

Journal of Nanoscience with Advanced Technology

Hydrogen and the State of Art of Fuel Cells

Paolo Di Sia

School of Engineering & Department of Neuroscience, University of Padova, Italy

***Corresponding author:** Paolo Di Sia, School of Engineering & Department of Neuroscience, University of Padova, Italy; E mail: paolo.disia@gmail.com

Article Type: Review, **Submission Date:** 19 February 2018, **Accepted Date:** 01 April 2018, **Published Date:** 25 April 2018.

Citation: Paolo Di Sia (2018) Hydrogen and the State of Art of Fuel Cells. J Nanosci Adv Tech 2(3): 6-13. doi: <https://doi.org/10.24218/jnat.2017.27>.

Copyright: © 2018 Paolo Di Sia. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Abstract

I present in this paper an overview of the main consolidated ways of using hydrogen as inexhaustible source of energy, focusing later on fuel cells technology. Production and storage of hydrogen affect its spread on large scale, so as the cost of required materials for realizing fuel cells. Hydrogen represents a very important direction for future; the constant growth of population, together with the decreasing availability of oil and people's health, require a change of methods for the world energy production. These reasons encourage the development of renewable energy production systems and clean nanotechnology. Fuel cells are currently one of the best alternatives to common thermodynamic cycles of electricity production, one of the cleanest and most energy-efficient technologies for the direct conversion of chemical fuels in electricity. The main types, features, advantages and disadvantages of current fuel cells are considered and analyzed. It is presumable and desirable that a fast replacement of oil by hydrogen in the near future is realized for the good of the whole world.

Keywords: Hydrogen, Fuel cell, Energy, Fuel, Nanotechnology, Environment, Sustainable future.

Introduction

This work gives an overview of the main consolidated ways of using hydrogen as an inexhaustible source of energy, focusing then in particular on fuel cells. Production and storage are problems affecting the spread of this technology on large scale, combined with the cost of materials and of processes required to realize fuel cells. Based on available information and scientific data about them, we aim to a reflection on the need for a change in the energy production.

Thanks to its characteristics, hydrogen offers indisputable possibilities; it has an energy content about three times higher than that of oil, commonly used worldwide as fuel. The exponential population growth occurred in the last century requires a change of methods of energy production and it is mandatory to reason

on the cost in terms of health corresponding to the use of oil as main source of energy. When we think on the cost of systems for making hydrogen available, we do not take into account the savings in terms of health and environmental protection.

One of the consequences of poor media information is the idea of a danger of hydrogen and that this fact is the cause of slowdown in the propagation of fuel cells. To this, is added the lack of incentives and investments for building a network of infrastructures about its production and transportation. A fundamental contribution to the thrust towards these systems is constituted by their high returns, sensibly greater than those manifested by the well-established technologies exploiting conventional fuels.

In this paper I consider the main methods, for effectiveness and diffusion, of hydrogen production. Apart from its specific energy, among the reasons of interest in using hydrogen as fuel for fuel cells, are as follows:

- a) the possibility to have it disposal anywhere in the world;
- b) it can be produced using energy deriving from renewable sources;
- c) the improvement of hydrogen technologies for getting the most by this resource.

Therefore, the first step for a completely clean production of energy should be to encourage the development of renewable energy production systems and clean nanotechnology [1-3].

Hydrogen and its characteristics

Hydrogen is the lightest gas in Nature and the most abundant element of the observable Universe. It is present in the atmosphere, even if in very small percentage, due to the its tendency to react with other elements, and presents three main isotopes. ¹H, called protium, is the most common hydrogen isotope and has an abundance greater than 99.98%. At normal conditions, i.e. at room temperature (conventionally 298 K) and atmospheric pressure (1 atm), hydrogen occurs in gaseous state

in bi-atomic molecular form H₂.

The orientation of most of research is to consider hydrogen as an energy vector, i.e. as an object that allows to obtain energy through a reaction process. It has a high specific energy per unit mass; the energy contained in 9.5 kg of hydrogen is equivalent to that of 25 kg of gasoline. Relatively to mass, it has the highest energy content compared to other fuels. Comparing the energy content in relation to mass and volume of the main fuels (Table), we can make some considerations:

- considering the energy actually usable by one kg of fuel, hydrogen is much higher having an energy content significantly greater than that of gasoline (and all other fuels);

- considering the energy usable by a quantity of material present in an equivalent volume of one cubic meter at room temperature and atmospheric pressure, hydrogen cannot compete with gasoline.

From this, it is clear that one of the problems affecting the use of hydrogen as fuel for cars, but also for stationary uses, is the need to store it at high pressures or in liquid form, with unavoidable disadvantages.

Methods for obtaining hydrogen

Various techniques and reactions have been studied for the production of hydrogen by its compounds already present in Nature. The main source from which it would seem natural to obtain it is water, given its abundance and its ease of retrieval. We can list three methods primarily used to get hydrogen:

a) water electrolysis;

b) reforming;

c) other production processes.

a) The electrolytic decomposition of water follows the reaction: $2\text{H}_2\text{O} + \text{electricity} \rightarrow 2\text{H}_2 + \text{O}_2$. The efficiency of the process depends on many factors such as the materials used for electrodes or the used catalysts. This method is considered less than other techniques because it requires a high expense in terms of electricity to allow the reaction [4].

About the electrolyzers, we list four categories:

i) **Traditional alkaline electrolyzers:** they ensure a good

compromise between conductivity of the electrolyte and effects of corrosion.

ii) **Advanced alkaline electrolyzers with high current density:** it is used the evident increase in conductivity with temperature of the electrolyte. Increasing efficiency, it results in a significant saving of electricity at parity of produced hydrogen.

iii) **Solid polymer electrolyzers or membrane electrolyzers:** they have a higher safety due to the absence of corrosive liquid electrolytes, ease of maintenance and possibility to operate at high current densities. A problem is certainly represented by the used materials as platinum and ion-exchange membranes that appreciably participate to the final cost.

iv) **High temperature electrolyzers:** the advantages are the efficiency (up to 100%) and the use of a solid ceramic electrolyte (oxygen-ions conductor) that is not corrosive and does not cause problems of liquid/gas leaks. It is a very advantageous technique, but far from a widespread use due to the cost of the process. If to start the process the energy were derived from renewable energy sources, it would be completely clean.

b) Despite the fact that the possibility to produce hydrogen in a clean way are always increasing, the greater quantity of hydrogen produced in the world comes from fuels such as methane (CH₄) according to reactions called "reforming reactions". Steam reforming is a method that allows the production of hydrogen from hydrocarbons (often methane). It consists in the chemical reaction of methane with water vapor at a temperature that varies from 700 °C to 1100 °C, combined with a pressure of 20 bar and with the presence of appropriate catalysts, usually based on nickel and alumina. According to the following reaction: $\text{CH}_4 + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO} + 3\text{H}_2 - 191.7 \text{ kJ/mol}$, it is produced "syngas", a mixture consisting primarily of carbon monoxide and hydrogen. The heat required for the endothermic reaction is generally provided by the combustion of a part of methane. Although the reaction is favored at low pressures, a higher pressure is used to save on any subsequent compression step [5].

First chemical reactions divide the methane molecules (CH₄) into hydrogen and carbon monoxide (CO). Subsequently the mixture containing CO reacts with other water vapor at the temperature of about 450 °C. The result is carbon dioxide (CO₂)

	Hydrogen	Methane	Gasoline	Diesel	LPG	Methanol
Content of energy per unit mass (MJ/kg)	119.90	49.89	44.48	42.6	46.44	19.85
Content of energy per unit volume (MJ/l)	8.47 (liq.)	20.88 (liq.)	31.15	35.7	25.5	15.88

Table: Comparison of Energy Content in Relation to Mass and Volume of the Main Fuels

and still hydrogen. This second reaction is called “shift reaction”: $\text{CO} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO}_2 + \text{H}_2 + 40.4 \text{ kJ/mol}$. During this reaction the oxygen atom (O) of the water vapor oxidizes the carbon (C) releasing hydrogen previously linked to oxygen. The efficiency of this process is commonly of 65-70% but with some attentions it can be carried also at 75-85%. The most modern systems are equipped with an energy recovery system contained in waste gas and steam.

The output steam can be used to produce electricity; gases containing a high percentage of the fuel are purified from carbon dioxide and reused to supply the process. The produced CO_2 is carefully controlled and cut down “in situ”. This process is the most used for the production of hydrogen. Coal gasification is an alternative to steam reforming for producing hydrogen industrially.

The coal is transformed into a mixture of syngas and methane. The coal is treated with water vapor to obtain the relation: $\text{C} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO} + \text{H}_2$. Various techniques have been developed, concerning cycles at low temperatures (400-500 °C) and these are more efficient than those commonly used to date. A fundamental part of these studies is covered by catalysts.

c) The listed processes are the most used ones; the attention is today focused also on processes of photosynthesis, that allow to obtain hydrogen by directly exploiting solar energy, without the need to resort to systems for producing the energy needed to get electrolysis.

By means of a process called “non-catalytic partial oxidation” it is possible to obtain hydrogen also from heavy hydrocarbons (naphtha), gasoline and methane, through reaction with oxygen or air. Combining steam reforming with partial oxidation reaction, it is possible to obtain hydrogen without adding fuel from outside. This combined process is called “auto-thermal reforming”. In this case the obtained hydrogen is pure, there is no CO_2 emission but the process requires a lot of energy. Its global access is 98% (close to the maximum); 48% of the modified energy is contained in hydrogen, 10% in steam and 40% in residual carbon, which is usually used in the tire industry. The Kvaerner process involves high plant costs (in particular costs of energy); the produced vapor is used for a subsequent production of electricity.

In addition to coal gasification, an interesting solution is the “gasification of biomass”. It is possible to obtain hydrogen directly from biomass as a collateral product of combustion and “pyrolysis process”. However, the hydrogen produced by the reaction is not enough pure for its common use; for eliminating unwanted substances it is necessary a purification system. Thanks to these processes it will be possible to obtain hydrogen from organic waste and make it available with an acceptable degree of purity for both stationary and vehicular applications.

With the “photoconversion”, or “photolysis”, water produces hydrogen and oxygen by reacting directly when exposed to

light, in presence of special catalysts. There are two possibilities: “photobiology” and “photoelectrochemistry”.

- *Photobiological processes*: these processes are based on the special ability of some algae and bacteria to produce hydrogen in particular conditions. These organisms, thanks to the catalyzing action of some enzymes present in their cells, are able to split water into hydrogen and oxygen. The dissociation of water occurs during the metabolism reactions of these photosynthetic organisms. The efficiency of these biological systems, among which the best known is “*rhodospirillum rubrum*”, is around 5%. The limit of this alga is represented by the fact that its enzymes are destroyed by oxygen produced in the water splitting process. Water is the source of electrons (e^-) and protons (H^+), while light supplies the necessary energy to realize the process according to relation: $2\text{H}^+ + 2e^- + \text{light} \rightarrow \text{H}_2$. Efforts have been invested in trying to genetically modify the enzymes of some bacteria for being able to efficiently produce gaseous H_2 even in the presence of oxygen and to increase the degree of purity of produced hydrogen.

- *Photoelectrochemical processes*: these systems use semiconductor electrodes to directly transform solar energy into hydrogen. This technology is still in a development phase. Thanks to current new technologies it is possible to study the involved materials and modify them at the atomic level. Nanocrystalline materials and particular coatings for electrodes are replacing common solid-state junction devices, often made of silicon. Iron oxide “hematite” has been involved in hydrogen research; taking advantage of superficial re-growth, allowing to smooth imperfections, the electric efficiency has been doubled[6-9].

Storage of hydrogen

Purity of produced hydrogen

As mentioned before, a process of purification is necessary before hydrogen can be stored, because fuel cells suffer significant loss of efficiency due to impurities present in the gas. There are several methods that allow to eliminate impurities from hydrogen. The process that seemed the most promising, allowing a higher purity than 99%, is PSA (Pressure Swing Adsorption). A more recent and advanced method based on PSA is DRPSA (Dual-Reflux Pressure Swing Adsorption). This technique allows to reach purity values like those of PSA, but with lower pressure values, and therefore lower energy cost. The 99.62% of CO_2 can be recovered with a purity of 99.18% through DRPSA process while the light product N_2 can be enriched up to 99.64% with a recovery of 99.56% under optimal operating conditions.

Methods for storing hydrogen

One of the most critical factor for the use of hydrogen as fuel in stationary systems is represented by its actual availability. The number of filling stations for this gas is practically zero when compared to the diesel and oil network.

The delivery of hydrogen to customers takes place mainly through classic steel cylinders. In general, the methods for accumulating

hydrogen are completely different in relation to the distance to travel for moving it; in the case of long distance, it prevails the need to store the maximum quantity. About tanks of hydrogen cars, some typical automotive factors become important: encumbrance, lightness, costs, safety. Hydrogen can be stored in two mean forms, that, together with cryo-compression, are suitable for both stationary systems (for the production of electric energy) and for vehicles [10-13].

Compressed gaseous state

Hydrogen is stored inside very resistant cylinders placed in protected areas or collected in warehouses. After the compression phase normally the hydrogen pressure is between 250-350 bar. If the quantity of gas is higher than 15000 Nm³, it is preferred to store it in containers with special spherical shape, this however has a higher specific cost (per unit volume unit). Modern tanks can withstand pressures from 350 to 700 bar. For vehicles, the problem of accumulation of gases on board is represented by their low value of energy per volume unit. The robustness of tanks, the introduction of explosion-proof fuses in case of fire and the adoption of special cut-off valves in the event of a collision make the storage of compressed hydrogen very secure on board.

Liquid state

Hydrogen at liquid state is available at the temperature of -253 °C. In order to be maintained in this physical state, it must be contained in special cryogenic tanks. The accumulation of hydrogen at liquid state allows, with the same geometric bulk of the tank, to transport a quantity of energy significantly higher than the gaseous state. Several reasons still restrain this type of storage, first of all the technological complexity of management of liquid hydrogen. In addition the overall costs to bring and maintain hydrogen at that temperature are higher than the case of compressed gas.

Fuel cells

Fuel cells are essentially primary cells in which the reducing agent (gaseous fuel) and oxidizing one (air or oxygen) are continuously put respectively in the anodic compartment and in cathodic one (Figure 1), respectively.

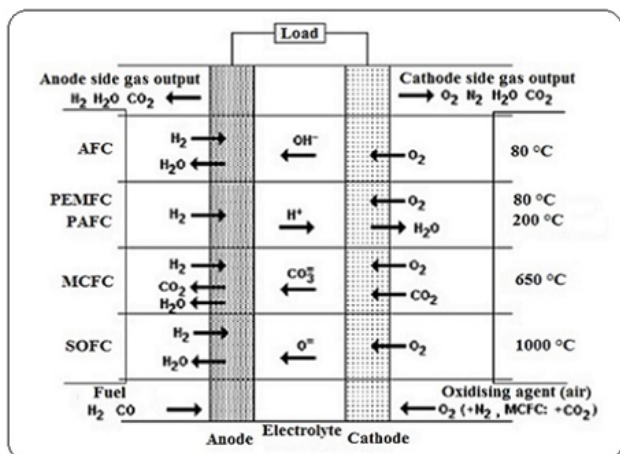


Figure 1: Schematic representation of a fuel cell

These cells operate a conversion of chemical energy into electrical energy; what mainly differentiates them from the other types of batteries and accumulators is the fact that, theoretically, they have the capacity to supply electrical energy until fuel and comburent are supplied to the cell, i.e. indefinitely if continuously powered. In practice, however, there are some problems such as degradation and dysfunctions, that sometimes limit its life [14-15].

Fuel cells are one of the most promising perspectives for replacing oil as main energy source.

Fuel cells mainly differ for type of used electrolyte and for their realization. There are several types:

- a) Proton Exchange Membrane Fuel Cells (PEMFC);
- b) Phosphoric Acid Fuel Cells (PAFC);
- c) Molten Carbonates Fuel Cells (MCFC);
- d) Solid Oxide Fuel Cells (SOFC);
- e) Direct Methanol Fuel Cell (DMFC) (uses methanol (CH₃OH) as the fuel, which is oxidized to directly produce CO₂ and H₂O);
- f) Alkaline Fuel Cells (AFC).

The most attractive use of these cells remains linked to the creation of electric and hybrid cars. All basic fuel cells consist of an electrolyte interposed between two porous layers called anode and cathode. Anode is powered by the fuel while cathode is being supplied by the comburent. The most commonly used fuel and oxidizer are hydrogen and oxygen in the gaseous state (g). Fuel cells use three-dimensional porous gas-diffusion electrodes consisting, for example, of porous graphite; in its pores a suitable catalyst is deposited for accelerate the redox process. These electrodes constitute triple contacts that allow the transit, through the electrode, of electroactive species and of reaction products (H₂O). At the same geometric dimensions, a porous electrode has a much larger exchange surface than a plane. In particular at low temperatures, materials must have excellent electrocatalytic characteristics [16].

Proton Exchange Membrane Fuel Cells PEMFC

The process that takes place in PEMFC is the classic combustion of H₂. The membrane allows the transfer of H⁺ ions from anodic to cathodic compartment. The reaction processes include also the problem of water elimination. The electrolyte that makes up these cells is a polymeric perfluorine-sulphonic membrane at proton conduction with thickness of about 100 μm. The membrane is between the two three-dimensional electrodes with dispersed catalyst. For obtaining a relevant power, several cells are connected in series using a bipolar plate of conductive material; often, in particular for the ease of processing, graphite is used. This bipolar plate has some grooves to supply the two electrodes of the respective gases.

Gases come from the respective compartments, through grooves, behind the porous electrode, through which come in contact

with the electrolyte for the electrochemical process. The plate is used for cooling the fuel cell too. There are channels through which a cooling fluid flows (air rather than water, because water causes electrode corrosion problems). The heated fluid is reused through the reforming process for producing H₂. These cells operate at a lower temperature than 100 °C and therefore the use of electrocatalytic materials (e.g. platinum) is necessary, in order to help the kinetics of electrochemical reactions. The porous-structure electrodes are obtained by deposition of the finely-dispersed electrocatalytic material on a layer of graphite powder supported on a graphitized carbon fiber. The graphite powder is bound with a polymer, often Teflon (PTFE polytetrafluoroethylene). There are also different ways to deposit platinum on electrodes. It is possible to integrate the hydrogen production method with the subsequent stage that through fuel cells produces current (Figure 2).

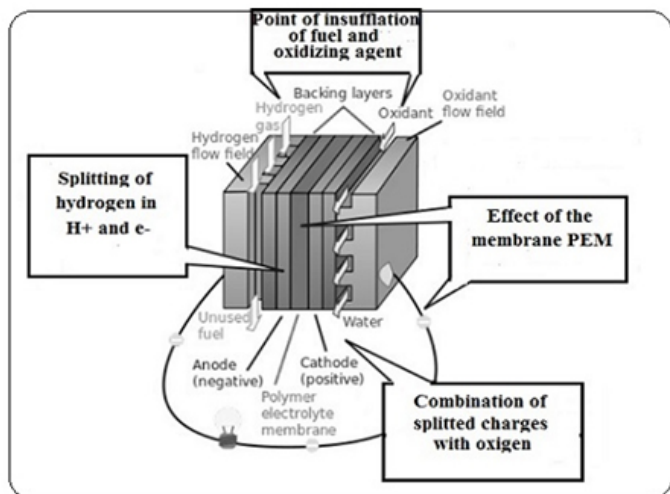


Figure 2: Simplified image of the components of a PEMFC cell

Currently with these type of cells, it is possible to obtain a power density of 1 kW/l. This value enables them to be used both as batteries for electronic devices and to the use of electrical production. The commercialization of cars with this integrated process (through mini-reactors installed on board, capable of converting gasoline or methanol into hydrogen) is expected by around 2020 [17-18].

Phosphoric Acid Fuel Cells PAFC

These cells perform the same anodic and cathodic reactions of PEMFCs. They are different from the previous ones in terms of the electrolyte, which in this case is 100% phosphoric acid (H₃PO₄). They work normally between 180-200 °C. The liquid acid is inside a silicon carbide matrix (SiC), thanks to the filling of micropores for capillarity. As for PEMFCs, electrodes are gas-diffusion, consisting of coal powder in which the platinum particles are dispersed. The coal powder is kneaded with Teflon so as to constitute a porous and at the same time quite robust structure (Figure 3).

This type of cell is not suitable for vehicular use, rather for the production of electricity, given the high working temperature

and the use of a liquid electrolyte. They do not need a particularly high degree of purity of gas, therefore can be powered directly from the gas mixture produced by the steam reforming process of methane. A concentration of CO in the gas up to 1% is accepted. The level of pollution is 10 to 100 times lower than that of conventional systems a diesel engines and gas turbines [19].

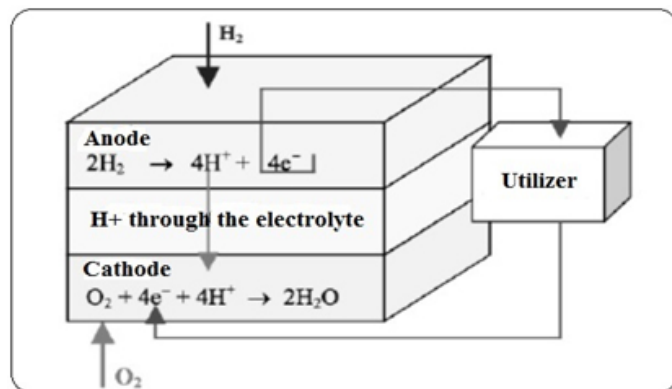


Figure 3: Schematic functioning of a PAFC cell

Molten Carbonates Fuel Cells MCFC

In these cells the anode consists of a porous structure of a nickel-chromium alloy (Ni-Cr 2-10%) and the cathode of a porous nickel oxide (NiO) structure doped with 1-2% lithium (Li). The electrolyte generally consists of a mixture of lithium and potassium (or sodium) carbonates, contained in a ceramic, chemically inert, porous, lithium aluminate γ -LiAlO₂ matrix. The operating temperature of the cell is higher than 600 °C. At this temperature the carbonate mixture is melted and is a good ionic conductor with a high CO₃²⁻ ion transport number, which contributes predominantly to the conductivity of electrolyte. The type of power supply is dual; the cell can be powered, from the anodic compartment, both with hydrogen (H₂) and carbon monoxide (CO). The process involves the consumption of CO₂ at the cathode, that must then be supplied with O₂.

The high temperature creates a problem of structural stability and also of costs, but it also has many advantages: it is possible to use less precious metal catalysts than platinum, that is a big part of cost of the other cells. The disadvantages include: high corrosiveness of the electrolyte, high temperatures, dissolution of the cathode nickel oxide [20].

Solid Oxide Fuel Cells SOFC

This type of cells has the potential to be one of the cleanest and energy-efficient technologies for the direct conversion of chemical fuels into electricity. Their peculiarity is that they are completely solid state; in particular the electrolyte is an ionic conducting oxide, so there are only two operating phases: solid and gaseous. One of current technical goals is the minimization of resistance to the "reduction reaction of oxygen" (ORR) to the cathode; in fact, especially at less temperatures than 700 °C, it contributes to the degradation of performance and to the loss of cells efficiency.

The components remain substantially the same, except for the

used materials for electronic connectors between multiple cells in series. The electrolyte material consists of zirconium oxide doped with 8-10% molar of yttrium oxide Y_2O_3 (Yttria Stabilized Zirconia (YSZ)); anodes are made of cermet Ni / YSZ (volume of nickel 50% and porosity 40%), cathodes (porosity of about 35%) are made by manganitic oxide $La_{1-x}Sr_xMnO_3$ ($x = 0.16$) and interconnections connecting the cathode of a cell to the anode of the other one are constituted by $LaCrO_3$, doped with Mg or Sr or metallic superalloys.

For this type of cells three different configurations have been developed:

Tubular configuration: Every single cell is made starting by a porous tube with closed bottom (between 30-150 cm) of 1-2 mm thickness, made of zirconium oxide stabilized with calcium oxide and sintered at 1650 °C. Subsequently the tube is covered with a lanthanum manganite, strontium doped ($La_{1-x}Sr_xMnO_3$) porous layer, with a thickness of about 1 mm, that constitutes the cathode of the cell. A film of YSZ impermeable to gases, of about 40 μm thickness, is deposited on this cathodic layer. The electrolyte is deposited so as to leave uncovered a strip of cathode material, with width of 9 mm and length equal to the support tube, subsequently covered with interconnection material, $LaCrO_3$ doped Mg. Finally, the entire electrolytic surface is covered with an anodic material (cermet). Single tubes, making up the cells, are connected to each other using nickel felts that are in constant contact with the reducing atmosphere, consisting of hydrogen H_2 . The supply of comburent (air) occurs through the hollow tubes. With this tubular configuration, the unused fuel is between 10 and 50%. Part of this gas flow is mixed with hydrogen and recycled into a cell, part is burned to preheat the supply gases. Natural gas is used as fuel. The high cost of every single cell unfortunately prevents its spread on large scale.

Monolithic configuration: The cell consists of a matrix with beehive structure in which a large number of canals are present, where fuel and oxidizer circulate. The channels in which gases flow are obtained with corrugated anodic and cathodic layers, separated by flat multilayers, so as to alternately produce the "cathode | electrolyte | anode" and "anode | interconnection | cathode" interfaces (Figure 4).

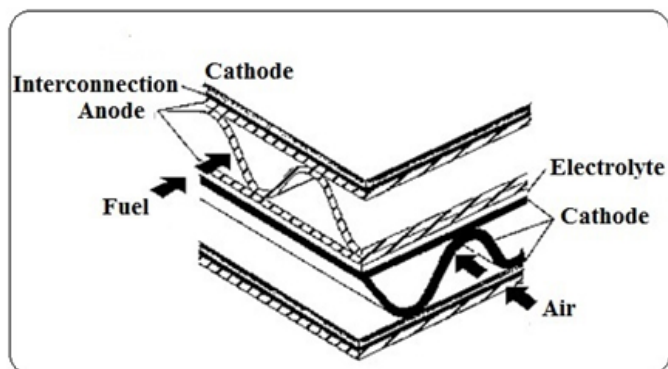


Figure 4: Monolithic configuration fuel cell with crossed flow

The performance of these cells is higher than that of the tubular

configuration; in fact, it has been obtained a current density of 1 A/cm² at 0.6 V, while for the tubular ones the maximum current is around 500 mA/cm². However, the problem of these cells occurs in the connection of multi-cell systems; the interaction of different materials during the sintering process and the low density of interconnection material in the planar layers degrade the operation of multi-cell devices.

Planar configuration: The cell consists of a cross-flow system in which the separation of gases is obtained with metal or ceramic tiles having supply fuel and oxidizer channels at the appropriate electrodes. The electrochemical cell consists of a cathode and an anode, both porous, among which is interposed a thin and thick electrolytic layer. With this technology single sized 3x5 cm² cells have demonstrated the possibility of delivering 0.4 W/cm³ at a voltage of 0.7 V (the tubular ones, instead, a power of about 0.25 W/cm³ at 1000 °C); the working temperature is 1000 °C e the supply uses pure hydrogen. This configuration presents the best electrical characteristics and the simplest implementing solutions, but still more work must be done to achieve the design of a marketable version [21,22].

Direct Methanol Fuel Cell DMFC

Methanol has been used in polymeric electrolyte fuel cells as reagent for hydrogen production through the reforming process. This reaction is much less endothermic than the other hydrocarbon reforming reactions, therefore requires less heating and low temperatures (250 °C), with cheaper catalysts such as copper (Cu) on zinc oxide (ZnO). To avoid the production of CO, the shift process is also used here, because CO in PEMFCs poisons the platinum catalyst. In direct-methanol cells, CH_3OH is used directly as fuel with which the anode is supplied instead of H_2 .

The problem is that the oxidation of methanol proceeds more slowly than that of H_2 , since it is a more complex process involving 6 electrons per molecule. As a result, there is a lower specific power. A second problem is the possibility of crossover for methanol; thanks to its water solubility, always present in the membrane, it reaches the cathode causing a decrease of the open circuit voltage.

The first advantage of methanol is its tendency to oxidise; it easily oxidizes into CO_2 , even if to do that it makes intermediate reactions. It is available, being a product of many spontaneous or gasification processes (for example of biomass or coal) or fermentation product of agricultural products and waste, therefore it has a low cost. It can be easily transported and produced by renewable sources. The oxidation reaction in DMFCs is as follows: $CH_3OH + 3/2 O_2 \rightarrow CO_2 + 2 H_2O$, with a corresponding $\Delta V_{rev} \approx 1.2$ V. In practice, the delivered voltage is much lower (from 0.6 to 0.3 V), for the previously listed reasons. Methanol can be used as fuel also in PEMFCs. In alkaline electrolyte fuel cells, the product of the anodic process: $CH_3OH + 6 OH^- \rightarrow CO_2 + 5 H_2O + 6 e^-$ would react with the alkaline electrolyte, consuming: $CO_2 + 2 OH^- \rightarrow CO_3^{2-} + H_2O$. For

this reason an acid electrolyte is used. The anodic process is not simple, but involves a transition through successive steps. The anodic reaction needs water as reagent, then the fuel cannot be pure methanol but an aqueous solution.

For not decreasing the already low specific energy of the system, it is good to provide water to the cell. The diluted solution of methanol (3%) helps to prevent the crossover; moreover the contact with the membrane (PEM) keeps it constantly hydrated, helping to ensure its better functioning. The polymeric electrolyte for DMFC is similar to that of PEMFC. Unfortunately, the various steps of the oxidation process of methanol are slow and this is the main cause of the low efficiency of these cells.

About the anodic process, at present some bimetallic catalysts, in particular Pt/Ru 50/50, appear to be quite efficient. The catalyst is produced through a technology that allows the dispersion of nanoparticles of the Pt/Ru alloy in the coal, for increasing the dispersion, thanks to the high porosity of the coal. This last acts also as electronic conductor, ensuring the contact with the current collector. The realization of nanocomposites allows a reduction in the amount of catalyst of an order of magnitude and, at the same time, the efficiency is increased by an order of magnitude [23,24].

Alkaline Fuel Cells AFC

These bio-electrochemical cells are a system for producing electric current through particular bacteria and reproducing the interactions between them in Nature. The idea of using microbes to produce electricity was conceived at the beginning of the twentieth century. Already in 1911 research showed that the excitation of a living protoplasm gives a not less electrical response than that of animal protoplasm [25]. In the condition of active metabolism, it gives an instantaneous electrical response to the influence of sunlight, modified according to the conditions that related to protoplasmic activity.

Today MFCs are made up of a bioanode and a biocathode, with a membrane to separate the anodic and cathodic compartments, where oxidation and reduction occur. Organic reducing agents are used and are oxidized to produce CO₂, protons and electrons. When microorganisms consume a substance such as sugar in aerobic conditions, they produce CO₂ and H₂O. When oxygen is not present, they produce CO₂, protons and electrons.

Connecting the two electrodes with a wire or an electrically conductive path and connecting the two compartments with a saline bridge or an exchange membrane, produced protons are allowed to pass from the anodic to the cathodic sector. The reducing agent brings electrons from the cell to the electrode, which is oxidized and loses electrons. Charges flow, through the wire, towards the second electrode that works as an "electrowire". These cells have found commercial use to date in the treatment of waste water [26].

Conclusions

Tools helping the design and implementation of fuel cells systems

are more and more common on the market, offering the most robust functionality for simulating all types of electrochemical behaviour and the affected surrounding processes [27].

Studied systems in this area include lead-acid batteries, lithium batteries, metal-hydride nickel batteries, SOFCs, DMFCs and PEMFCs; all these can be studied and analyzed using this software.

The reason of these theoretical and experimental efforts is the need to find an effective and efficient solution for ensuring a compatible future with the current required comfort standards [28-31]. Considering the most recent solutions regarding production cycle, storage and hydrogen transformation, we can conclude that this is a very important direction for future.

Although electrolysis is the cleanest process to produce hydrogen, steam reforming is still the most used one. For stationary applications of small-power electricity production, biomass treatments (bio-power) are also interesting when they come from waste products.

Through complex reforming processes it is possible to minimize the emissions of pollutant agents through the shift combined with the breakdown of carbon dioxide. As for hydrogen storage techniques, the most promising would seem the cryo-compression. Although it offers high returns, its demand of energy is very high; however, a part of this energy can be saved by focusing on processes of hydrogen production that provide gas with high purity.

Also the problem of hydrogen purity is a subject of careful study. For many cells, in fact, some impurities of hydrogen (such as CO), can cause large inefficiencies (CO particles can poison platinum).

Fuel cells are currently the best alternative to the common thermodynamic cycles of electricity production; the study on the constituent materials of cells continues incessantly, in the field of materials, especially electrodes and catalysts. To date the most performing material is platinum, but it is a precious metal and in fact constitutes a significant proportion of the cost of fuel cell. Solid oxide fuel cell seems to be one of the cleanest and most energy-efficient technologies for the direct conversion of chemical fuels in electricity.

It is not possible to expect a fast replacement of oil by hydrogen, but it is presumable and desirable that, in the near future, this change may occur[32].

References

1. Di Sia P. Present and Future of Nano-Bio-Technology: Innovation, Evolution of Science, Social Impact. The Online Journal of Educational Technology (TOJET). 2015; 442-49.
2. Di Sia P. Nanotechnologies among Innovation, Health and Risks. Procedia - Social and Behavioral Sciences Journal. 2017; 237:1076-1080. doi: <http://dx.doi.org/10.1016/j.sbspro.2017.02.158>.
3. Minic D, editor. Hydrogen Energy - Challenges and Perspectives. Rijeka: InTechOpen; 2012.

4. Bessarabov D, Wang H, Li H, Zhao N, editors. PEM Electrolysis for Hydrogen Production: Principles and Applications. Boca Raton: CRC Press; 2015.
5. Angeli SD, Turchetti L, Monteleone G, Lemonidou A. Catalyst development for steam reforming of methane and model biogas at low temperature. *ApplCatal B-Environ*. 2016; 181:34-46.
6. Willner I, Steinberger-Willner B. Solar hydrogen production through photobiological, photochemical and photoelectrochemical assemblies. *Int J Hydrogen Energ*. 1988; 13(10):593-604.
7. Minggu LJ, Daud WRW, Kassim MB. An overview of photocells and photoreactors for photoelectrochemical water splitting. *Int J Hydrogen Energ*. 2010; 35(11):5233-5244.
8. Di Sia P. Characteristics in Diffusion for High-Efficiency Photovoltaics Nanomaterials: an interesting Analysis. *Journal of Green Science and Technology (JGST)*. 2014; 1:1-4.
9. Du C, Yang X, Mayer MT, Hoyt H, Xie J, McMahon G, et al. Hematite-Based Water Splitting with Low Turn-On Voltages. *AngewChemInt Edit*. 2013; 52(48):12692-12695. doi: 10.1002/anie.201306263.
10. Zhevago NK, Chabak AF, Denisov EI, Glebov VI, Korobtsev SV. Storage of cryo-compressed hydrogen in flexible glass capillaries. *Int J Hydrogen Energ*. 2013; 38(16):6694-6703.
11. Di Sia P. On the Use of Hydrogen in the Automotive Sector. *Nano Energy Systems*. 2017; 1(2):50-58. doi: 10.24274/nes.2016.
12. Kampitsch TBM, Kircher O. "Cryo-Compressed Hydrogen Storage". In: Stolten D, Samsun RC, Garland N, editors. *Fuel Cells: Data, Facts and Figures*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2016. doi: 10.1002/9783527693924.ch17.
13. Grätzel M. Photoelectrochemical cells. *Nature*. 2001; 414.6861:338-344.
14. Perry ML, Fuller TF. A historical perspective of fuel cell technology in the 20th century. *J Electrochem Soc*. 2002; 149(7):S59-S67. doi: 10.1149/1.1488651.
15. Di Sia P. "The Nanotechnologies World: Introduction, Applications and Modeling". In: Sinha S, Navani NK, editors. *Nanotechnology, vol.1: Fundamentals and Applications*. Houston: Studium Press LLC; 2013.
16. Srinivasan S. *Fuel Cells: From Fundamentals to Applications*. New York: Springer; 2006.
17. Steele BCH, Heinzl A. Materials for fuel-cell technologies. *Materials for Sustainable Energy*. 2010:224-31. doi: https://doi.org/10.1142/9789814317665_0031.
18. Costamagna P, Srinivasan S. Quantum jumps in the PEMFC science and technology from the 1960s to the year 2000: Part II. Engineering, technology development and application aspects. *J power sources*. 2001; 102(1):253-269.
19. Available: <http://www.fuelcelltoday.com/technologies/pafc>.
20. Larminie J, Dicks A. *Fuel Cell Systems Explained*. Chichester: John Wiley & Sons Ltd; 2003.
21. Singhal SC. Advances in solid oxide fuel cell technology. *Solid State Ionics*. 2000; 135:305-313.
22. Ding D, Li X, Lai SY, Gerdes K, Liu M. Enhancing SOFC cathode performance by surface modification through infiltration. *Energy Environ Sci*. 2014; 7(2):552-575. doi: 10.1039/C3EE42926A.
23. Aricò AS, Srinivasan S, Antonucci V. DMFCs: From Fundamental Aspects to Technology Development. *Fuel Cells*. 2001; 1:133-161. doi:10.1002/1615-6854(200107)1:2<133::AID-FUCE133>3.0.CO;2-5.
24. Liu H, Song C, Zhang L, Zhang J, Wang H, Wilkinson DP. A review of anode catalysis in the direct methanol fuel cell. *J Power Sources*. 2006; 155(2):95-110.
25. Potter MC. Electrical effects accompanying the decomposition of organic compounds. *Proc R Soc Lond B*. 1911; 84:260-276. doi: 10.1098/rspb.1911.0073.
26. Jang JK, Pham TH, Chang IS, Kang KH, Moon H, Cho KS, et al. Construction and operation of a novel mediator- and membrane-less microbial fuel cell. *Process Biochem*. 2004; 39:1007-1012.
27. Available: <https://www.comsol.it/batteries-and-fuel-cells-module>
28. Di Sia P. Present and Future of Nanotechnologies: Peculiarities, Phenomenology, Theoretical Modelling, Perspectives. *Reviews in Theoretical Science (RITS)*. 2014; 2(2):146-180.
29. Di Sia P. Nanotechnology between Classical and Quantum Scale: Applications of a new interesting analytical Model. *AdvSciLett*. 2012; 17:82-86.
30. Di Sia P. An Analytical Transport Model for Nanomaterials. *J ComputTheor Nanos*. 2011; 8:84-89.
31. Di Sia P. An Analytical Transport Model for Nanomaterials: The Quantum Version. *J ComputTheor Nanos*. 2012; 9(1):31-34.
32. Di Sia P. Nanobiomaterials for environmental protection: state of the art, applications and modelling. *International Journal of Engineering Innovations and Research (IJEIR)*. 2014; 3(5):688-693.