



Report on
Energy

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5 Energy

5.4 Fuel cells and Hydrogen production & storage

5.4.1 Definition

5.4.1.1 Fuel cells

A fuel cell is a device dedicated to electrochemical conversion from fuel (for instance H_2) and air (for instance O_2) into electricity, water and heat (from $80^\circ C$ to $800^\circ C$, depending on the type of fuel cells).

It consists of three main parts: 2 electrodes (anode, on which flows hydrogen and cathode, on which flows oxygen) and in between an electrolyte. Hydrogen and oxygen are combined in a reaction which delivers water and electricity between the 2 electrodes through an external electrical circuit. In the case of low-temperature fuel cells ($<100^\circ C$), reactions occurring at the electrodes are thermodynamically possible but kinetically slow. That is why electrocatalysts have to be used to enhance reactions and to improve fuel cells performances.

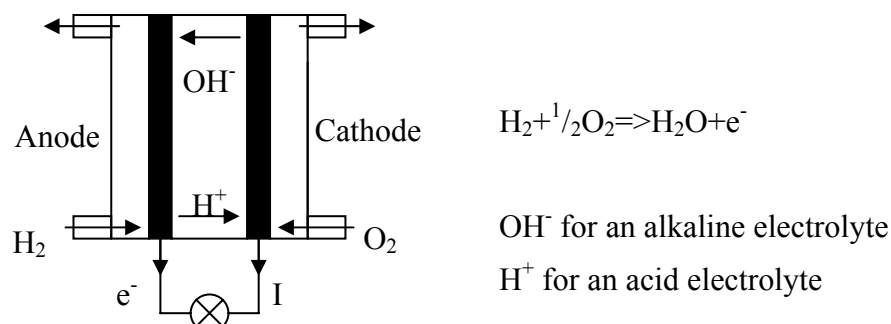


Figure 1: Basic scheme of hydrogen/oxygen fuel cell

The fuel used to run the fuel cell depends on the type of fuel cell considered: it can be pure hydrogen (or products like coal and natural gas able to supply hydrogen after reforming); methanol, glucose ... This fuel is stored in a tank, which can be part of the fuel cell or separated from it.

The main advantages are the following. Unlike a classical battery which stops producing electrical energy as soon as the chemical reactants are consumed, fuel cell produces power as long as fuel is provided. Fuel cells exhibit also high energy density storage. And finally, there are no moving parts in fuel cells, therefore mechanical problems are reduced.

The main problem remains the cost of those devices which most comes from the materials used for the electrodes, the electrolyte and the catalyst. The efforts of R&D focus on it.

5.4.1.2 Hydrogen production & storage

Hydrogen gas is a very promising energy vector, as fuel for fuel cells or space rocket. It is a way to store electric, chemical or heat energy, for many potential energy uses, which are mobile as well as stationary. It can indeed power vehicles or heat homes and offices. City buses, automobiles, mining equipment are some proposed mobile applications that have progressed to demonstration. Home generators and large electrical generating systems represent emerging stationary applications.

The main advantage of hydrogen use as fuel is that it is a non polluting one as the result products of fuel cell are water and electricity. Thus, hydrogen has many applications and advantages.

Furthermore, as electrical energy is difficult to store in large quantities, one possible way to solve this problem is to convert and store this energy into hydrogen, for large classes of applications.

Last, hydrogen could also be produced by using heat already available (sun or nuclear plants for instance).

However, if the use of hydrogen as fuel is developed, new technologies, concepts and support facilities to produce, distribute and store hydrogen are required.

5.4.2 Short description

5.4.2.1 Fuel cells

There are several types of fuel cells classified according to their electrolyte, their fuel, and operating temperature¹

FC (Fuel cell) type	Electrolyte	Operating temp. (°C)
AFC (Alkaline FC)	KOH	80
DMFC (Direct Methanol FC)	Proton exchange polymer	60 – 90
PEMFC (Proton Exchange Membrane FC)	Proton exchange polymer	90
PAFC (Phosphoric Acid FC)	H ₃ PO ₄	200
MCFC (Molten Carbonate FC)	Li ₂ CO ₃ /K ₂ CO ₃	650
SOFC (Solid Oxide FC)	ZrO ₂ -Y ₂ O ₃	700-1000
MFC (Microbial FC)		

The last kind of fuel cell differs from the previous one as it operates in living, biological medium: bio fuel cells.

The used hydrogen is stored as compressed gas, as liquefied hydrogen, or in hydride metals. It can also be produced by reforming of natural gas, methanol, coal ...

This transformation can be operated outside (low temperature fuel cells: AFC, PEMFC, PAFC) or inside (high temperature fuel cells: MCFC, SOFC). The product of reforming, rich in hydrogen also contains products like CO, CO₂ On one hand, carbon monoxide is poisonous for Pt-based catalysts used in low temperature fuel cells (AFC, PEMFC, DMFC and PAFC) and therefore should be precisely controlled. On the other hand, CO is one of the reactants for high temperature fuel cells (MCFC, SOFC). Furthermore, CO₂ degrades alkaline electrolyte and therefore must completely be removed.

In every case, the reforming decreases the efficiency of the reaction so it is interesting to directly use the fuel in the electrochemical process such as in DMFC.

In this chapter we are going to take into account this reforming when it is part of the fuel cell. Other cases will be treated in hydrogen production and storage chapter.

5.4.2.2 AFC

The Alkaline Fuel Cell has been developed since mid-1960s by NASA and was widely used in the US space program to produce electricity and water.

This fuel cell uses as electrolyte an aqueous alkaline solution such as high concentrated potassium hydroxide (30 to 45% KOH). The operating temperature, normally in a range of 80-90°C can be increased to a range of 200-230°C under pressure (Bacon fuel cell). The charge carrier is the hydroxyl ion (OH⁻).

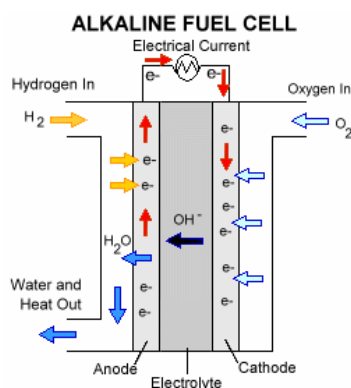


Figure 2: Work principle of an alkaline fuel cell

Advantages:

Alkaline media enhances reactions kinetics (for both hydrogen oxidation and oxygen reduction reactions). Moreover, the use of an alkaline media also makes it possible to use non-noble catalysts (Ni, Ag, ... instead of Pt).

The efficiency was around 60% in space applications (EERE).

Drawbacks:

Carbon dioxide (CO₂ from the air) reacts with hydroxyl ions to produce carbonates leading to the decrease of electrolyte ionic conductivity and blocking cathodic pores.

It is necessary to purify both the hydrogen and oxygen used in the cell. This purification process is costly.

Susceptibility to poisoning also affects the cell's lifetime, further adding to cost.

5.4.2.3 DMFC

Most fuel cells are powered by hydrogen, direct methanol fuel cells, however, are powered by pure methanol, which is mixed with steam and fed directly to the fuel cell anode. The operating temperature is in a range of 60-90°C.

Advantages:

Direct methanol fuel cells do not have many of the fuel storage problems typical of some fuel cells since methanol has a higher energy density than hydrogen.

Methanol is also easier to transport and supply to the public using current infrastructure since it is a liquid. These fuel cells don't require a hydrogen storage system and a reforming system.

Drawbacks:

Performances (power density) are lower than PEMFC

Methanol is flammable and very toxic.

The permeation of methanol through the membrane is high. This methanol "crossover" thus decreases the efficiency of the cells and wastes fuel.

Carbon monoxide (CO) is an intermediate product of the anode reaction which is poisonous for Pt, blocking catalytic sites and reducing the performance of the cells. Finally, the global efficiency is around 20%.

To reduce CO-poisoning, bimetallic catalysts (Pt alloys such as Pt-Ru) are necessary. These catalysts are also very expensive..

Another kind of fuel cell using directly fuel that is not hydrogen is DBFC (direct borohydride fuel cell). This system is increasingly studied because of its great interest for portable application due to high theoretical energy density.

5.4.2.4 PEMFC

Proton exchange membrane fuel cells are also called polymer electrolyte membrane fuel cells. These fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst.

Other parts of these fuel cells are the bipolar plates used to distribute gases and evacuate water and the backing used to diffuse gases towards electrodes and transfer electrons from anode to cathode.

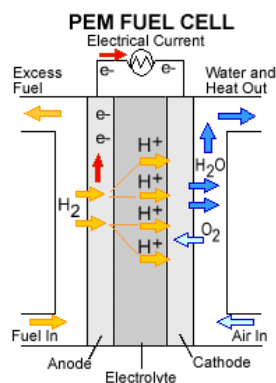


Figure 3: Work principle of a proton exchange membrane fuel cell

Advantages:

They deliver high power density

They are of low weight and volume, compared to other fuel cells.

They need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids. They are typically fuelled with pure hydrogen supplied from storage tanks or onboard reformers.

They operate at relatively low temperatures (around 80°C). Low temperature operation allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability.

Drawbacks:

The low operating temperature requires the use of a noble-metal catalyst (typically platinum) to separate the hydrogen's electrons and protons, adding to system cost.

The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost. Finally bipolar plates and membranes are also expensive.

5.4.2.5 PAFC

This fuel cell is considered as the "first generation" of modern fuel cells. It is one of the most mature cell types and the first to be used commercially, with over 200 units currently in use.

This fuel cell uses as an electrolyte liquid phosphoric acid (PO_4H_3). This electrolyte is not circulating but is contained in a silicon carbide matrix. The electrodes are made of porous carbon containing Pt catalyst.

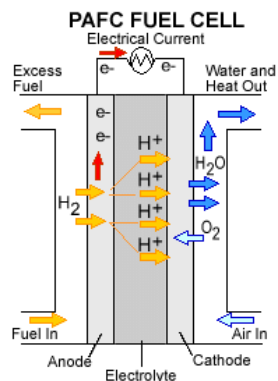


Figure 4: Work principle of a phosphoric acid fuel cell

Advantages:

Phosphoric acid does not react with CO₂.

They are well tolerant to impurities in fossil fuels that have been reformed into hydrogen. Therefore, it is possible to use gases produced by reforming.

Their operating temperature and their size suit particularly to a use in co-generation of electricity and heat. They are 85 % efficient when used for the co-generation, but less efficient at generating electricity alone (37 to 42 %). This is only slightly more efficient than combustion-based power plants, which typically operate at 33 to 35 % efficiency

Drawbacks:

It has to be noted that phosphoric acid solidifies below 40°C, making start-up difficult and restraining PAFCs to be stored at a temperature above this limit when not used.

PAFCs are also less powerful than other fuel cells, given the same weight and volume. As a result, these fuel cells are typically large and heavy.

PAFCs are also expensive. Like PEMFC, they require an expensive platinum catalyst, which raises the cost of the fuel cell.

5.4.2.6 MCFC

This fuel cell is considered as the "second generation" of modern fuel cells. They have been developed only recently.

The electrolyte is composed of a molten carbonate salt mixture (Li₂CO₃ – K₂CO₃, 62% – 38%), suspended in a porous, chemically inert ceramic matrix. The electrode is gas porous. In addition, as this fuel cell can operate at extremely high temperatures of 650°C and above, non-precious metals such as Ni can be used as catalysts at the anode and cathode, reducing indeed costs and they can be used for the co-generation of electricity and heat. The charge carrier is the carbonate ion (CO₃²⁻).

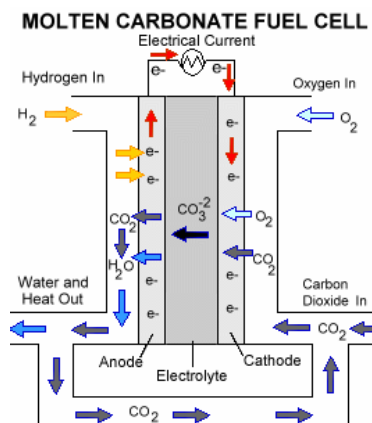


Figure 5: Work principle of a molten carbonate fuel cell

Advantages:

Unlike other fuel cells, MCFCs don't require an external reformer to convert fuels to hydrogen. Due to the high temperatures at which MCFCs operate, these fuels are converted to hydrogen within the fuel cell itself by a process called internal reforming.

Thanks to the high operating temperature, these fuel cells can reach efficiencies approaching 60% and 85% if the waste heat produced is captured and used.

Drawbacks:

The working environment is high temperature and corrosive one. There is therefore a degradation of the electrolyte.

These fuel cells can also suffer leaking problem.

5.4.2.7 SOFC

Solid oxide fuel cells use a hard, non-porous ceramic compound as the electrolyte. Since the electrolyte is a solid, the cells do not have to be constructed in the plate-like configuration typical of other fuel cell types. The electrodes are porous to have a quick access to gases. The charge carrier is the oxygen ion O²⁻.

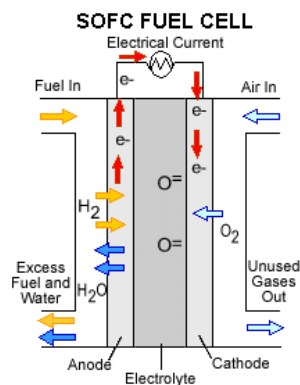


Figure 6: Work principle of a solid oxide fuel cell

Advantages:

These fuel cells operate at very high temperatures (around 1,000°C) and therefore there is no need for precious-metal catalyst. Cost is thereby reduced.

Thanks to the high operating temperature, they can reform fuels internally, which enables the use of a variety of fuels and reduces the cost.

As carbon monoxide (CO) is not poisonous for these fuel cells, it can be used as fuel. This allows SOFCs to use gases made from coal.

These fuel cells are expected to be around 50-60 percent efficient at converting fuel to electricity. In applications of co-generation (capture and use the system's waste heat), overall fuel cell efficiency could top 80-85 percent.

Drawbacks:

High operating temperature results in a slow start-up and requires significant thermal shielding to retain heat and protect personnel.

The high operating temperatures also place stringent durability requirements on materials. The development of low-cost materials with high durability at cell operating temperatures is the key technical challenge facing this technology.

5.4.2.8 MFC

A microbial fuel cell (MFC) is a device that mimicks bacterial interactions found in nature. It converts chemical energy to electrical energy by the catalytic reaction of micro-organisms or enzymes. A typical microbial fuel cell consists of anode and cathode compartments separated by a cation specific membrane. In the anode compartment, fuel such as glucose², acetate, butyrate or wastewater³ is oxidized by microorganisms, generating electrons and protons. Electrons are transferred to the cathode compartment through an external electric circuit, and the protons are transferred to the cathode compartment through the membrane. Electrons and protons are consumed in the cathode compartment, combining with oxygen to form water.

5.4.2.9 Hydrogen production & storage

5.4.2.9.1 Hydrogen Production⁴

Hydrogen can be produced through several methods. First it can be obtained from fossil resources such as natural gas or coal. Second, it can be obtained from renewable resources. Biomass, microorganism, algae allow a direct production of hydrogen whereas water allows a production of hydrogen by electrolysis, electricity being produced by wind, solar or hydroenergy.

Chemical, biological, electrolytic, photolytic, thermo-chemical process technologies are useable to achieve the production of hydrogen.

Among those processes, natural gas reforming and water electrolysis are the most mature ones. They are proven technologies that can be used in the early stages of developing a hydrogen infrastructure.

The different hydrogen production renewable methods are sum up in the following figure.

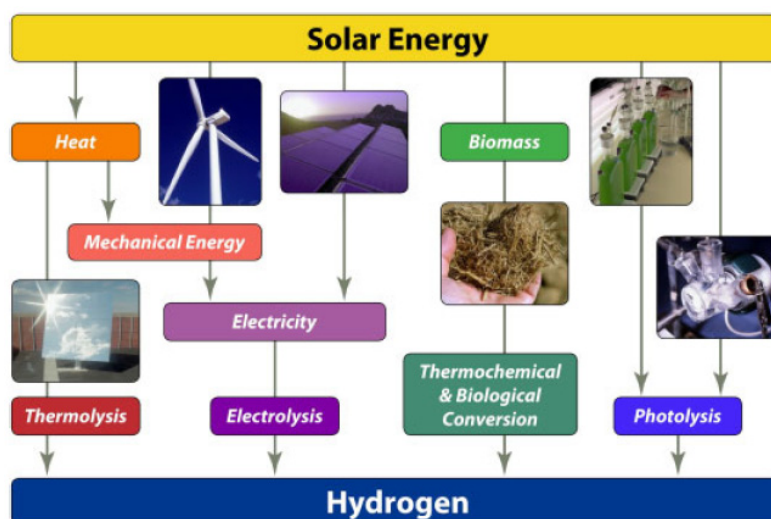


Figure 7: Renewable pathways for hydrogen production⁵

5.4.2.9.1.1 Hydrogen from fossil fuels

Concerning the hydrogen production from natural gas, 3 chemical processes exist. The first one is the steam reforming which is the endothermic conversion of methane and water vapour into hydrogen and carbon monoxide. The second one is partial oxidation which is the partial combustion of methane with oxygen gas to yield hydrogen and carbon monoxide. The third one is the autothermal reforming, a combination of steam reforming and partial oxidation.

The first process is an efficient, low emissions and low costs for large units one but is a complex system, sensitive to natural gas qualities. The second and third processes are low costs for small units, simple systems but have lower efficiency, need hydrogen purification and exhibit noxious emissions.

The production of hydrogen from coal is obtained through several gasification processes. To maximise the carbon conversion to gas, and avoid the formation of pollutant, high temperature entrained flow processes are preferred.

5.4.2.9.1.2 Hydrogen from splitting of water

The basic process is the water electrolysis which is the splitting of water into hydrogen and oxygen thanks to electrical energy. High temperature processes are preferable as the required electrical energy decreases. Several electrolyser are available. First, the alkaline electrolyser uses an aqueous solution of potassium hydroxide as an electrolyte that circulates through the electrolytic cell. This one is suitable for stationary applications. Second, the polymer membrane electrolyser uses an acidic polymer membrane, which is therefore not liquid. It is suitable for stationary and portable applications. Third, the high temperature electrolysis is based on high temperature fuel cells technology.

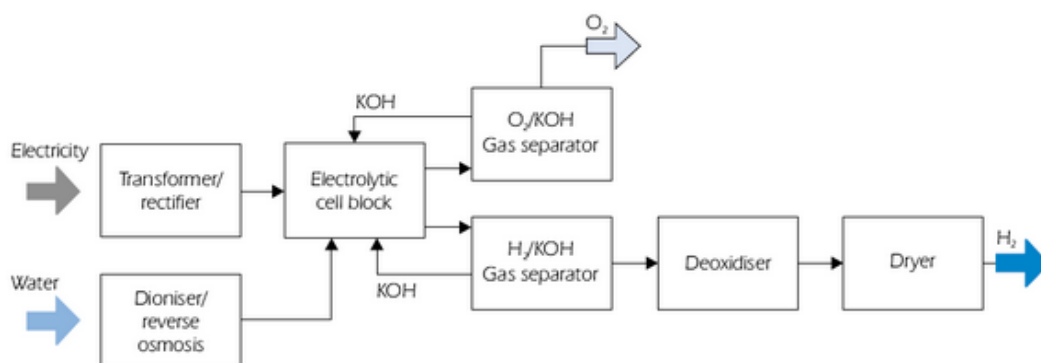


Figure 8: Example of water electrolysis: process diagram of alkaline electrolysis

A second way to produce hydrogen is through photo-biological process or biophotolysis. This production is based on 2 steps: photosynthesis followed by a hydrogen production catalysed by hydrogenases such as green algae or cyanobacteria. This method is still under development but holds a great potentiality.

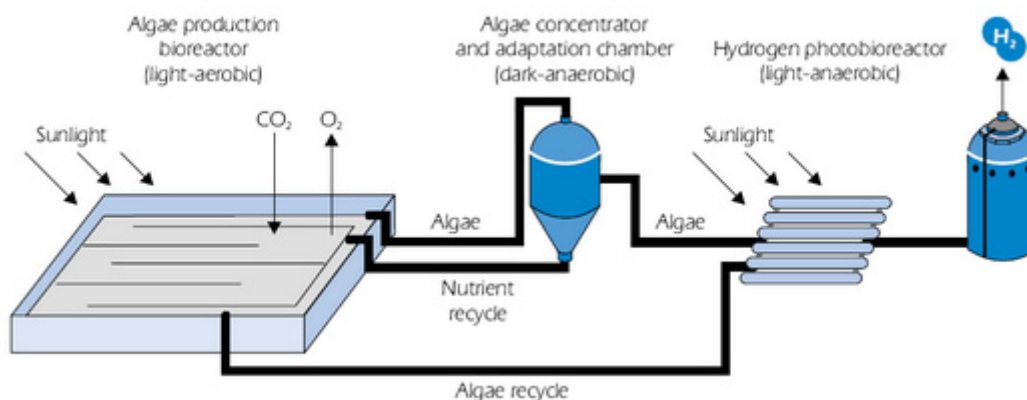


Figure 9: Photo-biological hydrogen production

Another way to obtain hydrogen is to split water thermo-chemically, which is the conversion of water into hydrogen and oxygen after a series of thermally driven chemical reactions. The matter remains the development of a commercial low cost and high efficiency system.

The last process, which is already commercially available, is the photo-electrolysis or photolysis. It is the coupling of a photovoltaic cell and an electrolyser. This system offers a double output: electricity from solar cell and hydrogen from electrolyser. The production of hydrogen can be obtained in one or two steps. The direct photo-electrolysis combine electricity production and hydrogen production in a single apparatus: light split water directly into hydrogen and oxygen. Since water and light are naturally abundant, the photoassisted water splitting procedure can be considered as an economic route to generate hydrogen.

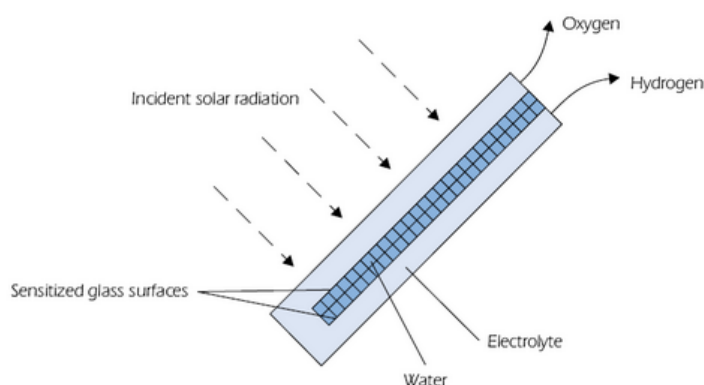


Figure 10: Photo-electrolytic cell

5.4.2.9.2 Hydrogen storage⁶

Different possible ways to store hydrogen are available. The US Department of Energy requires that a suitable storage system should at least have the following characteristics: a weight capacity of 6.5 wt-%¹ and a volume capacity of 62 kg H₂/m³

First, hydrogen can be stored under gas form.⁷ It is then transported in the same pipelines as natural gas and stored in tanks. However, the storage in steel tanks requires high pressure (200 to 300 bars) and the storage capacity is limited (less than 1 wt-%) because of the weight of the tank. The use of composite material tank can solve this problem as it is lighter and then increase the storage capacities but the material is still bulky and avoids flexible design.

The second possibility is the storage of hydrogen under liquid form in metal vessels at high pressure.⁸ Even if the storage needs small volume and if the storage capacity is higher than in gas storage, the limitations of those systems are quite restricted. First, the temperature required to liquefy hydrogen is very low (-253 °C), which consumes one third of the energy content. Second, tanks need effective insulation, which is indeed costly and nevertheless, due to warming and evaporation, a continuous lost of hydrogen occurs.⁹

¹ x wt-% = x g of H₂ in 100 g of material

Another possibility is, at last, to store hydrogen under solid form. Two categories of solid-state hydrogen storage appear: first, the chemisorption where the materials used, named dissociative materials, store hydrogen under atomic form mainly by dissociation of hydrogen molecules and atomic absorption; second, the physisorption, where the materials used, named non-dissociative materials, store hydrogen primarily under molecules form. Chemisorption appears mainly in metal hydrides whereas physisorption appears in metal organic framework, carbon and carbon-based nanostructures ... At low temperatures occurs the physisorption but the gravimetric performances are limited because of the weight of the metal. At high temperatures occurs the chemisorption and therefore the performances increase but then the desorption temperature is high too so it requires high energy. To solve this problem, the use of lighter materials to reduce the weight and of catalytic materials to accelerate absorption/desorption dynamics can be proposed. An interesting material will be one with a high surface area where hydrogen can be absorbed and where the binding of hydrogen high enough to allow a great storage density but low enough to avoid the need of high energy for hydrogen desorption.

The main problem of this gas storage remains that the size of the molecules is very small causing problem of leakage and reducing the lifetime of the storage method. Another problem is the security because of the storage under pressure.

5.4.3 State of R&D

5.4.3.1 Fuel cells

5.4.3.1.1 Electrodes

To reduce electrodes' lightweight it is possible to use a network of single-walled carbon nanotubes. Electrodes are then 10 times thinner and lighter than conventional ones. The long, thin shapes of the nanotubes give them a higher conductivity than that of amorphous carbon.¹⁰

To improve the exchange between the electrodes and the electrolyte, it has been proposed to use fullerenes materials as electrodes in DMFC. This would help to deliver methanol-based fuel cells with fast response times at ambient temperature.¹¹

It has also been proposed, for DMFC, to maximise the area where chemical reactions take place. For that purpose, a good solution is to use the high surface area geometry of nanowires made of mixed electronic-ionic conductor materials such as Pd metal and Ru oxide. Results have to be published for validation.¹²

Concerning MFC, to enhance response times, one possibility is to suppress the mediator used in most biofuel cells. This can be accomplished by engineering carbon electrodes with carbon nanotubes. It is therefore possible to bound the oxidising enzyme onto the electrode surface and then increasing the speed of the electron transfer.

5.4.3.1.2 Electrolyte

One way to increase the performance of a fuel cell is to increase the ion conductivity of the electrolyte or of the membrane. Several solutions have been proposed, mostly depending on the type of fuel cell considered.

First, a constant purpose of R&D activities consists in the nanostructuring of the membrane to increase the active surface and decrease the amount of Nafion™.¹³ This Nafion™ reduction allows also increasing the cyclability and therefore, the lifetime.

For PEMFC it is possible to increase the proton conductivity by incorporation of sulfonic acid functionalised single-walled carbon nanotubes (S-SWCNTs) into the Nafion™ membrane. It increased indeed the number of sulfonic acid groups in the membrane. This would also help increase the mechanical stability of the composite membranes over that of Nafion™ membranes.¹⁴

Materials such as nanocrystalline Zr films have been studied as a new electrolyte membrane material. This should allow to reduce the thickness of the electrolyte and therefore to increase the ionic conductivity and the gas permeability.¹⁵

Furthermore, composite membranes containing nanoparticles allow higher water retention and protonic conduction.¹⁶ Moreover properly designed membranes with appropriate incorporation of functionalised carbon nanotubes could help decrease the methanol cross-over and therefore increase the proton conductivity.¹⁷

Replacement of Nafion™ is also of great interest for many research teams. Indeed, this organic material displays mean performance, and has relatively bad mechanic properties. The elaboration of new inorganic structures having high specific surface but also short paths for protons requires control of the material at the nanoscale. This also requires a fine knowledge of the protonic transport process through the electrolyte.

SOFCs are conventionally operating at high temperature so ceramic is the best electrolyte choice that are durable at such high temperatures. However the use of thin electrolyte film decreases the energy loss during the electrochemical conversion of the fuel energy. But it is a fragile material not suitable for applications. Such weaknesses of the SOFC against thermal shock could be improved by substituting a metallic porous electrode for the ceramic-based porous support. Metal is flexible and persistent, so that metallic electrode support is desirable from both the thermal and the mechanical stresses. The use of a porous metal substrate with nanosize but uniform pores can afford high power density and quick start-up. In addition the developed nanoporous metal could be applied as gas separation filters and as catalytic support for exhaust gas treatments.¹⁸

However, most nanotechnologies are limited for high temperature applications. The nanostructuring disappear indeed under temperature effect.

5.4.3.1.3 Catalyst

Because of the low operating temperature of most fuel cells the catalyst used is usually Pt. The matter is that this material is expensive due to its limited supply. The R&D concerning catalyst mostly focuses on ways to reduce the amount of Pt.

Several solutions appear:

The most drastic one is the replacement of Pt by other catalyst.

A smoother one is the replacement of Pt film by nanostructured Pt (nanowires, nanoparticles) to increase the catalyst surface to volume ratio.

The first solution can be afforded by using Ag and Ag-alloy catalyst which have comparable overvoltages and similar activities as Pt, it can be useful in AFC at a much lower cost than Pt. Ag particles deposited on carbon nanotubes had similar performance to electrodes with Pt (Hacker). Another approach is the development of Ag nanowires carbon nanotubes and PTFE (Teflon) matrix.¹⁹

The second solution can be afforded by using Pt nanoparticles on multiwalled carbon nanotubes for example. It indeed may increase the catalytic activity and enhance the tolerance to poisoning species in methanol oxidation for DMFC for example.

Another proposal consists in the use single-crystal nanowires of Pt synthesised on nanospheres of carbon black, a commonly used catalyst support in fuel cells. These nanostructures enhance also the catalytic activity. The main advantage is that Pt nanowires display less single crystal surfaces and present less structural defects than Pt nanoparticles. These Pt nanostructured catalysts present a 50% higher mass activity than the commercial cathode.²⁰

Pt alloy single crystal surfaces display higher specific activities than pure Pt so it can be interesting to realise Pt alloy nanowires.

5.4.3.2 Hydrogen production & storage

5.4.3.2.1 Hydrogen production

Most developments of nanotechnology in hydrogen production are performed for the photo-electrolysis cells. Indeed, photo-electrode materials and their associate process displaying great performances (high efficiency) and longevity (corrosion-resistance) are required. At first, one method of hydrogen production by photo-electrolysis is the light-induced photo-oxidation of water, where metal oxides are often employed as the photocatalyst. TiO₂ is an effective catalyst for hydrogen production from water but its efficiency needs to be improved. The global idea is to use nanostructured catalyst to improve the efficiency such as vanadium oxide, which exhibited a high quantum efficiency of ~38.7 % when synthesized as nanorods. The implementation of aligned vanadium oxide nanorods into thin film allows tuning the hydrogen production by varying the incident angle of UV light on the films. Then, a high rate is obtained under UV light. It allows therefore possible commercial applications of this material as photoassisted hydrogen generators.

5.4.3.2.2 Hydrogen storage

Nanotechnologies are useful essentially for solid-state hydrogen storage. Some other usages of nanotechnologies can be considered to strengthen the mechanical strength of the hydrogen storage tank. Here the report focused on the use of nanotechnologies in solid-state storage.

5.4.3.2.2.1 Chemisorption

Magnesium hydride is considered as a promising hydrogen storage material thanks to its nominal capacity of 7.6 wt-% higher than those of other metal hydrides. The limitation of the bulk material is the slow absorption/desorption of hydrogen, the high temperature required for dehydrogenation and the durability, i.e. the resistance to cyclic hydrogenation/dehydrogenation.

The addition of a catalyst²¹, the ball milling to reduce the crystallite and particle size²², as well as mechanochemical methods²³ have been developed to increase the hydrogen absorption rate and to reduce the desorption temperature.

It has to be noted that the small size of nanostructured materials has a strong influence on the rate of hydrogen absorption and dissociation as the diffusion rate indeed increases and the diffusion length decreases. For example, it has been shown that the hydrogen absorption kinetics and the storage capacity improve when the crystallite size in magnesium powders prepared with similar particle size. In addition, a small amount of catalyst (e.g. nanoparticles of Pd or Fe) improved the absorption kinetics. Catalyst addition offsets the negative effects of surface oxidation and eliminates the need for activation.²⁴

The use of nanocrystalline alloys can be another solution. Nanocrystalline materials using high energy milling lead to a hydrogen absorption obtained within minutes whereas it can take hours in conventional material. In addition, the add of catalysts reduced absorption temperature and allow desorption at not too high temperature whereas pressure is maintained at low level²⁵: hydrogen absorbed at 523 K increase from 1.02 wt-% to 2.13 wt-% and hydrogen desorbed at 613 K increase from 0.5 wt-% to 5.12 wt-%.

The use of vanadium powder mixed with mechanically milled magnesium hydride leads to the possibility to desorb hydrogen at low temperature (200 °C) and to obtain a rapid re-absorption of hydrogen at room temperature.²⁶

5.4.3.2.2.2 Physisorption

The first solution of hydrogen storage based on physisorption is the use of metal oxide framework (MOF), that are networks of transition metal atoms bridged by organic ligands. Those ligands have been used to as structured nanoporous materials for hydrogen storage.²⁷ The main advantages are that they present large overall pore volumes and surface areas, adjustable pore sizes, the adsorption is tuneable thanks to the functionalization of the ligand and the choice of the metal, and at least, the bulk volume is totally accessible.

Thanks to these structures, the adsorption is better at low temperature (77 K) and has to be improved at room temperature but it can be compensated by a higher pressure.²⁸

Carbon nanostructures such as carbon nanofibres, nanotubes or fullerenes were supposed to have very high hydrogen storage capability. But it seemed that it was much a speculative value: it has been proven that only an undetected amount of hydrogen at least stored. Since then, studies are still performed because of the great theoretical potential of these structures.

High value of hydrogen adsorption in graphite nanofibers was indeed reported in 1998 (60wt-%)²⁹ but has never been reached again.³⁰

Several studies on single walled nanotubes and multi walled nanotubes have been performed. A record of 8 wt-% hydrogen capacity for purified single walled nanotubes³¹ has been reported but has never been reached again. For now, it seems that the hydrogen storage capacity of carbon materials depend on their specific surface area but not on their nanostructure.³² The hydrogen storage capacity can be improved by the addition of an alkali metal, by activation of the carbon³³ or by spillover.

Another possible hydrogen storage material is the zeolites. These 3D sieves with mesh size of 3 and 1 Å have the ability to reach adsorption of 20 to 30 wt-% of water at ambient temperature and pressure. Hydrogen storage needs rather high temperature (300 °C) and high pressure to get the possibility to press hydrogen into cavities. Cooling keeps hydrogen into cavities and release is obtained thanks to a new heating.

A last solution proposed to store hydrogen was the alkal metal alanates as they can liberate a large amount of hydrogen under soft operating conditions. The problem is that this process is irreversible. A first solution proposed was to dope alanates with titanium based catalyst. Other solutions are now developed based on new catalyst and on new preparation methods such as nanostructured magnesium alanates with achieve good storage capacities whereas the loading release rates stay reasonable.³⁴

5.4.4 Additional demand for research

5.4.4.1 Fuel cells

Fuel cells are very promising systems for mobile electronic devices as well as automotive applications or stationary electric plants. Nevertheless, researchers have to cope with fuel cell core lifetime which is one major issue. Increasing the durability of fuel cell components is a growing focus for research. There is still a wide gap between industrial specifications and the state-of-art. For instance, for transportation applications, fuel cell have to work under a wide range of environmental conditions (temperature from -20°C to 60°C) with a durability around 5000h, which is far from today's reality. Researchers have to tackle several issues of fuel cell core components (catalysts, electrolyte, and electrodes) to get a better understanding of failure modes.

5.4.4.1.1 Electrodes

One the main component of electrode is gas diffusion layer (GDL). Its function includes mechanical support, gas and water transports, and electronic conduction. Gas transport is permitted by hydrophilic pores and water transport is permitted by hydrophobic pores. The number of these pores should remain stable to maintain the transport balance. The degradation of these pores leads to an imbalance between water production and removal leading to an electrode flooding or drying.

Another major component of PEMFC electrodes is carbon. Carbon is a widely used material for supporting catalysts (good electrical and morphological properties). Although its stability is quite good under normal conditions, under extreme conditions (high temperature, high potential, low pH, high oxygen concentration, etc), carbon suffers from corrosion. This corrosion leads to a catalyst degradation (for instance, separation of platinum form carbon support) leading to a drastic decrease of fuel cell electrical performances.

5.4.4.1.2 Electrolytes

As for electrolytes, PEMFC are facing membrane degradation problems, resulting from chemical (platinum migration into membrane ...), thermal damages (degradation of the polymer...) and mechanical damages (stress, cracks...)

5.4.4.1.3 Catalyst

Researchers' attention also focuses on catalysts lifetime. The degradation of catalysts comes from metal particles migration and agglomeration, electrolyte dissolution or delamination of active layers leading to a decrease of ionic and electronic contact or to a catalyst structure modification. These degradations depend on factors such as electrode potential, humidity, temperature, pollutants (causing poisoning effects) and carbon support corrosion.

5.4.4.2 Hydrogen production & storage

5.4.5 Applications and perspectives

5.4.5.1 Fuel cells

The applications of fuel cells mainly depend on their operating temperature.

- AFC:

The first applications of those fuel cells and the one they were developed to was the aerospace. Some applications in the automotive have been developed. Some stationary applications can be proposed but not for mass product much more for tailored and therefore expensive applications.

- DMFC:

The main applications of this type of fuel cell are portable applications. Several companies developed indeed micro fuel cells for mobile phones, computer or PDA. A small market in automotive applications is possible. The stationary applications are limited because of the concurrence with PEMFC.

- PEMFC:

PEMFC suit particularly to automotive applications thanks to their low operating temperature, their quite easy manufacturing ... They can be used for stationary applications, especially in the domestic domain. Last but not so developed applications concerned the portable domain.

- PAFC:

These fuel cells are now almost completely developed and they are mostly used for stationary applications.

- MCFC:

The main applications are stationary for the production of electricity in electric plants or for industry applications and global building when they are used in co-generation systems

- SOFC:

The applications are mostly stationary like those of MCFC. But it is also possible to use them in automotive applications for auxiliary power units.

5.4.5.2 Hydrogen production & storage

The application of hydrogen storage and production is improvement of the hydrogen economical sectors

5.4.6 Current situation within EU

5.4.7 References & Literature

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