layers. Several types of advanced high-pressure cylinders could be designed to improve volumetric and gravimetric density in dependence of the weight ratio between metal and composite: from a whole metal to a plastic liner or a fully wound composite overwrap, passing by different percentages of metal liner and composite overwrap.

In order to match the safety issues, future pressure vessels include three layers: an inner polymer liner, overwrapped with a high-strength and high-elasticity carbon fiber composite, and an outer layer of an aramid-material capable of withstanding mechanical and corrosion damage [107].

Recent approaches aimed at improving the unsatisfactory gravimetric and volumetric capacities are based on compressed cryogenic technique [110]. In particular by cooling a tank to nitrogen liquefaction temperature (77 K) the volumetric capacity results three times higher with respect to conventional high pressure tank.

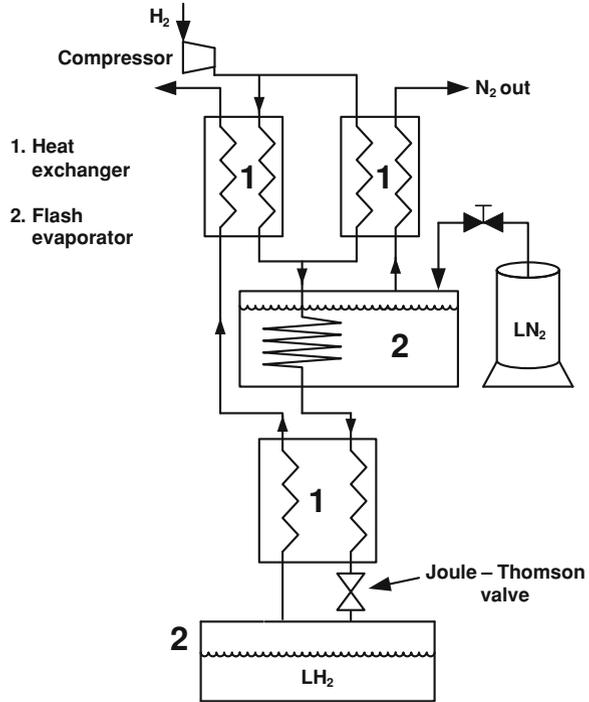
2.3.2 Hydrogen Storage in Liquid Cryogenic Form

The liquid cryogenic technology might represent a valid alternative to high-pressure gas storage approach [113]. It can be used to increase significantly (see Table 2.2) the unsatisfactory volumetric density values of hydrogen stored as gaseous compound. At a very high pressure (700 bar), the gravimetric density of hydrogen in gaseous form does not reach 40 kg/m^3 , while as liquid it reaches about 70 kg/m^3 . However, some technical aspects need to be considered for an overall analysis of this technology.

The Linde cycle is a simple cryogenic process based on Joule–Thomson effect. It is composed of different steps: the gas is first compressed, then preliminarily cooled in a heat exchanger using liquid nitrogen, finally it passes through a lamination throttle valve to exploit the benefits of Joule–Thomson expansion. Some liquid is produced, and the vapour is separated from the liquid phase and returns back to the compressor through the heat exchanger. A simplified scheme of the overall process is reported in Fig. 2.9.

The process is rather expensive because of high electricity costs for compression and the low Joule–Thomson inversion temperature of hydrogen (203 K), that involves high energy consumption necessary to maintain the hydrogen continuously cooled (about 30% of its LHV) [114].

Fig. 2.9 H₂ liquefier block diagram (Linde cycle)



Furthermore, the boil-off effects must be considered because of the liquefaction temperatures (21 K). A very low external thermal exchange fluctuation could produce appreciable vaporization. The font of these variations could be originated by the exothermic transformation of electronic configuration of hydrogen molecule from *ortho* to *para* [107], by the thermal irreversibility of fluid compression, or by the different heat exchange mechanisms with outside. This problem is emphasized for tanks of small size (100 l, typical value for cars), because heat leaks are proportional to the surface to volume ratio, and the high initial density could significantly decrease during the time.

The materials used in the different size vessels are based on stainless steel or aluminium alloys, but also on polymeric materials, such as Teflon. The sphere form is ideal for the minimization of vapour release, due to its minimum surface to volume ratio with respect to all other possible geometries, and for the limitation of stress and uniformity of strain distribution. On the other hand, the manufacturing costs for spheres are too high, in compared with cylindrical shape which is the most economical solution.

Recently, a new liquefaction approach based on the magnetocaloric effect has been proposed [115]. The method is based on the characteristics of some magnetic materials that heat up when placed in a magnetic field and cool down when removed from it. The magnetic refrigeration can develop its potentialities in terms of overall efficiency for liquefaction process, as it is theoretically able to exploit

almost completely (up to 90%) the efficiency of the Carnot cycle, which represents the reference cycle for the cooling process. However, the practical feasibility of an integrated plant based on this method is far to be experimentally verified.

2.3.3 Hydrogen Storage in Solid Materials

Hydrogen storage devices based on high pressure gas and cryogenic liquid technologies do not reach the storage performance of conventional transportation liquid fuels. On the other hand, they suffer also of important safety issues related to the utilization of severe operative conditions necessary to improve, even if only partially, the very low gravimetric and volumetric energy densities typical of hydrogen molecules. An interesting alternative is the storage of hydrogen based on the principle of forming hydrogen containing carriers from which the fuel can be extracted when necessary. Then the idea is to develop materials able to soak up and release hydrogen, thank to absorption and/or adsorption processes [116].

Metal hydrides are ‘hydrogen atom’-carriers usable as storage system [107, 110, 116, 117]. The method is based on specific properties of some metals that readily absorb gaseous hydrogen, thanks to their capability to accept hydrogen atoms, derived by its molecule splitting, inside their interstitial sites in reasonable operative conditions.

The *absorption* process is a reaction of hydrogen gas with a metal, and results moderately exothermic. Then during the charging phase, which occurs typically at 30–60 bar, some heat needs to be removed, while during discharging phase slight changes in operative conditions (temperature and pressure) permit the quantitative amounts of gaseous hydrogen molecules previously charged to be released, according to:



where M indicates the metal used for hydrogen storage.

A schematic hydrogen absorption mechanism consists in the following three steps:

1. mass transport of gas molecules to the solid surface
2. physical adsorption with successive molecule dissociation
3. transition of hydrogen atoms to the metal bulk with formation of new solid phases.

During the third step, at a specified temperature value, the metals bind hydrogen (previously dissociated as atoms in the adsorption step) producing an intermediate solid solution [107, 118]. Increasing the pressure the interaction between hydrogen atoms and metal framework sites becomes stronger, nucleation and growth steps start bringing to the formation of a hydride solution. The concentration limits relative to the formation of the two above solutions (intermediate and hydride)

change with temperature, typically the concentration difference decreases when temperature increases, and becomes zero when the critical point is reached. Until the two solid phases coexist the temperature remains practically constant, and the hydrogen concentration increases inside the intra-metallic mixture, evidencing that the hydrogen amount is reversibly stored at the fixed temperature with slight pressure variations. Finally, the intermediate solution disappears and all hydrogen atoms are entangled in the hydride solid solution. Further hydrogen absorption could occur when the hydrogen concentration increases up to the maximum value compatible with the atom insertion inside the voids of the metal framework.

The strong interest towards metal hydrides is strictly related to the potential of significantly increasing the volumetric density of hydrogen packing (up to 0.2 kg/m^3) that largely exceeds the density of liquid hydrogen (about 0.07 kg/m^3). The operative temperature and pressure of the absorption process depend on the type of hydride, and are the key parameters affecting the efficiency of a hydrogen storage device for automotive application.

The different metal hydrides can be classified in two main categories:

1. Low desorption temperature.
2. High desorption temperature.

The first class is characterized by those metals and metal alloys (iron, titanium and nickel) which require only a small amount of heat to release hydrogen. This heat might be easily withdrawn by the process fluids of a fuel cell powertrain. On the other hand, some hydrogen can be released also at room temperature, but this problem could be overcome by preliminary tank pressurizing, followed by a gradual pressure diminution when hydrogen content within the hydride decreases.

Beside the basic advantages of high volumetric density and low energy inputs, this class of hydrogen storage materials is attractive also for the operational safety. Unfortunately the gravimetric energy density does not reach the targets useful for road vehicle application, essentially because of the high molar mass of metal framework.

The second class includes other hydrides based on light elements, such as alkali and alkaline-earth metals, first of all the metal alloys of magnesium [107, 117–121]. These materials are very interesting because of their acceptable gravimetric hydrogen storage capability, but their poor kinetic properties at moderate temperature strongly limit the practical application. In particular MgH could contain theoretically hydrogen up to about 8% in MgH form, but absorption and desorption processes occur only at elevated temperatures ($>200^\circ\text{C}$), and then require large amount of heat to release hydrogen. The catalytic role of different additional materials such as metal oxides or transition metals has been extensively investigated in magnesium alloys to reduce release temperature and improve kinetics [122, 123], but the results do not evidence significant improvements of their performance.

Recently, metal-doped aluminium hydrides have been proposed as further potential hydrogen storage materials [107, 123]. Among lightweight metal hydrides the lithium and sodium alanates (NaAlH_4 , LiAlH_4) have been widely

studied for their characteristics of high hydrogen content and low release temperatures [124–126]. Reversibility and kinetic of the hydrogen absorption/desorption cycle are critical issues also for this class of compounds. NaAlH_4 hydride can provide 5.5 wt% of hydrogen under reasonable conditions, by a decomposition reaction made reversible thank to the usage of a catalyst [127], while lithium alanate utilization appears not possible because of the irreversibility of the first decomposition step.

Other solid materials are able to storage H_2 storage thanks to the *adsorption* method. The process may be physical or chemical, in dependence of the energetics of the adsorption mechanism. Physisorbed hydrogen is weakly bound to the solid surface because of the ‘attraction’ between the adsorbate (hydrogen) and the adsorbent (solid material); this is due to the induced dipole moment of a non-polar adsorbate interacting with its own image charge in the polarizable solid. On the other hand, chemisorbed hydrogen is strongly ‘attached’ to the material active sites as result of a chemical bond formation between the adsorbent and the adsorbate in a monolayer on the surface. Both the processes can occur especially on porous materials as they require high surface area to maximize the available sites for hydrogen uptake, while molecular affinity is a key parameter which determines the selectivity of the material towards a particular molecule, especially for chemical adsorption.

In the last decade high storage capacities have been claimed for carbon nanostructures, theoretically able to match the automotive targets by means of adsorption [107, 109]. Activated carbon has been first proposed and has shown promising storage capability of about half of liquid, at 50 bar, but exclusively at 77 K [128]. Other types of carbon materials based on nanostructured frameworks have been then selected and proposed. In particular, the narrow pore size distribution of single-walled carbon nanotubes (SWNTs) makes them attractive candidates as adsorbents for hydrogen molecules [129, 130], but the early promising experimental results have been the object of controversy [131, 132].

On the other hand, also carbon nanofibers based on stacked graphite layers seem show appreciable gravimetric storage capacity at room temperature and at moderate pressure (about 120 bar) [133], but other experimental results obtained on similar nano-materials appear contradictory [134], and the hydrogen storage mechanism is still far to be understood.

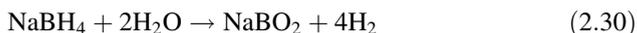
Zeolites, which are a well-known class of molecular sieves and have been proposed in the past for several industrial applications (ion exchange, adsorption, heterogeneous catalysis), are also investigated, but their storage capacity remains not satisfactory also at 77 K [135].

A recent scientific interest has been addressed towards a new class of structured nanoporous materials, constituted by metal organic frameworks (MOFs), whose potentialities are related to their low bulk density and very high specific area, ranging from 1000 to 6000 m^2/g [136]. They are synthesized by linking inorganic clusters with various organic linkers [137], through strong bonds. The interest towards MOF compounds is related to the theoretical possibility to optimize the hydrogen storage exploiting both selective binding energy and high specific area

effects. Several MOF have shown promising results at 77 K with adsorption capacities up to 7.3%, while at room temperature hydrogen uptakes is still not higher than 1% [138, 139].

Recent strategies for improving carbon nanostructures performance based on the spillover mechanism have been investigated. Hydrogen spillover uses a supported metallic catalyst able to dissociate the hydrogen molecule. During the successive phase of the process hydrogen atoms migrate to the substrate and finally permeate through the substrate surfaces and/or into the bulk materials [140]. Thanks to this technique, an appreciable higher storage capability at room temperature (up to about 2.4%) has been obtained by some authors for different types of materials [141].

Chemical hydrogen storage could represent another interesting alternative approach. It consists of on-board hydrogen generation through a chemical reaction which starts from a hydrogen-containing material, characterized by high gravimetric energy density, followed by final off-board regeneration. The storage material needs to be produced, and usually involves hydrolysis reaction. Specific chemical hydrides are used, such as sodium borohydride (NaBH_4) [142]. The following chemical equation describes the process occurring in aqueous solution:



Equation 2.30 is irreversible, moderately exothermic, and can be controlled in the presence of a suitable catalyst. When used on-board of vehicle the residual compounds must be removed and regenerated off-board. This technique could represent an applicative approach especially if liquids are used to store hydrogen, but results too expensive and limited by very high regeneration energy requirements [143]. Recently, the Los Alamos laboratories have proposed a new process able to improve the efficiency of the regeneration phase by addition of appropriate digesting and reducing agents to the spent fuel [144].

References

1. Mcdowall W, Eames M (2006) Forecast, scenarios, visions, backcasts and roadmaps to the hydrogen economy: a review of the hydrogen future literature. *Energy Policy* 34:1236–1250
2. Hetland J, Mulder G (2007) In search of a sustainable hydrogen economy: how a large-scale transition to hydrogen may affect the primary energy demand and greenhouse gas emissions. *Int J Hydrogen Energ* 32:736–747
3. Ball M, Wietschel M (2009) The future of hydrogen—opportunities and challenges. *Int J Hydrogen Energ* 34:615–627
4. Holladay JD, Hu J, King DL, Wang Y (2009) An overview of hydrogen production technologies. *Catal Today* 139(4):244–260
5. Chorkendorff I, Niemantsverdriet JW (2003) Heterogeneous catalysis in practice: hydrogen. In: *Concepts of modern catalysis and kinetics*. Wiley-VCH Verlag GmbH & Co, Weinheim
6. Rostrup-Nielsen T (2005) Manufacture of hydrogen. *Catal Today* 106:293–296
7. Armor JN (1999) The multiple role for catalysis in the production of H_2 . *Appl Catal A* 176:159–176

8. Farrauto RJ (2005) Introduction to solid polymer membrane fuel cells and reforming natural gas for production of hydrogen. *Appl Catal B* 56:3–7
9. Trimm DL (1991) Thermal stability of catalyst supports. In: Bartholomew CH, Butt JB (eds) *Catalyst deactivation*. Elsevier, Amsterdam, p 29
10. Gitzen WH (1970) Alumina as a ceramic material. American Ceramic Society, Columbus
11. Rostrup-Nielsen DJR (1974) Coking on Ni catalysts for steam reforming of hydrocarbons. *J Catal* 33:184–201
12. Trimm DL (1999) Catalysts for the control of coking during steam reforming. *Catal Today* 49:3–10
13. Rostrup-Nielsen J, Dybkjaer I, Christiansen LJ (1993) Steam reforming opportunities and limits of the technology. In: de Lasa HI, Dogu G, Ravella A (eds) *Chemical reactor technology for environmentally safe reactors and products*. Kluwer, Dordrecht, p 249
14. Kikuchi E (2000) Membrane reactor application to hydrogen production. *Catal Today* 56:97–101
15. Barelli L, Bidini G, Gallorini F, Servilli S (2008) Hydrogen production through sorption-enhanced steam methane reforming and membrane technology: a review. *Energy J* 33:554–570
16. Brejc H, Supp E (1993) Partial oxidation of hydrocarbons. In: Elvers B, Hawkins S, Ravenscroft M, Rounsaville JF, Schulz G (eds) *Ullmann's encyclopedia of industrial chemistry*, vol A12. VCH, New York, pp 207–243
17. Silberova B, Venvik HJ, Walmsley JC, Holmen A (2005) Small-scale hydrogen production from propane. *Catal Today* 100(3–4):457–462
18. Tsang SC, Claridge JB, Green MLH (1995) Recent advances in the conversion of methane to synthesis gas. *Catal Today* 23(1):3–15
19. Wang HY, Ruckenstein (1999) Catalytic partial oxidation of methane to synthesis gas over γ - Al_2O_3 -supported rhodium catalysts. *Catal Lett* 59:121–127
20. Koh ACW, Chen L, Leong WK, Johnson BFG, Khimyak T, Lin J (2007) Hydrogen or synthesis gas production via the partial oxidation of methane over supported nickel-cobalt catalysts. *Int J Hydrogen Energ* 32(6):725–730
21. Lanza R, Jaras SG, Canu P (2007) Partial oxidation of methane over supported ruthenium catalysts. *Appl Catal A-Gen* 325(1):57–67
22. Pavlova SN, Sazonova NN, Ivanova JA, Sadykov VA, Snegurenko OI, Rogov VA, Zolotarskii IA, Moroz EM (2004) Partial oxidation of methane to synthesis gas over supported catalysts based on Pt-promoted mixed oxides. *Catal Today* 91–92:299–303
23. De Groot AM, Froment GF (1997) The role of coke formation in catalytic partial oxidation for synthesis gas production. *Catal Today* 37:309–329
24. Enger BC, Lodeng R, Holmen A (2008) A review of catalytic partial oxidation of methane to synthesis gas with emphasis on reaction mechanism over transition metal catalysts. *Appl Catal A* 346:1–27
25. Zhang J, Wang Y, Ma R, Wu D (2003) Characterization of alumina-supported Ni and Ni-Pd catalysts for partial oxidation and steam reforming of hydrocarbons. *Appl Catal A-Gen* 243(2):251–259
26. Kikuchi R, Iwasa Y, Takeguchi T, Eguchi K (2005) Partial oxidation of CH_4 and C_3H_8 over hexaaluminate-type oxides. *Appl Catal A-Gen* 281(1–2):61–67
27. Corbo P, Migliardini F (2007) Hydrogen production by catalytic partial oxidation of methane and propane on Ni and Pt catalysts. *Int J Hydrogen Energ* 32:55–66
28. Schulze K, Makowski W, Chyzy R, Dziembaj R, Geismar G (2001) Nickel doped hydrotalcites as catalyst precursors for the partial oxidation of light paraffins. *Appl Clay Sci* 18:59–69
29. Liu S, Xu L, Xie S, Wang Q, Xiong G (2001) Partial oxidation of propane to syngas over nickel supported catalysts modified by alkali metal oxides and rare-earth metal oxides. *Appl Catal A-Gen* 211:145–152
30. Beretta A, Forzatti P (2004) Partial oxidation of light paraffins to synthesis gas in short contact-time reactors. *Chem Eng J* 99:219–226

31. Caglayan BS, Onsan ZI, Aksoylu AE (2005) Production of hydrogen over bimetallic Pt-Ni/ δ -Al₂O₃: II. Indirect partial oxidation of LPG. *Catal Lett* 102(1-2):63–67
32. Otsuka K, Sunada YWE, Yamanaka I (1998) Direct partial oxidation of methane to synthesis gas by cerium oxide. *J Catal* 175:152–160
33. Passos FB, de Oliveira ER, Mattos LV, Noronha FB (2005) Partial oxidation of methane to synthesis gas on Pt/Ce_xZr_{1-x}O₂ catalysts: the effect of the support reducibility and of the metal dispersion on the stability of the catalysts. *Catal Today* 101:23–30
34. Muradov N (2001) Hydrogen via methane decomposition: an application for decarbonization of fossil fuels. *Int J Hydrogen Energ* 26:1165–1175
35. Ahmed S, Aitani A, Rahman F, Ali Al-Dawood, Al-Muhaish F (2009) Decomposition of hydrocarbons to hydrogen and carbon. *Appl Catal A-Gen* 359:1–24
36. Aiello R, Fiscus JE, Loye HC, Amiridis MD (2000) Hydrogen production via the direct cracking of methane over Ni/SiO₂: catalyst deactivation and regeneration. *Appl Catal A-Gen* 192:227–234
37. Choudary TV, Sivadinarayana C, Chusuei CC, Klinghoffer A, Goodman DW (2001) Hydrogen production via catalytic decomposition of methane. *J Catal* 199:9–18
38. Suelves I, Lazaro MJ, Moliner R, Corbella BM, Palacios JM (2005) Hydrogen production by thermo catalytic decomposition of methane on Ni-based catalysts: influence of operating conditions on catalyst deactivation and carbon characteristics. *Int J Hydrogen Energ* 30:1555–1567
39. Konieczny A, Mondal K, Wiltowski T, Dydo P (2008) Catalyst development for thermocatalytic decomposition of methane to hydrogen. *Int J Hydrogen Energ* 33:264–272
40. Li J, Smith KJ (2008) Methane decomposition and catalyst regeneration in a cyclic mode over supported Co and Ni catalysts. *Appl Catal A-Gen* 349:116–124
41. Muradov N (2001) Catalysis of methane decomposition over elemental carbon. *Catal Commun* 2:89–94
42. Pinilla JL, Suelves I, Lazaro MJ, Moliner R (2008) Kinetic study of the thermal decomposition of methane using carbonaceous catalysts. *Chem Eng J* 138:301–306
43. Serrano DP, Botas JA, Guil-Lopez R (2009) H₂ production from methane pyrolysis over commercial carbon catalysts: kinetic and deactivation study. *Int J Hydrogen Energ* 34:4488–4494
44. Lee KK, Han GY, Yoon KJ, Lee BK (2004) Thermocatalytic hydrogen production from the methane in a fluidized bed with activated carbon catalyst. *Catal Today* 93–95:81–86
45. Pinilla JL, Moliner R, Suelves I, Lázaro MJ, Echegoyen Y, Palacios JM (2007) Production of hydrogen and carbon nanofibers by thermal decomposition of methane using metal catalysts in a fluidized bed reactor. *Int J Hydrogen Energ* 32:4821–4829
46. Weizhong Q, Tang L, Zhanwen W, Fei W, Zhifei L, Guohua L, Yongdan L (2004) Production of hydrogen and carbon nanotubes from methane decomposition in a two-stage fluidized bed reactor. *Appl Catal A-Gen* 260:223–228
47. Muradov N, Smith F, Huang C, Raissi AT (2006) Autothermal catalytic pyrolysis of methane as a new route to hydrogen production with reduced CO₂ emissions. *Catal Today* 116:281–288
48. Fulcheri L, Schwob Y (1995) From methane to hydrogen, carbon black and water. *Int J Hydrogen Energ* 20:197–202
49. Fridman A (2008) *Plasma chemistry*. Cambridge University Press, Cambridge
50. Tsai CH, Chen KT (2009) Production of hydrogen and nano carbon powders from direct plasmolysis of methane. *Int J Hydrogen Energ* 34:833–838
51. Muradov N, Smith F, Bockerman G, Scammon K (2009) Thermocatalytic decomposition of natural gas over plasma-generated carbon aerosols for sustainable production of hydrogen and carbon. *Appl Catal A-Gen* 365:292–300
52. Figueiredo JL, Moulijn JA (1985) Carbon and coal gasification science and technology. In: *Proceedings of the NATO advanced study institute on carbon and coal gasification*. Science and Technology Series: NATO Science Series E, vol 105, p 672

53. Rostrup-Nielsen JR (2000) New aspects of syngas production and use. *Catal Today* 63:159–164
54. Stiegel GJ, Ramezan M (2006) Hydrogen from coal gasification: an economical pathway to a sustainable energy future. *Int J Coal Geol* 65:173–190
55. Joshi MM, Lee S (1996) Integrated gasification combined cycle—a review of IGCC technology. *Energy Source* 18:537–568
56. Damen K, van Troost M, Faaij A, Turkenburg W (2006) A comparison of electricity and hydrogen production systems with CO₂ capture and storage. Part A: review and selection of promising conversion and capture technologies. *Prog Energy Combust* 32:215–246
57. Cormos CC, Starr F, Tzimas E, Peteves S (2008) Innovative concepts for hydrogen production processes based on coal gasification with CO₂ capture. *Int J Hydrogen Energy* 33:1286–1294
58. Bohm MC, Herzog HJ, Parsons JE, Sekar RC (2007) Capture-ready coal plants—options, technologies and economics. *Int J Greenh Gas Control* 1:113–120
59. Galvita V, Messerla VE, Urtimenko AB (2007) Hydrogen production by coal plasma gasification for fuel cell technology. *Int J Hydrogen Energy* 32:3899–3906
60. Saxena RC, Seal D, Kumar S, Goyal HB (2008) Thermo-chemical routes for hydrogen rich gas from biomass: a review. *Renew Sust Energy Rev* 12:1909–1927
61. Orecchini F, Bucci E (2007) Biomass to hydrogen for the realization of closed cycles of energy resources. *Energy J* 32:1006–1011
62. Florin N, Harris A (2007) Hydrogen production from biomass. *Environmentalist* 27:207–215
63. Koroneos C, Dompros A, Roumbas G (2008) Hydrogen production via biomass gasification—a life cycle assessment approach. *Chem Eng Process* 47:1261–1268
64. Devi L, Ptasinski KJ, Janssen FJJG (2003) A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenerg* 24:125–140
65. Bangala DN, Abatzoglou N, Martin JP, Chornet E (1997) Catalytic gas conditioning: application to biomass and waste gasification. *Ind Eng Chem Res* 36:4184–4192
66. Koros W, Mahajan R (2000) Pushing the limits on possibilities for large scale gas separation: which strategies? *J Membr Sci* 175:181–196
67. Abanades S, Charvin P, Flamant G, Neveu P (2006) Screening of water-splitting thermochemical cycles potentially attractive for hydrogen production by concentrated solar energy. *Energy J* 31:2805–2822
68. Lattin WC, Utgikar VP (2009) Global warming potential of the sulfur-iodine process using life cycle assessment methodology. *Int J Hydrogen Energy* 34:737–744
69. Orhan MF, Dincer I, Rosen MA (2008) Energy and exergy assessments of the hydrogen production step of a copper–chlorine thermochemical water splitting cycle driven by nuclear-based heat. *Int J Hydrogen Energy* 33:6456–6466
70. Engelhardt V (1904) *The electrolysis of water; processes and applications*. Chemical Publishing Company, Easton
71. Pletcher D, Walsh FC (1990) *Industrial electrochemistry*, 2nd edn. Kluwer, Dordrecht, London, p 256
72. Rosen MA, Scott D (1998) Comparative efficiency assessments for a range of hydrogen production processes. *Int J Hydrogen Energy* 23:653–659
73. Hall DE (1981) Electrodes for alkaline water electrolysis. *J Electrochem Soc* 128:740
74. Dyer CK (1985) Improved nickel anodes for industrial water electrolyzers. *J Electrochem Soc* 132:64
75. Rami A, Lasia A (1992) Kinetics of hydrogen evolution on Ni–Al alloy electrodes. *J Appl Electrochem* 22:376–382
76. Barbir F (2005) PEM electrolysis for production of hydrogen from renewable energy sources. *Sol Energy* 78:661–669
77. Sherif SA, Barbir F, Veziroglu TN (2005) Wind energy and the hydrogen economy—review of the technology. *Sol Energy* 78:647–660
78. Schiller G, Ansar A, Lang M, Patz O (2009) High temperature water electrolysis using metal supported solid oxide electrolyser cells (SOEC). *J Appl Electrochem* 39:293–301

79. Millet P, Andolfatto F, Durand R (1996) Design and performance of a solid polymer electrolyte water electrolyzer. *Int J Hydrogen Energ* 21:87–93
80. Marshall A, Borresen B, Hagen G, Tsykin M, Tunold R (2007) Hydrogen production by advanced proton exchange membrane (PEM) water electrolyzers—reduced energy consumption by improved electrocatalysis. *Energy J* 32:431–436
81. Grigoriev SA, Poremsky VI, Fateev VN (2006) Pure hydrogen production by PEM electrolysis for hydrogen energy. *Int J Hydrogen Energ* 31:171–175
82. Onda K, Kyakuno T, Hattori K, Ito K (2004) Prediction of production power for high-pressure water electrolysis. *J Power Sources* 132:64–70
83. Marangio F, Santarelli M, Cali M (2009) Theoretical model and experimental analysis of a high pressure PEM water electrolyser for hydrogen production. *Int J Hydrogen Energ* 34:1143–1158
84. Grigoriev SA, Millet P, Fateev VN (2008) Evaluation of carbon-supported Pt and Pd nanoparticles for the hydrogen evolution reaction in PEM water electrolyzers. *J Power Sources* 177:281–285
85. Granovskii M, Dincer I, Rosen MA (2006) Life cycle assessment of hydrogen fuel cell and gasoline vehicles. *Int J Hydrogen Energ* 31:337–352
86. Jorgensen C, Ropenus S (2008) Production price of hydrogen from grid connected electrolysis in a power market with high wind penetration. *Int J Hydrogen Energ* 33:5335–5344
87. Mingyi L, Bo Y, Jingming X, Jing C (2008) Thermodynamic analysis of the efficiency of high-temperature steam electrolysis system for hydrogen production. *J Power Sources* 177:493–499
88. Ni M, Leung MKH, Leung DYC (2008) Technological development of hydrogen production by solid oxide electrolyser cell (SOEC). *Int J Hydrogen Energ* 33:2337–2354
89. Fujiwara S, Kasai S, Yamauchi H, Yamada K, Makino S, Matsunaga K, Yoshino M, Kameda T, Ogawa T, Momma S, Hoashi E (2008) Hydrogen production by high temperature electrolysis with nuclear reactor. *Prog Nucl Energy* 50:422–426
90. Coughlin RW, Farooque M (1980) Consideration of electrodes and electrolytes for electrochemical gasification of coal by anodic oxidation. *J Appl Electrochem* 10:729–740
91. Sathe N, Botte GG (2006) Assessment of coal and graphite electrolysis on carbon fiber electrodes. *J Power Sources* 161:513–523
92. Jin X, Botte GG (2007) Feasibility of hydrogen production from coal electrolysis at intermediate temperatures. *J Power Sources* 171:826–834
93. Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238:37–38
94. Penner SS (2006) Steps toward the hydrogen economy. *Energy J* 31:33–43
95. Bak T, Nowotny J, Rekas M, Sorrell CC (2002) Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects. *Int J Hydrogen Energ* 27:991–1022
96. Ni M, Leung MKH, Leung DHC, Sumathy K (2007) A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. *Renew Sust Energy Rev* 11:401–425
97. Kelly NA, Gibson TL (2008) Solar energy concentrating reactors for hydrogen production by photoelectrochemical water splitting. *Int J Hydrogen Energ* 33:6420–6431
98. Burgess G, Velasco JGF (2007) Materials, operational energy inputs, and net energy ratio for photobiological hydrogen production. *Int J Hydrogen Energ* 32:1225–1234
99. Kapdan IK, Kargi F (2006) Bio-hydrogen production from waste materials. *Enzyme Microb Technol* 38:569–582
100. Moore RB, Raman V (1998) Hydrogen infrastructure for fuel cell transportation. *Int J Hydrogen Energ* 23:617–620
101. Haeseldonckx D, D'haeseleer W (2007) The use of the natural-gas pipeline infrastructure for hydrogen transport in a changing market structure. *Int J Hydrogen Energ* 32:1381–1386
102. Padro C, Putsche V (1999) Survey of the economics of hydrogen technologies. DOE National Renewable Energy Laboratory Report no. NREL/TP-570-27079, September

103. Siddiqui RA, Abdullah HA (2005) Hydrogen embrittlement in 0.31% carbon steel used for petrochemical applications. *J Mater Process Technol* 170:430–435
104. Markert F, Nielsen SK, Paulsen JL, Andersen V (2007) Safety aspects of future infrastructure scenarios with hydrogen refuelling stations. *Int J Hydrogen Energy* 32:2227–2234
105. Hugo A, Rutter P, Pistikopoulos S, Amorelli A, Zoia G (2005) Hydrogen infrastructure strategic planning using multi-objective optimization. *Int J Hydrogen Energy* 30:1523–1534
106. Leung WB, March NH, Motz H (1976) Primitive phase diagram for hydrogen. *Phys Lett A* 56:425–426
107. Zuttel A (2008) Hydrogen storage. In: Zuttel A, Borgschulte A, Schlapbach L (eds) *Hydrogen as a future energy carrier*. Wiley-VCH Verlag GmbH & Co, Weinheim
108. Zhou L (2005) Progress and problems in hydrogen storage methods. *Renew Sust Energy Rev* 9:395–408
109. David E (2005) An overview of advanced materials for hydrogen storage. *J Mater Process Technol* 162–163:169–177
110. Satypal S, Petrovic J, Read C, Thomas G, Ordaz G (2007) The U.S. Department of Energy's National Hydrogen Storage Project: progress towards meeting hydrogen-powered vehicle requirements. *Catal Today* 120:246–256
111. de Wit MP, Faaij PC (2007) Impact of hydrogen onboard storage technologies on the performance of hydrogen fuelled vehicles: a techno-economic well to wheel assessment. *Int J Hydrogen Energy* 32:4859–4870
112. Aceves SM, Berry GD, Martinez-Frias J, Espinoza-Loza F (2006) Vehicular storage of hydrogen in insulated pressure vessels. *Int J Hydrogen Energy* 31:2274–2283
113. Peschka W (1992) *Liquid hydrogen, fuel of the future*. Springer, Wien
114. Berstad DO, Stang JH, Neksa P (2009) Comparison criteria for large-scale hydrogen liquefaction processes. *Int J Hydrogen Energy* 34:1560–1568
115. Sherif SA, Barbir F, Veziroglu TN (2005) Towards a hydrogen economy. *Electr J* 18:62–76
116. Ross DK (2006) Hydrogen storage: the major technological barrier to the development of hydrogen fuel cell cars. *Vacuum* 80:1084–1089
117. Sandrock G (1999) A panoramic overview of hydrogen storage alloys from a gas reaction point of view. *J Alloy Compd* 293–295:877–888
118. Suda S (2008) Hydrogen–metal systems: technological and engineering aspects. *Encyclopedia of Materials: Sci Tech* 4:3970–3976
119. Yvon K, Bertheville B (2006) Magnesium based ternary metal hydrides containing alkali and alkaline-earth elements. *J Alloy Compd* 425:101–108
120. Ouyang LZ, Qin FX, Zhu M (2006) The hydrogen storage behavior of Mg_3La and $Mg_3LaNi_{0.1}$. *Scripta Mater* 55:1075–1078
121. Andreasen A (2008) Hydrogenation properties of Mg–Al alloys. *Int J Hydrogen Energy* 33:7489–7497
122. Jung KS, Lee EY, Lee KS (2006) Catalytic effects of metal oxide on hydrogen absorption of magnesium metal hydride. *J Alloy Compd* 421:179–184
123. Sakintuna B, Lamari–Darkrim F, Hirscher M (2007) Metal hydride materials for solid hydrogen storage: a review. *Int J Hydrogen Energy* 32:1121–1140
124. Hauback BC (2008) Metal hydrides: properties and applications of alanates. *Encyclopedia of Materials: Sci Tech* 1–5
125. Bogdanovic B, Brand RA, Marjanovic A, Schwikardi M (2000) Metal-doped sodium aluminium hydrides as potential new hydrogen storage materials. *J Alloy Compd* 302:36–58
126. Corbo P, Migliardini F, Veneri O (2009) Hydrogen release properties of lithium alanate for application to fuel cell propulsion systems. *J Power Sources* 193:285–291
127. Onkawa M, Zhang S, Takeshita HT, Kuriyama N, Kiyobayashi T (2008) Dehydrogenation kinetics of Ti-doped $NaAlH_4$ —influence of Ti precursors and preparation methods. *Int J Hydrogen Energy* 33:718–721
128. Dillon AC, Heben MJ (2001) Hydrogen storage using carbon adsorbents: past, present and future. *Appl Phys A* 72:133–142

129. Dillon AC, Jones KM, Bekkedahl TA, Kang CH, Bethune DS, Heben MJ (1997) Storage of hydrogen in single-walled carbon nanotubes. *Nature* 386:377–379
130. Bethune DS (2002) Carbon and metals: a path to single-wall carbon nanotubes. *Phys B- Phys Condens Matter* 323:90–96
131. Bénard P, Chahine R (2007) Storage of hydrogen by physisorption on carbon and nanostructured materials. *Scripta Mater* 56:803–808
132. Züttel AA, Sudan P, Maunon PH, Kiyobayashi T, Emmenegger CH, Schlapbach L (2002) Hydrogen storage in carbon nanostructures. *Int J Hydrogen Energ* 27:203–212
133. Chambers A, Park C, Terry R, Baker K, Rodriguez NM (1998) Hydrogen storage in graphite nanofibers. *J Phys Chem B* 102:4253–4256
134. Orimo S, Züttel A, Schlapbach L, Majer G, Fukunaga T, Fujii H (2003) Hydrogen interaction with carbon nanostructures: current situation and future prospects. *J Alloy Compd* 356–357:716–719
135. Dong J, Wang X, Xu H, Zhao Q, Li J (2007) Hydrogen storage in several microporous zeolites. *Int J Hydrogen Energ* 32:4998–5004
136. Hirscher M, Panella B (2007) Hydrogen storage in metal-organic frameworks. *Scripta Mater* 56:809–812
137. Yaghi OM, Li G, Li H (1995) Selective binding and removal of guests in a microporous metal-organic framework. *Nature* 378:703
138. Mulder FM, Dingemans TJ, Schimmel HG, Ramirez-Cuesta AJ, Kearley GJ (2008) Hydrogen adsorption strength and sites in the metal organic framework MOF5: comparing experiment and model calculations. *Chem Phys* 351:72–76
139. Latroche M, Surblé S, Serre C, Mellot-Draznieks C, Llewellyn PL, Lee JH, Chang JS, Jung SH, Férey G (2006) hydrogen storage in the giant-pore metal-organic frameworks MIL-100 and MIL-101. *Angew Chem Int Ed* 45:8227–8231
140. Cheng H, Chen L, Cooper AC, Sha X, Pez GP (2008) Hydrogen spillover in the contest of hydrogen storage using solid-state materials. *Energy Environ Sci* 1:338–354
141. Yang RT, Li Y, Lachawiec AJ (2006) Hydrogen storage in graphite nanofibers and the spillover mechanism. DOE hydrogen program. Annual Progress Report. http://www.hydrogen.energy.gov/annual_progress06_storage.html#c. Accessed 12 February 2010
142. Kojima Y, Suzuki K, Fukumoto K, Sasaki M, Yamamoto T, Kawai Y, Hayashi H (2002) Hydrogen generation using sodium borohydride solution and metal catalyst coated on metal oxide. *Int J Hydrogen Energ* 27:1029–1034
143. Cakanyildirim C, Guru M (2008) Hydrogen cycle with sodium borohydride. *Int J Hydrogen Energ* 33:4634–4639
144. Davis BL, Dixon DA, Garner EB, Gordon JC, Matus MH, Scott B, Stephens FH (2009) Efficient regeneration of partially spent ammonia borane fuel. *Angew Chem Int Ed* 48(37):6812–6816



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