Fuel Cells: Technologies and Applications

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Abstract: A deep analysis of the Fuel Cells technologies state of the art has been done in this article. After a general description of the fuel cell base structure the six most important fuel cell technologies Polymeric Electrolyte Membrane Fuel Cells (PEMFC), Direct Methanol Fuel Cells (DMFC), Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), Solid Oxide Fuel Cell (SOFC) are explained, describing advantages and disadvantages of each one and pointing out their principal use. The future development are also shown.

1. INTRODUCTION

Fuel cells are seen by many people as a key solutions for the 21st century, enabling clean efficient production of power and heat from a range of primary energy sources.

Fuel cells are electrochemical devices that use hydrogen (H_2), or H_2-rich fuels, together with oxygen from air, to produce electricity and heat. However there are many variants of this basic process, depending on the Fuel Cell type and the fuel used.

This technology is very interesting for a many different applications including micro power generators, auxiliary power generators, stationary power generators, distributed power generators and portable power generators for transportation, military projects and the automotive market.

These are all applications that will be used in a large number of industries and environments on a worldwide scale [1].

The principle of the fuel cell was discovered by German scientist C. F. Schönbein in 1838. Based on this work, the first fuel cell was demonstrated by Welsh scientist Sir W.R. Grove in 1839 [2, 3]. In 1939, British engineer F.T. Bacon successfully developed a 5 kW stationary fuel cell. In 1955, W.T. Grubb, a chemist working for the General Electric (GE) Company (USA), further modified the original fuel cell design by using a sulphonated polystyrene ion-exchange membrane as the electrolyte. Three years later another GE chemist, L. Niedrach, devised a way of depositing platinum onto the membrane, which served as catalyst for the necessary hydrogen oxidation and oxygen reduction reactions. GE

went on to develop this technology with NASA, leading to its use during Project Gemini. This was the first commercial use of a fuel cell. In 1959, a team led by H. Ihrig built a 15 kW fuel cell tractor for Allis-Chalmers, which was demonstrated across the U.S. at state fairs. This system used potassium hydroxide as the electrolyte and compressed hydrogen and oxygen as the reactants. In the 1960s, Pratt and Whitney licensed Bacon's U.S. patents for use in the U.S. space program to supply electricity and drinking water (hydrogen and oxygen being readily available from the spacecraft tanks).

International Fuel Cells (IFC, later UTC Power) developed a 1.5 kW alkaline fuel cell (AFC) for use in the Apollo space missions. The fuel cell provided electrical power as well as drinking water for the astronauts for the duration of their mission. IFC subsequently developed a 12 kW AFC, used to provide onboard power on all space shuttle flights.

Earlier, General Motors had experimented with its hydrogen fuel cell powered Electrovan fitted with a Union Carbide fuel cell. Although the project was limited to demonstrations, it marked one of the earliest road-going fuel cell electric vehicles (FCEV).

From the mid-1960s, Shell was involved with developing direct methanol fuel cell (DMFC), where the use of liquid fuel was considered to be a great advantage for vehicle applications. Several German, Japanese and US vehicle manufacturers and their partners began to experiment with FCEV in the 1970s, increasing the power density of PEMFC stacks and developing hydrogen fuel storage systems. By the end of the century, all the world's major carmakers had active FCEV demonstration fleets as a result of these early efforts. The focus by then had shifted back to pure hydrogen fuel, which generates zero harmful tailpipe emissions.

Prompted by concerns over energy shortages and higher oil prices, many national governments and large companies initiated research projects to develop more efficient forms of energy generation in the 1970s. One result of this was important advances in phosphoric acid fuel cell (PAFC) technol-

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ogy, in particular in stability and performance. There were significant field demonstrations of large stationary PAFC units for prime, off-grid power in the 1970s, including a 1 MW unit developed by IFC. Funding from the US military and electrical utilities enabled developments in molten carbonates fuel cell (MCFC) technology, such as the internal reforming of natural gas to hydrogen. The use of an established natural gas infrastructure was a key advantage in developing fuel cells for large stationary prime power applications.

Substantial technical and commercial development continued in the 1980s, notably in the area of PAFC. A bright future for the technology was widely predicted around this time for stationary applications and buses. Ambitious conceptual designs were published for municipal utility power plant applications of up to 100 MW output. Predictions of tens of thousands of units in operation by the end of the century were made, but only hundreds were to actually appear by that date. Several experimental large stationary PAFC plants were built, but saw little commercial traction in the 1980s. With subsequent advancements in membrane durability and system performance, PAFC were rolled out in greater numbers almost two decades later for large-scale combined heat and power applications.

In 1983 the Canadian company Ballard began research into fuel cells, and was to become a major player in the manufacture of stacks and systems for stationary and transport applications in later years.

Attention turned to polymer electrolyte membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC) technology in the 1990s, particularly for small stationary applications. These were seen as offering a more imminent commercial possibility, due to the lower cost per unit and greater number of potential markets - for example backup power for telecoms sites and residential micro-CHP. In Germany, Japan and the UK, there began to be significant government funding devoted to developing PEMFC and SOFC technology for residential micro-CHP applications.

Government policies to promote clean transport also helped drive the development of PEMFC for automotive applications. In 1990, the California Air Resources Board (CARB) introduced the Zero Emission Vehicle (ZEV) Mandate. This was the first vehicle emissions standard in the world predicated not on improvements to the internal combustion engine (ICE) but on the use of alternative power trains. Carmakers such as the then-DaimlerChrysler, General Motors, and Toyota, all of which had substantial sales in the US, responded to this by investing in PEMFC research. Companies other than automakers, such as Ballard, continued PEMFC research for automotive and stationary clean power. Ballard went on to supply PEMFC units to Daimler and Ford. The programs initiated in the 1990s still continue, albeit with some changes to the strategic focus of some key players.

Significant advances in DMFC technology occurred around the same time, as PEMFC technology was adapted for direct methanol portable devices. Early applications included portable soldier-borne power and power for devices such as laptops and mobile phones. MCFC technology, first developed in the 1950s, made substantial commercial advances in the 1990s, in particular for large stationary applications in which it was sold by companies such as Fuel Cell Energy and MTU. SOFC technology also underwent substantial developments in terms of power density and durability for stationary applications. Boosted by general optimism in high-technology industries, many fuel cell companies listed on stock exchanges in the late 1990s, only for prices to fall victim to the crash in technology stocks shortly after.

Fuel cells began to become commercial in a variety of applications in 2007, when they started to be sold to end-users with written warranties and service capability, and met the codes and standards of the markets in which they were sold. As such, a number of market segments became demand driven, rather than being characterized by oversupply and overcapacity. In particular, thousands of PEMFC and DMFC auxiliary power units (APU) were commercialized in leisure applications, such as boats and campervans, with similarly large numbers of micro fuel cell units being sold in the portable sector in toys and educational kits. Demand from the military also saw hundreds of DMFC and PEMFC portable power units put into service for infantry soldiers, where they provided power to communications and surveillance equipment and reduced the burden on the dismounted solider of carrying heavy battery packs.

A large-scale residential CHP program in Japan helped stimulate commercial stationary PEMFC shipments. These units began to be installed in homes from 2009, and more than 13,000 such units have been installed to date. Demonstration programs for backup power systems in the USA gave further impetus to the stationary sector. This was also driven by practical concerns over the need for reliable backup power for telecoms networks during emergencies and rescue operations. The inadequacy of diesel generators was illustrated during the Gulf of Mexico Hurricane Katrina disaster, when many ran out of fuel, disrupting the telecoms network and hampering relief efforts. The need for reliable on-grid or off-grid stationary power in developing countries also gave a boost to fuel cells. In the late 2000s, hydrogen and natural gas fuelled PEMFC units began to be sold in parts of India and east Africa to provide primary or backup power to mobile phone masts. The rapidity of mobile phone adoption in these regions means that the conventional grid infrastructure cannot keep pace with new power demands, or is too unreliable for an effective mobile network. Fuel cells provide a solution to this previously unmet need.

In transport applications, the greatest commercial activity occurred in the materials handling segment, where there is a strong business case for their use in place of the incumbent technology, lead acid batteries. Funding for demonstration fleets of fuel cell materials handling vehicles saw increasing numbers deployed in warehouses across the USA, although the overall numbers remained small compared with those for stationary and portable fuel cells. Fuel cell buses have been commercially available for several years and their usefulness has been well demonstrated. However their cost, at around five times that of a diesel bus, plus the cost of hydrogen infrastructure means that they are only used where a city deems the environmental benefit to be worth the extra investment. Fuel cell cars are currently only available for

lease; these vehicles are being made available by manufacturers to gain experience ahead of a commercial launch planned from 2015.

Over the last five years growth in shipments of fuel cells has accelerated rapidly as various applications have become commercial. Portable fuel cells saw the most rapid rate of growth over the period since 2009 as increasing numbers of fuel cell educational kits were sold to consumers. This genuine commercial market generated much-needed revenue for several key players and has allowed those companies to invest in research into larger stationary and transport applications. The portable sector has also been boosted by shipments of APU products for the leisure market, in particular camping and boating. Shipments in the portable sector were also augmented by the launch of Toshiba's Dynario fuel cell battery charger in 2009. On a limited production run of 3,000, demand for the Dynario far outstripped supply. Stationary fuel cell adoption has increased rapidly as the roll-out of the Japanese Ene-Farm project took place and fuel cells for uninterruptible power supplies (UPS) were adopted in North America.

The fuel cell industry has faced and continues to face challenges as it comes through a period of recession and completes the transition from R&D to commercialization. On the whole, it has survived extremely difficult circumstances. Although many fuel cell companies are still far from being profitable, the opportunities for growth in the future are very promising. The success of certain application segments in recent years means that there has been a move to consolidate particular technologies into a standard reference design for a particular type of fuel cell. This has led to fue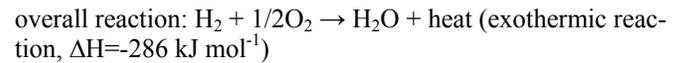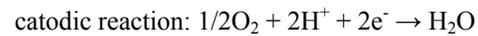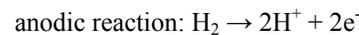l cells increasingly being developed as scalable energy solutions capable of serving several different market segments, be they APU or to power devices such as unmanned aerial vehicles (UAV).

1.1. The Base Structure of Fuel Cells

A fuel cell is an electrochemical device which converts the chemical energy of a fuel and an oxidant directly into electrical energy. The basic physical structure of a single cell consists of an electrolyte layer in contact with a porous anode and cathode on either side.

In a typical fuel cell, gaseous fuels are fed continuously to the anode (negative electrode) and an oxidant (i.e., oxygen from air) is fed continuously to the cathode (positive electrode) compartment; the electrochemical reactions take place at the electrodes to produce an electric current (Fig. **1**).

In the case of a fuel cell with an acid electrolyte the electrochemical reactions are:

anodic reaction: $H_2 \rightarrow 2H^+ + 2e^-$

catodic reaction: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

overall reaction: $H_2 + 1/2O_2 \rightarrow H_2O$ + heat (exothermic reaction, $\Delta H = -286 \text{ kJ mol}^{-1}$)

A fuel cell, although having components and characteristics similar to those of a typical battery, differs in several respects. The battery is an energy storage device and the available energy is determined by the chemical reactant stored within the battery itself. The battery will cease to produce electrical energy when the chemical reactants are consumed (i.e., battery discharged). In a secondary battery (fuel cell), the reactants are continuously supplied from an exter-
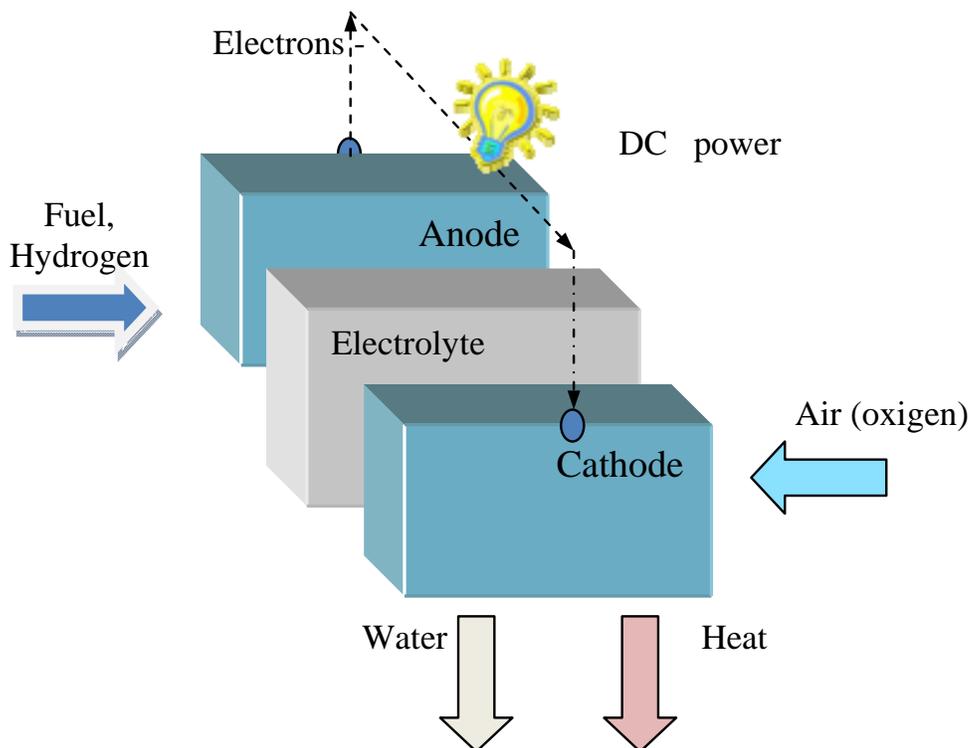

Fig. (1). Fuel Cells Concept.

nal source.

The fuel cell, on the other hand, is an energy conversion device that theoretically has the capability of producing electrical energy for as long as the fuel and oxidant are supplied to the electrodes.

Degradation, primarily corrosion, or malfunction of components are the limits to the practical operating life of fuel cells [4].

1.2. The Advantages and Disadvantages of Fuel Cells

If compared with conventional fossil fuel propelled electric generators, the use of fuel cells brings about many advantages [1]:

- Higher volumetric and gravimetric efficiency
- Low chemical, acoustic, and thermal emissions
- Modularity and siting flexibility
- Low maintenance
- Fuel flexibility (depending on type of fuel cell)
- No production of pollutants

1.2.1. Higher Efficiency

The higher efficiency of fuel cells is a consequence of the direct (chemical) production of electric energy from the fuel used. As a consequence the technology is not affected by the limitations derived from the Carnot thermic cycle which burdens all the combustion based electric generation systems.

1.2.2. Low Chemical, Acoustic, and Thermal Emissions

Due to higher efficiencies and lower fuel oxidation temperatures, fuel cells emit less carbon dioxide and nitrogen oxides for kilowatt of power generated. Another characteristic is that since fuel cells have no moving parts (except for the ancillary pumps, blowers, and transformers), noise and vibration are negligible.

1.2.3. Modularity and Siting Flexibility

A single fuel cell will produce less than one volt of electrical potential. To produce higher voltages, fuel cells are stacked on top of each other and connected in series. Cell stacks consist of repeating fuel cell units, each comprised of an anode, cathode, electrolyte and a bipolar separator plate. The number of cells in a stack depends on the desired power output and individual cell performance. The stacks have sizes which ranges from a few hundreds of W to several hundred of kW (up to some MW).

1.2.4. Low Maintenance

Due to the high modularity of generator systems it is relatively easy, for same type of fuel cells, to localize and substitute a damaged or malfunctioning cell contained inside a stack. This characteristic obviously leads to lower maintenance costs.

1.2.5. Fuel Flexibility

Hydrogen is the most used fuel (especially for the low temperature technologies of fuel cells which requires pure

gasses to operate); however fuel flexibility has been demonstrated in many technologies using natural gas, propane, landfill gas, anaerobic digester gas, military logistic fuels, and coal gas. This flexibility depends for the most on the operative temperature range of the type of fuel cells used (in principle, the higher the temperature the less pure the gas that the fuel cell can use).

Even if they are able to provide many important advantages, all the fuel cells technologies are still in a development phase and are burdened by many problems which makes their use less convenient than the other technologies which are already in use.

The problems are the following:

- Fuel cells costs for stationary electric generation (€/Wh) are still too high and unsuitable for the substitution of the technologies based on fossil fuels.
- The life cycle and the degradation time of many technologies of fuel cells (especially the high temperature technologies which are the best for electric power generation) is still not totally known.
- Hydrogen, which is one the main fuel for fuel cell technologies, is expensive and it does not still exist a network for his production and distribution.
- The use of low temperature fuel cells in the car market is limited by the fact that it is difficult to confine a suitable quantity of hydrogen in small fuel containers and by the fact that hydrogen is a flammable and potentially explosive gas (especially if compressed in small containers).

These are the reasons which prevents fuel cells to substitute many others technologies with lower efficiency and a much higher environmental impact.

The result is that an high effort in research and development is still needed to render this technology approachable, especially regarding the reduction of energy production costs [5-7] the use of new materials [8,9] and the improvement of conductivity mechanism in the electrolytes [10], also because the development of new materials remain in progress [11].

1.3. Fuel Cells Technologies

Actually there are many technologies of fuel cells available on the market, and each one of those is characterized by: the operative temperature range, the type of fuels which can be used, the type of catalyst used by the cell and the efficiency ratio of the energy conversion.

The main technologies available on the market are the following (Table **1**):

- Polymeric Electrolyte Membrane Fuel Cells (PEMFC):
- Direct Methanol Fuel Cells (DMFC)
- Alkaline Fuel Cells (AFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Molten Carbonate Fuel Cell (MCFC)
- Solid Oxide Fuel Cell (SOFC)

Table 1.   The Different Fuel Cells that have been Realized and are Currently in Use and Development

	AFC\nAlkaline	PEMFC\nPolymer Electrolyte Membrane	DMFC\nDirect Methanol	PAFC\nPhosphoric Acid	MCFC\nMolten Carbonate	SOFC\nSolid Oxide
Operating temp.($^\bullet$C)	<100	60-120	60-120	160-220	600-800	800-1000\nLow temperature (500-600) possible
Electrolyte	KOH	Perfluoro sulfonic acid (Nafion membrane)	Perfluoro sulfonic acid (Nafion membrane)	H_3PO_4 immobilized in SiC matrix	Li_2CO_3-K_2CO_3 eutectic mixture immobilized in γ-$LiAlO_2$	YSZ (yttria stabilized zirconia)
Charge carrier in the electrolyte	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}
Anode reaction	$H_2 + 2OH^- \rightarrow$ $2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ +$ $2e^-$	$CH_3OH + H_2O$ $\rightarrow$ $CO_2 + 6H^+ + 6e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow$ $H_2O + CO_2 + 2e^-$	$H^2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode reaction	$\frac{1}{2}O_2 + H_2O +$ $2e^- \rightarrow 2OH^-$	$\frac{1}{2}O_2 + 2H^+ +$ $2e^- \rightarrow H_2O$	$3/2\ O_2 + 6H^+ +$ $6e^- \rightarrow 3H_2O$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow$ CO_3^{2-}	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$
Electrode materials	Anode: Ni\nCathode : Ag	Anode: Pt, PtRu\nCathode: Pt	Anode: Pt, PtRu\nCathode: Pt	Anode: Pt, PtRu\nCathode: Pt	Anode: Ni-5Cr\nCathode: NiO(Li)	Anode: Ni-YSZ\nCathode: lanthanum strontium manganite (LSM)
Applications	Transportation Space, Military Energy storage systems			Combined heat and power for decentralized stationary power systems	Combined heat and power for stationary decentralized systems and for transportation(trains, boats, …)	
Realised Power	Small plants 5-150 kW modular	Small plants 5-250 kW modular	Small plants <5 kW	Small-medium sized plants 50 kW-11 MW	Small power plants 100 kW-2 MW	Small power plants 100-250 kW
Main producers	AFC Energy (UK)\nUTC Power (USA)\nActa Power (Italy)	Ballard (Canada)\nHeliocentris (Germany)	SFC Energy (Germany)	UTC Power (USA)\nFuji Electric (Japan)	Fuel Cell Energy (USA)	Ceramic Fuel Cells Limited (Australia)\nHexis & Vaillant (Germany)\nSOFC Power (Italy)\nBloom Energy (USA)
Lifetime*	Not available	2,000-3,000 h	1,000 h	>50,000 h	7,000-8,000 h	1,000 h

*Estimated values from literature data.

Some of these technologies are used for: static or distributed electrical generation, vehicle propulsion, mobile electric generation while others are simply used as auxiliary power generators.

The main aim of the following chapters of this paper will be the analysis of the of each one of those technologies listed before in regards of the structure of the fuel cell, the advantages and disadvantages of the technology and the actual applications of that technology in the fuel cells market [6].

2. POLYMERIC ELECTROLYTE MEMBRANE FUEL CELLS (PEMFCS)

Polymer electrolyte fuel cells (PEMFCs) are environmental friendly and efficient energy conversion devices that are expected to play a dominant role in future energy solutions.

They obtain the conversion of the chemical energy of a fuel into electricity by the hydrogen oxidation reaction and oxygen reduction reaction over a proper catalyst; the only side products of this process are water and heat.

PEMFC operates at temperature between 70 °C and 100 °C with a polymer electrolyte membrane, separating the fuel (hydrogen) from the oxidant (air or oxygen), which is a material that allows hydrogen ions to move through the membrane layer.

The low operating temperature allows them to be started quickly (low warm-up time) and results in less wear on system components thus increasing the cell durability. However a noble-metal catalyst (typically platinum) is required in order to start the electrochemical process at low temperatures.

This fuel cell is fed with hydrogen, which is oxidized at the anode, and oxygen that is reduced at the cathode. The protons released during the oxidation of hydrogen are conducted through the proton exchange membrane to the cathode. Since the membrane is not electronically conductive, the electrons released from the hydrogen travel along the electrical external load, provided thus generating an electrical current.

This technology has drawn the most attention because of its simplicity, viability, quick start-up (due to the low operative temperature), and it has been demonstrated like a valid solution for the generation of static and mobile electrical power.

The PEMFC has been even proposed as a power source for zero emission vehicles. PEMFC systems are particularly well suited for vehicle applications since they do not require the use of hazardous fluids, and they enjoy high power densities and low operating temperatures. However, cold start issues should be improved for a successful vehicle application of PEM fuel cells.

2.1. PEMFC Structure

The PEMFC, like all fuel cells, consists of three basic parts (see Figs. **2** and **3**); the anode, the cathode, and the membrane. These three areas are often manufactured from separate sheets, and the PEM is no exception.
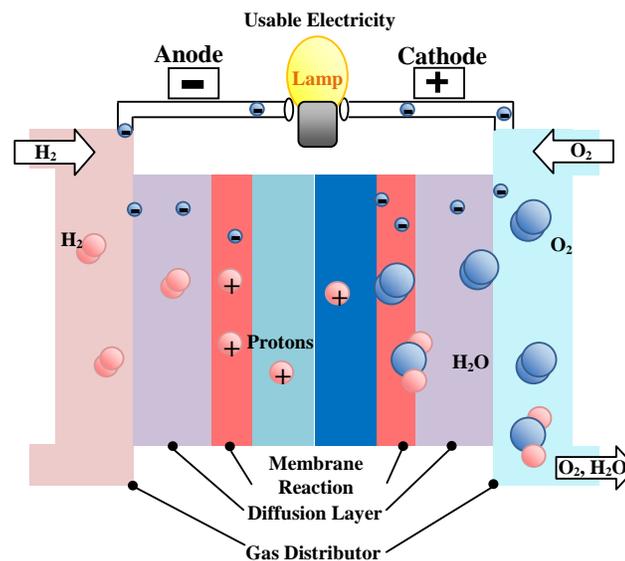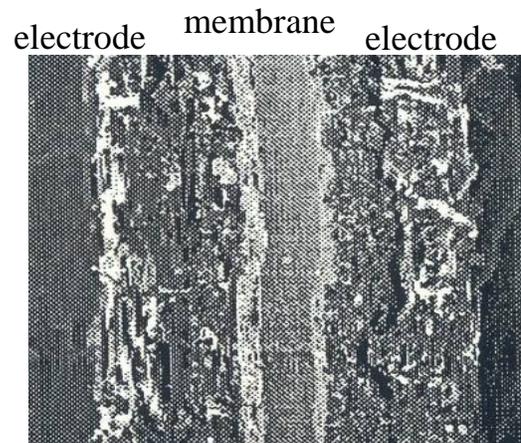

Fig. (3). MEA structure.

The electrodes and the electrolyte layer are then joined together, by hot pressing process, in order to create a "membrane electrode assembly" (MEA) [1, 4, 12].

The MEA is composed by a proton exchange membrane, two catalyst layers, and two gas diffusion layers (GDL). Typically, these components are individually fabricated and then pressed to together at moderate temperatures and pressures.

2.1.1. The Membrane

Although many different types of membranes are used, by far that most common is Nafion (DuPont), a sulphonated polymer with a PFTE backbone [13]. The Nafion is created through the addition of sulfonic acid groups into the bulk of a polymer matrix of Teflon and its layer has a thickness between 50 and 175 μm. The thinner Nafion membrane allows a higher conductivity of the cell, but introduces a more problematic water management; a thicker membrane slows down the conductivity.

Fig. (2). PEMFC structure.

The function of this structure is to act as an electrolyte (ionic conduction) and a separator between oxygen and hydrogen.

Other types of membranes that being researched are: polymer-zeolite nanocomposite proton exchange membrane [14], sulfonated polyphosphazene based membranes [15] and phosphoric acid-doped poly (bisbenzoxazole) high temperature ion-conducting membrane [16].

However the Nafion membrane is so commonly used (due to his high chemical stability) that it is considered an industry standard, and all new membranes are compared to it.

The main characteristics of the membrane are:

- high water uptake;

- good proton (H^+) conductor if well hydrated, but doesn't allow the conduction of electrons which are constricted to follow an external path thus generating an electrical current;

- does not allow the intermixing of the hydrogen and oxygen thus maintaining the two gas separated;

- high chemical and mechanical resistance due to the properties of Teflon backbone.

2.1.2. The Catalyst Layer

The catalyst layer is in direct contact with the membrane and the gas diffusion layer. It is also referred to as the active layer. In both the anode and cathode, the catalyst layer is the location of the half-cell reaction in a PEM fuel cell. The catalyst layer is either applied to the membrane or to the gas diffusion layer. In either case, the objective of the catalyst layer is to place catalyst nanoparticles (generally 5-15 nm platinum or platinum alloys, such as Pt_xRu_y) within close proximity of the membrane [17]. The aim is to generate a gas/solid/membrane triple contact to allow to take place the electrochemical reactions.

2.1.3. The Gas Diffusion Layer

The porous gas diffusion layer in PEM fuel cells ensures that reactants effectively diffuse to the catalyst layer. In addition, the gas diffusion layer is the electrical conductor that transports electrons to and from the catalyst layer.

The functions of the backing layer are to: (1) act as a gas diffuser; (2) provide mechanical support, (3) provide an electrical pathway for electrons, and (4) channel product water away from the electrodes.

Typically, gas diffusion layers are constructed from porous carbon paper, or carbon cloth, with a thickness in the range of 100–300 μm, coated with a layer of microporous carbon powder/PTFE. The function of polytetrafluoroethylene is to prevent water from "pooling" within the pore volume of the backing layer so that gases freely contact the catalyst sites. Furthermore, it facilitates product water removal on the cathode as it creates a non-wetting surface within the passages of the backing material.

The gas diffusion layer also assists in water management by allowing an appropriate amount of water to reach and be held at the membrane for hydration.

In addition, gas diffusion layers are typically wet-proofed with a PTFE (Teflon) dispersion coating to ensure that the pores of the layer do not become congested with liquid water [17].

Those parts and their characteristics permits the general fuel cell process. Hydrogen at the anode separates into electrons and protons. The membrane allows the passage of only protons so the electron externally travels thus generating an electrical current. Meanwhile protons travel through the ionic conductive membrane to the cathode. The H^+ protons then reach the cathode where they generate water through their combination with oxygen.

Since high temperatures are not necessary to hydrate the membrane, the PEM can be run at very low temperatures, typically at 80 °C or lower.

A typical fuel cell provides a voltage between 0.6 and 0.7 V @ 0.5 A/cm^2 so, in order to provide greater voltage and power, a great number of cells is placed in series creating a structure called cell stack.

Inside a cell stack each MEA assembled is placed between two bipolar plates with the exception of the first and the last cell (Fig. **4**).
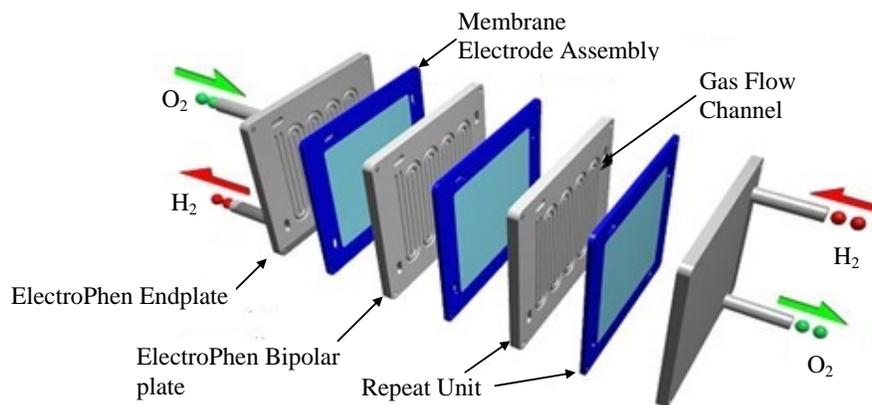

Fig. (4). PEMFC Cell Stack.

Many different materials can be used for the realization of a traditional bipolar plate however some requirements must always be guaranteed:

- functionality of the electrical connection between two consecutive cells;

- a constant and homogeneous supply of hydrogen and oxygen to the electrodes of the different cells;

- an efficient thermal dissipation;

- the removal of the water produced by the reactions.

2.2. PEMFC Advantages and Disadvantages

Advantages of the PEMFC are as follows [18]:

- The power density of the cell stack is very high, particularly in pressurized systems.

- The operative pressure difference between the anode and the cathode can be very large due to the mechanical properties of the solid polymer electrolyte. Therefore, operating with a pressurized system it is quite easy.

- A wide variety of cell component materials can be adopted on account of its low operating temperature (80 °C). In particular, use of low cost carbon materials may contribute to the cost reduction of cell stack.

On the other hand, the PEMFC technology shows the disadvantages listed below [18]:

- PEMFC catalysts are susceptible to CO poisoning due to their low operating temperature. Therefore, the CO concentration has to be reduced below 10 ppm with CO removal if the reformate from hydrocarbons or alcohols is used as a fuel for the PEMFC.

- The temperature of recovered waste heat is lower than that of other fuel cells. As a result recovered heat can be utilized only as hot water.

- The water management of the membrane electrolyte is very important for the cell performance, because it secures the appropriate amount of water to show its sufficient ionic conductivity.

On account of these features, PEMFC development for electric vehicle and portable power applications still needs more time. The PEMFC technology is also promising for residential cogeneration systems if combined with small-scale natural gas fuel processors.

2.3. PEMFC Applications

PEM Fuel cells can generate power from some W to hundreds of kW. Because of this, they may be used in almost every application where local electricity generation is needed. PEMFC are already being tested inside applications such as automobiles, buses, utility vehicles, scooters, bicycles, aerospace/military applications (e.g. Shuttle and submarines). PEMFC are also being tested for distributed power generation inside individual homes, buildings or communities due to their modularity and excellent flexibility in power supply [19, 20].

PEMFC fuel cell used for different applications have at the same time different configurations whose characteristics change in order to achieve the requirements needed by the different environments in which they are involved.

This document will now analyze the three most important application environments for PEM fuel cells which are the followings:

- Transportation (up to 70 kW);

- stationary power applications (up to 500 kW);

- portable power applications (up to some kW).

2.3.1. Applications for Transportation and Automotive Sector

Transportation is a competitive and promising sector for PEMFC fuel cells due to two factors:

- the future expected deplete of fossil fuels;

- the possibility to guarantee environment friendly vehicles.

The development of a Fuel Cell Vehicle (FCV) requires the on-board integration of a fuel-cell system and electric energy storage devices with an appropriate energy management system.

Actually most of the major car makers and the governments of some states (like USA and JAPAN) are actively engaged in the development of FCVs [19]. However the most important factor for the success of a FCV is the success of the hydrogen economy and its related technology.

It is a fact that FCV systems equipped with direct-conversion fuel processors (which is the most secure FCV technology since it does not imply the storage of hydrogen that can easily cause an explosion) can successfully compete with conventional Internal Combustion Engine (ICE) vehicles in all aspects except for the cost and maintenance [19].

However direct conversion fuel processors are hybrid systems (which converts fuels into hydrogen and then into energy with fuel cells) that requires great spaces inside vehicles and a complex feedback control system. The consequence is that actually they are integrated only inside bigger vehicles like buses which have more space to house the fuel processor.

The main requirements that the automotive PEM stack technology still needs to fulfill in order to became a major technology on the market are:

- a very short start-up time (fraction of a minute);

- small size and weight of the PEMFC systems;

- an operating life time which spans from 3000 to 5000 operational hours.

2.3.2. Stationary Applications for Distributed Power Generation

Distributed power generation is another sector in which PEMFC developments holds great interest.

The high modularity, high efficiency and lower emission of PEMFC stacks allow their use for the expansion of the electric network. As a result part of the loads of the network can be directly managed by many power systems which are

distributed inside different types of buildings and structures, thus lowering the burden placed on the power plants.

Stationary fuel cells for distributed generation could be used inside in many different places [20]:

- as the main power source in places not reached by the electric power grid;

- as supplemental power source working in parallel with the electric grid;

- as complementary power source in power systems based on renewable energy like photovoltaic and wind turbines (thus generating power when these energy sources cannot meet the demand);

- as emergency power generators to cover the malfunctions of the electric grid;

The requirements that these systems have to fulfill are:

- a lower noise level since the power unit are usually installed indoor;

- short start-up time for emergency power systems;

- power units designed for outdoor use must be able to operate in extreme ambient conditions;

- an operational life cycle which spans from 40,000 to 80,000 hours (five to ten years).

2.3.3. Applications for Portable Power Systems

Portable power systems based upon PEMFC technology consists in 2 main types of applications [20]:

- power cells for battery replacements with power below 100 W;

- portable generators with at least 1 kW power based on power cells;

The main factors that must be considered in those systems are:

- The operative time of the battery;

- The size and weight of the system.

Power units with significantly higher power densities or larger energy storage capacities are suited for applications like portable computers, communication and transmission devices, power tools, remote meteorological or other observation systems.

PEMFC detains many advantages like fast startup, simplicity of operation, zero emissions, and potential for low capital and maintenance costs that have attracted many interest regarding DG (Distributed Generation) applications [21].

There is however one major problem in the use of this types of fuel cells for the those applications: the need to refuel them with hydrogen.

Due to its characteristics, hydrogen is a gas that has both a low ration of energy per volume of gas stored (thus requiring large storage spaces) and an high penetration in solid materials which means that the gas escapes on the storage device on normal conditions.

In order to minimize storage spaces and to ensure that it remains inside the storage device, the hydrogen have to be highly pressurized. However pressurization is a process that requires energy and that increases the magnitude of an eventual explosion.

Another problem which prevents portable PEMFC to be used inside military environments is that the cells are easily detectable by enemy sensors.

2.3.4. Considerations

PEM fuel cells have actually reached a partial commercialization phase due to many different initiatives being issued all over the world (USA, Japan, Europe) by the bigger car constructors and the governments. Those initiative mainly focus on further development of the cells at many demonstrative applications which are at the same time used to deepen the knowledge on the life cycle of PEMFC.

Although each applications of the PEMFC has its own issues there two main problems shared between all applications: the need to provide a stable supply of pure hydrogen and to reduce the actual costs for the production of the cells.

Regarding the realization of an hydrogen distribution network there are three issues that actually prevents that from becoming a reality. The first issue is the difficulty to realize an highly efficient storage of hydrogen for long time periods. Adding to this we must count the actual lack for a detailed normative which has to provide functional and security standards for the development of such devices.

The second issue regards the use of platinum as catalyst. The minimum Pt load in the electrodes 0.2 mg$_{Pt}$ cm^{-2}. Even though the value is low, this still raises the cost of the fuel cell production, while at the same time, the performance is reduced compared to electrodes with higher Pt content. Decreasing the amount of Pt has been one of the major concerns during the past decade; one of the effort has focused on the increase of utilization efficiency of the catalyst. To fully exploit the catalyst, all the Pt nanoparticles must have simultaneous access to the gas, the electron-conducting medium, and the proton conducting medium. In the catalyst layer prepared by the conventional ink-process, this condition is achieved via a suitable blending of Pt-supporting carbon particles and Nafion. However, there is still a significant portion of Pt that is isolated from the external circuit, resulting in a low utilization. Even with the most advanced conventional electrodes, Pt utilization in commercial prototype fuel cells remains very low (20–30%). Nanomaterials can hold new perspectives in solving the above mentioned problems, especially in the effort to increase the catalytic activity of the system. Nanostructured materials are intrinsically materials with very high specific surface, which is a basic requirement for enhanced catalytic activity.

The third issue regards the actual high costs for the production of hydrogen. There are many different studies and ideas regarding methods (most of all concerning electrolysis) to produce hydrogen, however no one has still found a way to produce hydrogen with fossil fuels comparable costs.

Actually the costs for PEMFC ranges between 3,000-5,000 €/kW against those of 300 – 500 €/kW of fossil fuels and about 80% of those comes from the cost of the bipolar plates, the electrodes, the membranes, the catalyst used (usually platinum) and hydrogen production [22].

These costs are far too high to allow the technology to be competitive with those based upon fossil fuels.

In conclusion further development focused on the reduction of the cell costs (like finding new catalysts and building materials) is still needed for a mass introduction of PEMFC on the market.

The water electrolysis is the best way to produce high purity hydrogen without using fossil fuels. Unfortunately, the electrolysis requires high energy consumption of electrical power. Therefore, the only way to efficiently produce H_2 by this technology is to use the off-peak electrical power obtained by nuclear or hydroelectric plants.

3. DIRECT METHANOL FUEL CELLS (DMFCS)

DMFCs are another technology of fuel cells, based upon a polymer electrolytes membrane (PEM) which operates at temperatures between 70 and 100 °C.

The differences between DMFC and PEMFC resides in the fuel used, which in this case is constituted by liquid methanol dissolved in water. As the PEMFC, the DMFC are considered an environmental friendly technology since there is no production of sulfur or nitrogen oxides (only carbon dioxide).

The main advantage of DMFC resides in the fuel used, since methanol is a cheap and easy to produce fuel which can be directly injected and used inside the cell itself thus allowing a simple cell structure and consequently lower weights.

3.1. DMFC Structure

The core of a Direct Methanol Fuel Cell is the polymer electrolyte ion exchange membrane. As the PEMFC the state of the art in membranes is Nafion. This polymer has sites with strong ionic properties acting as proton exchange sites [1, 4].

The membrane faces are in direct contact with the anode and the cathode which both consists in a three layer structure made by: a catalytic layer, a diffusion layer and a backing layer (Fig. **5**).

The catalytic layer is composed by a mixture of a catalyst, which is usually a combination of platinum (at the cathode) and platinum-ruthenium alloy (at the anode) nano-particles and a ionomer. As the membrane the ionomer is composed by a perfluorosulfonic acid polymer. The main characteristic of the catalytic layer is its mixed conductivity for both protons and electrons.

The diffusion layer is composed by a mixture of carbon and Teflon with hydrophobic properties which allows both the transportation of oxygen molecules to the catalyst layer of the cathode and the escape of CO_2 molecules from the anode.

The combination of the membrane and the electrodes gives life to the MEA assembly which thickness is usually around 1 millimeter [23-25].

When the cell is activated a liquid flux of methanol is injected into the anode from where it is diffused inside the diffusion layer. The methanol reaches the catalytic layer where it is oxidized into carbon dioxide, protons and electrons. At this point the protons diffuse trough the Nafion membrane and electrons trough the catalytic layer but, while the electrons are collected by the cathode thus generating an electrical current, the protons that diffuses through the membrane react at the cathode with oxygen to produce water.

3.2. DMFC Characteristics and Applications

Due to the capacity of injecting the fuel directly into the cell, the air breathing and their low operative temperature, the DMFC are the smallest fuel cell actually on development. In addition due to the same characteristics deriving from their structure the DMFC are a quite noiseless and environment friendly technology [23].

Another main point of these cells is that they work on methanol which is much more easy to store and to produce than hydrogen, without the hazard of explosions as in the case of the hydrogen.

Thanks to the small dimensions, the low temperature operative range and the high usability of the fuel, DM fuel cells are actually a well seen technology for portable applications and generators.
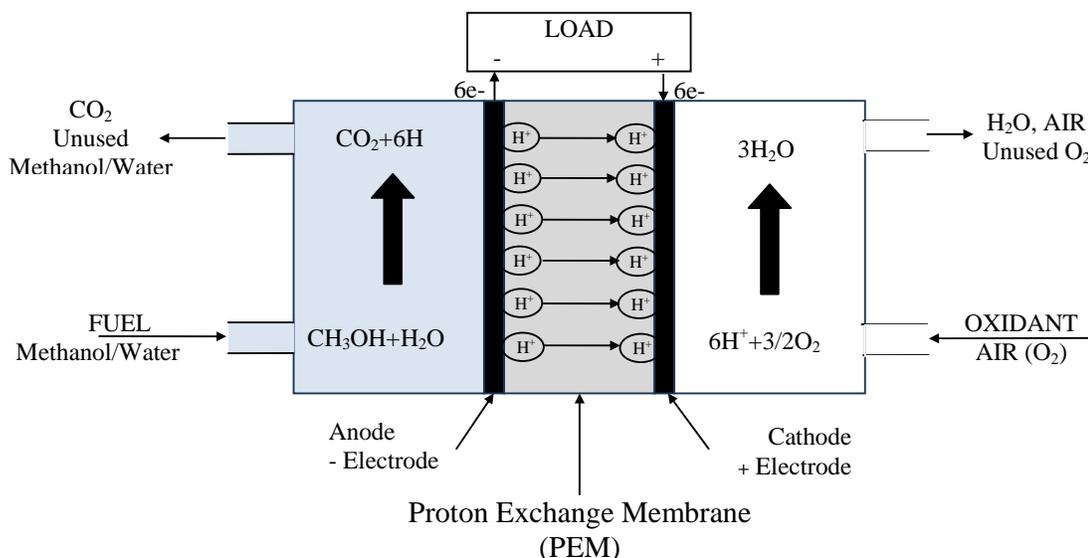
Fig. (5). DMFC structure.

The drawback of the technology is that DMFC actually detain an efficiency around 35% which is the lowest among all the fuel cells.

Actually DMFC have two main applications on the market [22]:

- portable power generation;
- low weight substitute of the batteries for both civil and military environments.

Still, due to the low efficiency, the power density that the DMFC are able to provide, which is around 200-400 mW/cm^2, is still too low. As a consequence DMFC can't at the moment meet the energy production requirements for many of their actual portable applications.

In conclusion DMFC are an under development technology, yet recently the raising interest for small power portable applications has significantly and consistently raised the development efforts regarding this technology. These efforts focus on the resolution of the following problems:

- the increase of the low reactivity of methanol through the development of new catalysts;
- the development of new membranes to avoid methanol cross-over and capable of working with higher temperatures thus increasing the cell operative temperature range (which directly affects the efficiency);
- the optimization of the electrodes and the MEA assembly.

However the performances of the DMFC prototypes realized for military and consumer electronics are still too low to guarantee a proper commercialization of the technology.

The constructors involved in this environment are Mesoscopic Devices, MTI MicroFuel Cells, Neah Power Systems and Ultracell inside USA, Smart Fuel Cells in Europe, Hitachi, Motorola Labs, NEC, Sanyo Electric and Toshiba inside Japan and, at last, Samsung Advanced Institute of Technology in Korea [22].

4. ALKALINE FUEL CELLS (AFCS)

The Alkaline Fuel Cells were the first type of fuel cells used inside power generators. As many more technologies the AFC were developed by the space sector due to their wide operative temperature ranges; at the time the aim was the development of a power source for the alimentation of space aircrafts.

There are many types of Alkaline fuel cells with different operative temperatures ranges while the technology allows for a general temperature between 30 °C and 250 °C (AFC for space applications can start up even at temperatures lower than zero). AFCs use liquid KOH (a solution of potassium hydroxide) as the electrolyte and are fueled by hydrogen. The oxidant must be pure oxygen, not air, due the carbonatation of the electrolyte by CO_2 contained in the air (300 ppm). Each cell generates a voltage between 0.5 V and 0.9 V depending on the design with an electrical efficiency that can be up to 65% [26].

4.1. Alkaline Fuel Cells Structure

The general structure of an AFC is composed by a porous anode and a porous cathode, usually made with a cheap catalyst as nickel or silver, separated by a liquid KOH solution as the electrolyte (Fig. **6**).

In the cell oxygen is feed to the cathode while the hydrogen is feed to the anode [27]. The electrolyte operates by transporting ions between the cathode and the anode thus generating an electrical current through an electrochemical reaction. A wide variety of materials (e.g., potassium titanate, ceria, asbestos, zirconium phosphate gel) have been used in the microporous separators for AFC's. Nowadays, the asbestos is not used due to its carcinogenicity.

There are however 3 different designs of Alkaline Fuel Cells that have to be accounted:

- Mobile electrolyte AFC's
- Static electrolyte AFC's
- Dissolved fuel AFC's

Mobile Electrolyte AFC's: this design sends pure hydrogen at the anode and air at the cathode while the electrolyte is pumped inside the cell by an external circuit. Since it tends to evaporate the water product, the hydrogen have to be done to circulate in order to extract the evaporated water solution with a condenser.

The bigger problem inside this design is the chemical reaction between the potassium hydroxide (KOH) and the carbon dioxide (CO_2) that is present in the air. This reaction is unfavorable because the efficiency of the fuel cell depends upon the purity of the potassium hydroxide solution.

In order to solve this problem a carbon dioxide scrubber (very expensive) is used to maintain the solution as pure as possible. This type of design is the one that was used inside the Apollo space shuttle [3], where the cost was not a problem [28].

Static electrolyte AFC'S: in this design, the potassium solution is held inside asbestos with a matrix structure which prevents the electrolyte to circulate.
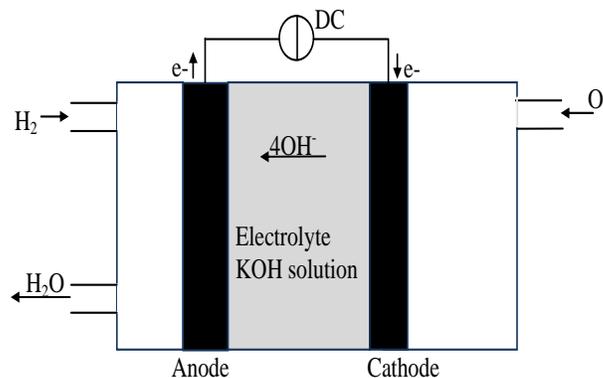

Fig. (6). AFC structure.

This AFC variant, in order to work, requires the injection of pure oxygen inside the cathode. As the other design the hydrogen is done to circulate in order to remove the gaseous water product while a cooling system works to keep the fuel cell within the required operational temperature range [3, 28].

Dissolved fuel AFC's: this is the simplest type of AFC regarding the realization. Inside this design, like in the others, potassium hydroxide is used but this time the electrolyte is combined with a fuel like hydrazine or ammonia. This type of AFC, which is not suitable for large power generators, have high problems regarding the fuel crossover but they can be ignored since the catalyst used is not platinum (thus greatly reducing the costs for the substitution of the catalyst)[28].

Another big problem is that the most suitable fuel for this cell is the hydrazine (due to the capacity to dissociate into hydrogen and nitrogen) which is a toxic, carcinogen and explosive fuel [3].

4.2. Alkaline Fuel Cell Characteristics and Applications

Summarizing up what have been said alkaline fuel cells can boast many advantages:

- wide operating temperature range;
- high simplicity of the cell structure;
- fast start up;
- competitive costs for the cell construction (due to the simplicity of the materials involved);
- capacity to reach an electrical efficiency of 65% (which is really high for cold fuel cells);
- a life cycle time between 10,000 and 15,000 hours due to the good compatibility of the materials in the cell (however life cycles of 40,000 hours are required in order to a full commercialization of a fuel cell technology).

As a result if compared with PEM fuel cells the AFCs are cheaper and more efficient. The reason which prevents the AFCs to become the dominant fuel cell technology on the market is the CO_2 poisoning of the electrolyte [29].

In fact due to the high reactivity of OH^- ions with carbon and its composites even the slightest quantity of CO_2 can greatly compromise the cell efficiency. This implies that the cell must be fueled with pure hydrogen and oxygen which is not a problem inside an environment like space but it becomes a great burden inside the earth atmosphere. As a matter of fact very expensive purification systems are required in order to guarantee the gases purity thus greatly increasing the effective cost of a power generator based on AFCs. The result is that the AFCs are still the main technology used inside the space environment as well as inside many applications regarding submarines, but they are not considered a suitable technology for static or mobile applications on earth.

If we don't take into consideration the space and defense sector up to today only a few power units between 1 and 10 kW have been realized. The constructors involved on those initiatives are Astris Energy and Apollo Energy Systems in USA and AFC energy, Hydro Cell OY and Vito in Europe [22].

5. PHOSPHORIC ACID FUEL CELL (PAFC)

While AFC where the first type of cell to be used inside power applications, the Phosphoric Acid Fuel Cells (PAFC) were the first type of cell to be commercialized. Firstly developed in the mid-1960s and field-tested since the 1970s, up to today these types of cells have been constantly improved in both stability, performance, and cost.

The electrolyte used inside PAFCs is phosphoric acid (H_3PO_4) that, due to its bad ionic conductivity, requires operative temperatures between 150 ºC and 220 ºC to properly work. As a result a PAFC cell is no more a quick start, low temperature fuel cell.

The fuel required for the cell is always hydrogen however due to the high temperature range of the cells pure hydrogen is not required. This allows the cell to be fueled with relatively impure hydrogen which can be easily derived from fuel reforming process.
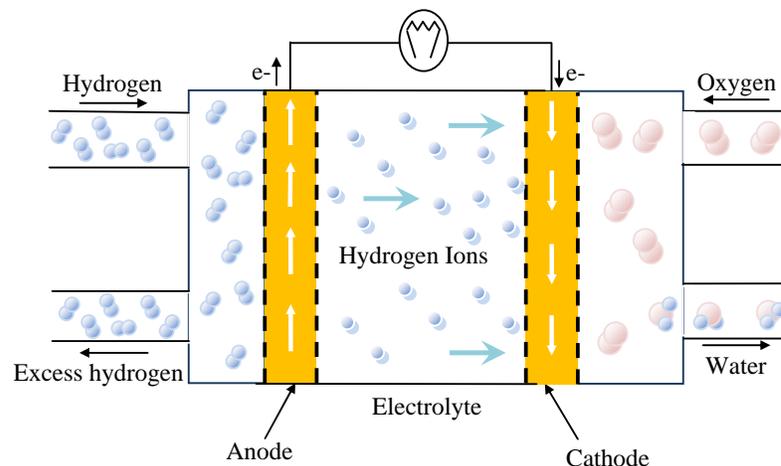

Fig. (7). PAFC structure.

The overall cell efficiency is between 37% and 42% however, if the heated water/steam generated by the cell is used inside a combined heath system, the total efficiency can go over 60%.

5.1. Phosphoric Acid Fuel Cell Structure

The basic cell structure Fig. (**7**) is made of a ceramic matrix impregnated with a solution of phosphoric acid which is surrounded by a couple of porous electrodes used to collect the ions and to diffuse the gasses [1, 12].

The ceramic matrix which contains the phosphoric acid is made of approximately 1 µm silicon carbide particles thus reaching a matrix thickness around 0.1÷0.2 mm. Thanks to this structure the matrix is thick enough to maintain the acid within the layer through capillary action and to avoid gasses cross-over from the anode to the cathode.

The gas diffusion electrodes are made using platinum nanocatalyst, supported on high surface carbon, dispersed inside a layer made of carbon bonded with polytetrafluoro-ethelyne (PTFE). This generates a porous structure with a well dispersed high conductive catalyst, which have the duty
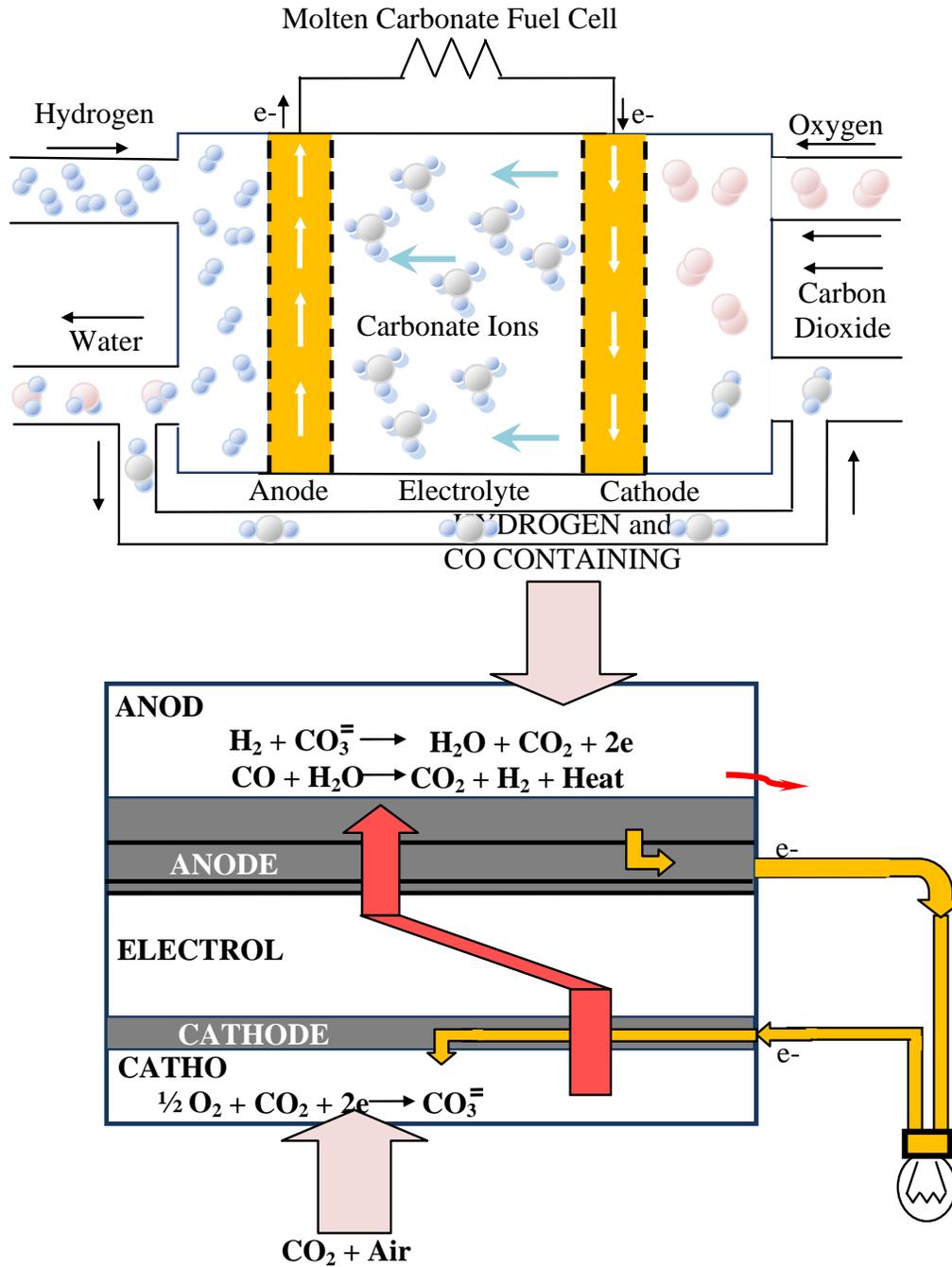

Fig. (8). MCFC structure.

to both efficiently disperse the reactant gasses up to the matrix layer interface and to collect the electrons.

The cell works by dissociating the hydrogen fueled to the anode into protons and electrons. The electrons are collected by the anode thus generating an electrical current. Meanwhile the protons diffuses in the phosphoric acid through the matrix layer until they reach the cathode where they recombine with the oxygen generating heated water [30].

The electrolyte used is phosphoric acid since it is the only inorganic acid with the thermal, chemical and electrochemical stability required in order to be actively used inside PA fuel cell.

Also since phosphoric acid requires high operative temperature ranges, and does not react with CO_2 to form carbonate ions, both carbon monoxide poisoning and the formation of carbonate are not an issue for PAFCs.

5.2. Phosphoric acid fuel cell characteristics and applications

PAFC technology above all the other fuel cell technologies is the one with the most extensive operational experience with more than 400 systems (mostly 100 kW to 400 kW power systems) installed worldwide (but the majority is installed inside the U.S. and Japan).

In Japan, over 150 PAFC plants ranging from 50 kW to 500 kW capacity have been developed and installed, together same plants 1-5 MW. The largest demonstration PAFC plant is also in Japan with 11 MW capacity that went into operation in 1991 in the Tokyo Electric Power Company system at the Goi Thermal station.

Thanks to the data derived from all those applications the PAFCs are the most reliable fuel technology on the market characterized by the qualities which are listed below [31] [32]:

- an operating life cycle which exceeds 65,000 hours with an operative temperature between 150 ºC and 220 ºC;

- an electric efficiency up to 40% which can be boosted up to 60% through the use of combined heath systems;

- partial immunity from carbon monoxide poisoning (it is immune only if there is not an high concentration of this element inside the gas);

- capability to use hydrogen fuels without high level of purity like reformed carbon fuels thus reducing the costs for power generation.

However PAFCs can't really be consider an high temperature fuel cell but more likely a technology between the low temperature fuel cells and the high temperature fuel cells.

The operative temperature of the PAFCs is in fact too low to be successfully used inside big stationary power generating applications (>5 MW) due to the following reasons:

- fuels with high levels of carbon monoxide like natural gasses and coal gasified gas can't be used without poisoning the platinum catalyst inside the cell;

- heated steam generated by PAFCs is too low in temperature to be used inside big combined heath systems.

Such characteristics have made the PAFC an ideal candidate for early small and medium stationary applications. However in order to began a massive commercialization of the technology there are still some objectives that must be reached [31, 32]:

- an operative life cycle of at least 80,000 hours;

- a cost for power generation below 1,200 €/kW.

The major constructors involved into the development of PAFC are up to today the UTC Power and Hydrogen in the USA, Fuji Electric Advanced Technology and Toshiba Internationals Fuel Cells in Japan [22].

6. MOLTEN CARBONATE FUEL CELLS (MCFC)

Molten carbonate fuel cells (MCFC) represent an high temperature technology of fuel cells which are currently being developed as a solution for static electrical power generation or to work with other static generation applications which are already on the market like coal based power plants or some industrial facilities.

MCFC are a technology of fuel cells which operates at temperatures up to 650 °C using a liquid solution of alkali carbonate salts as the electrolyte.

MCFC represent an high temperature fuel cell technology which can reach an efficiency of 45% that can be potentially raised up to 60% - 70% if the waste heat is correctly utilized.

Due to the high temperature, MCFCs can be fueled with gases like methane, natural gas or coal reformed gases. However due to the same high temperature they suffers from many problems such as fast degradation of the cell structure, due to mechanical/corrosion problems, and constant loss of the electrolyte, due to evaporation, inside the cell (which implies the need to refuel it continuously).

6.1. Molten Carbonate Fuel Cell Structure

The base structure of a MCFC is made with a ceramic matrix containing the electrolyte Fig. (**8**) which is surrounded by the anode, fueled by hydrogen rich fuel, and the cathode, fueled by oxygen (usually air).

There are actually two mixtures of molten carbonate salts (the high temperature is required in order to melt this mixture) that could be used as the electrolyte. The two mixtures can be a combination of lithium carbonate and potassium carbonate or lithium carbonate and sodium carbonate.

Those electrolytes are dispersed inside a porous and chemically inert ceramic matrix made with lithium aluminate ($LiAlO_2$). Inside this structure ceramic powder and fibers are used in order to reinforce the whole mechanical strength. Furthermore a special polymer is used to create many sheets with constant thickness which are then impregnated with the electrolyte to confine it.

Regarding the electrodes thanks to the high operating temperature, a relatively cheap catalyst like nickel can be used instead of the much expensive ones like platinum.

The metal material used for the construction of the anode and the cathode result exposed to both highly oxidizing and reducing environments. This implies that in order to be used those metal have to respect a certain array of strict requirements.

The anode is a porous electrode made with a nickel alloy (Ni-5Cr, Ni-xAl) as the catalyst. This alloys containis a small percent of aluminum or chromium in order to suppress the hot creep inside the electrode structure.

The cathode is realized with a porous nickel catalyst. During the cell start-up, the nickel in contact with the electrolyte (eutectic mixture of Li_2CO_3 and K_2CO_3) is converted to high conductive lithium doped nickel oxide ($Li_xNi_{1-x}O_2$).

The cell requires time in order to start since it needs to reach a temperature of 650 °C. Upon reaching this temperatures the carbonate salts begin to melt and becomes conductive by carbonate ions (CO_3^{2-}). These ions are transported from the cathode to the anode where they combine with hydrogen to produce water, carbon dioxide and electrons. These electrons are then collected by the anode and routed, through an external circuit, to the cathode thus generating electricity and heat [12, 33, 34].

A particular configuration of MCFCs do not need external reformers in order to convert fuels into hydrogen. In fact due to the high temperatures the fuels can be directly converted to hydrogen through a process called catalytic internal reforming which takes places in a pre-chamber inside the anode compartment. The main problem of this configuration is the coarseness of the reforming catalyst, which reduce the life-time of the system.

6.2. Molten Carbonate Fuel Cell Characteristics and Applications

MCFCs are currently being developed and demonstrated in several countries around the world like USA, Japan, Korea and Germany. The applications that are being demonstrated ranges, regarding the generated power, between 125 kW and 1 MW [35, 36].

The main advantages that the technology detain are summarized as follows:

- MCFCs efficiency goes up to 45% and, since high temperature and steam is generated, if they are used with combined cycles heath systems the efficiency of the MCFCs applications exceeds 50% – 60%;

- MCFCs can use a wide array of hydrogen rich fuel like natural gas or coal gasified gasses and, if the fuel reforming takes place inside the cell, the construction of an external reformer is not needed. These characteristics greatly reduce power generation costs;

- the possibility to use standard and low cost materials such as stainless steel and nickel based alloys greatly participate in the reduction of the cell construction costs.

However the high temperatures involved and the electrolytes chemistry are the cause of the following disadvantages:

- a low operative life cycle due to the corrosion caused by the electrolyte used, the loss of the electrolyte due to the

- high temperatures and the dissolution of the cathode inside the electrolyte matrix, with the possibility to short-circuit the cell;

- slow starting times determined by the need to reach an operative temperature of 650 °C;

- impossibility to re-start the cell stack after a shut-down.

Therefore although there are demonstration programs all around the world, there is still a large effort in terms of research and development which is being carried on by many organizations, industrial companies and universities. Those efforts are focused upon the improvement of the cell operative life cycle and the increase of the power density of the cell.

The main actors involved in this environment of research are FuelCell Energy (FCE, USA), CFC Solutions (Germany), Ishikawajima Harima Heavy Industries (IHI, Japan), POSCO/KEPCO consortium and Doosan Heavy Industries (Korea), GenCell Corportation (USA) [22].

7. SOLID OXIDE FUEL CELLS (SOFC)

Solid Oxide Fuel Cells (SOFC) are another technology of high temperature fuel cell which was developed for stationary power applications of all sizes. SOFC operative temperature ranges between 800 °C and 1000 °C. Thanks to the high temperatures a wide array of different fuels containing hydrogen (coal gas, bio gas, propane, natural gas, hydrogen) can be used since the fuel reforming takes place directly inside the cell.

SOFC detain a very good power efficiency, near 60%, a long term performance stability and an high thermal efficiency. It is due to the high quality waste heat that the steam generated can be used, when pressurized, with a gas turbine based combined heat system which is theoretically able to boosts the electrical efficiency up to 80%.

Another characteristic derived by the high temperatures is the possibility to start the electrochemical reaction by simply supplying air and without the help of noble metals used as catalysts. This greatly reduces the costs sustained for the construction of the fuel cell.

As a result these type of fuel cell has been the object of intensive efforts in research and development on a worldwide basis.

However the high temperature drawback is that heat control inside this type of fuel cell becomes really difficult. The result is that these cells can hardly be integrated on portable systems for electric generation.

7.1. Solid Oxide Fuel Cells Structure

Two types of Solid Oxide Fuel Cells actually exists: the oxygen ion conducting type and the hydrogen ion conducting type. However since up to today no chemically stable electrolytes where found for the hydrogen ion type, R&D around the world have principally focused on the oxygen ion type.

The base structure of the cell is the same as always: an electrolyte layer sandwiched between the anode and the cathode (Fig. **9**).
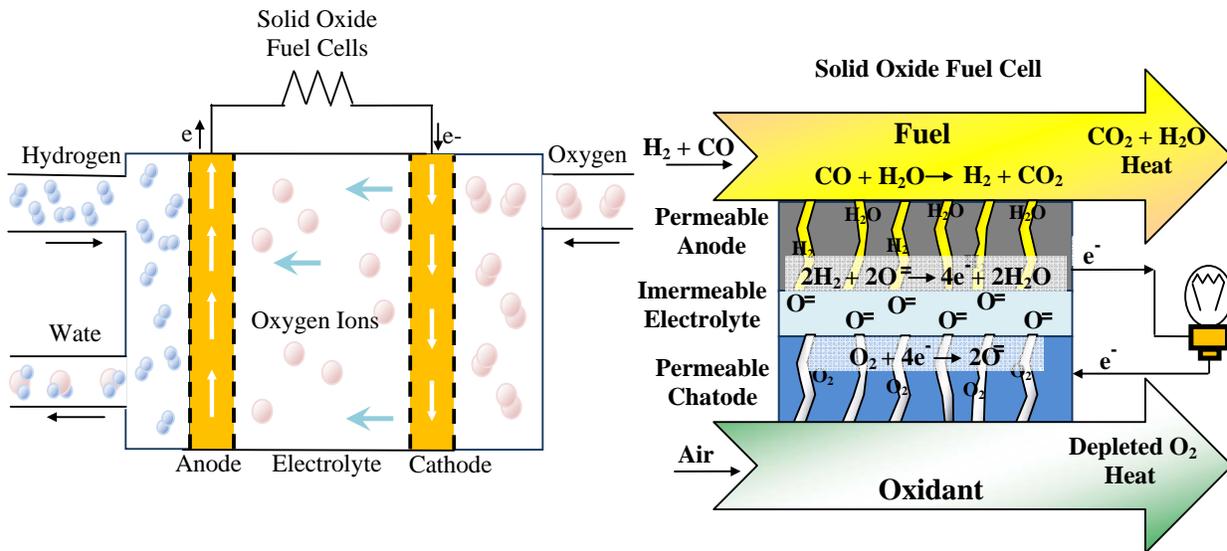
Fig. (9). SOFC structure.

The electrolyte layer is composed by a thin solid ceramic material which is usually a Yttrium doped zirconium oxide (YSZ) which is used due to its good ionic conductivity, chemical stability and mechanical strength. The problem of this electrolyte is that it requires high temperatures in order to reach the required conductivity needed by the cell to work properly.

Regarding this argument there are many efforts focused on the research of other materials to use as the electrolyte. One example is scandium doped zirconium which has an higher ionic conductivity but is not used due to the high costs it involves. Another solution is gadolinium or samarium doped cerium oxide, which is being currently used by Ceres Power Limited (UK); this material have an higher ionic conductivity but in order to work properly it must operate around 600 °C. Many others electrolytes are under research but they still don't have reached a good chemical stability.

Regarding the electrodes the cathode needs to have a porous structure in order to allow the diffusion of the gaseous oxygen inside the interface between the cathode and the electrolyte. In order to do this and due to the high temperatures involved there are strict mechanical and chemical requirements (chemical stability and a reasonable thermal expansion) so the material usually involved in the construction is strontium-doped $LaMnO_3$ [37-39].

The anode as the cathode needs to have a porous structure and it is usually made with a composite cermet of nickel and yttrium doped zirconium oxide (Nickel-YSZ). The nickel works as a catalyst for the fuel oxidation but has many problems like high thermal expansion and coarsening of the microstructure. YSZ works in order to constrain these characteristics and provides a good adhesion of the anode to the electrolyte interface.

The cell works by supplying air to the cathode where the oxygen molecules are split into oxygen ions (O^{2-}) with the addition of four electrons. The ions are transported through the electrolyte and when they reach the anode they recombine with the hydrogen supplied thus releasing the additional electrons and generating heated water. The electrons are then collected by the anode which generates the electrical current.

7.2. Solid Oxide Fuel Cells Characteristics and Applications

Solid Oxide Fuel Cells represents one of the most efficient and interesting technology among fuel cells.

Currently there are many high temperature SOFCs systems with a power around 10 kW which are being demonstrated. Moreover there is a big interest into the development of low temperature SOFCs for the use in automotive systems [39].

Compared to the other fuel cell technologies SOFCs presents the following advantages [37,40]:

- the highest electric and thermal efficiency (up to 80% with combined heath systems) among all the fuel cells;

- no need to use noble metals as catalysts inside the cell or other expensive materials;

- possibility to use many different low cost hydrocarbon fuels (biogas, coal gas, natural gas);

- a long operative life cycle due to the low degradation of the materials (to be demonstrated);

- the structural simplicity of the cell permits the simplification of the production lines;

- very low emissions both in terms of NOx and SOx if the cell is supplied with hydrocarbon fuels (zero emissions if the cell is supplied with pure hydrogen);

- low noise production system.

The disadvantages are the long starting times (which is a common disadvantage among high temperature fuel cells) needed in order to reach the proper operative temperature required by the cell electrolyte and the thermo-mechanical problems due to coupling of materials with different thermal expansion coefficients.

The poor ability to thermal cycling of the SOFC cells impose to use this type of fuel cell only for stationary applications to achieve significant lifetime

Due to their high efficiency, low costs and environment friendly characteristics SOFCs will be a candidate, after the PAFC technology, to reach a full commercialization on the fuel cell market.

In particular high expectations are placed on stationary and distributed power applications both inside North America and Europe.

Since SOFCs characteristics are highly suitable even for portable applications there are a lot research efforts focused on the reduction of the cell operative temperature. The aim of those researches is to obtain a reduction around 450-600 °C.

Steady progress is also being made in terms of the development of auxiliary power sources for private homes and automobiles.

The main worldwide actors involved on this technology are: Siemens Power Generation, Acumetrics, Bloom Energy, Ceramics Fuel Cells, Hexis AG, Kyocera/Osaka Gas, Mitsubishi Heavy Industries, Mitsubishi Materials Kansai Electric Power, Tokyo Gas, Versa Power, Wartsilla Corp and SOFCPower [22].

8. COST AND DURABILITY OF FUEL CELLS

The high capital cost for fuel cells is by far the largest factor contributing to the limited market penetration of this technology. In order for fuel cells to compete realistically with other contemporary power generation technologies, they must become more competitive from the standpoint of both capital and installed cost (the cost per kilowatt required to purchase and install a power system) [41].

In the stationary power market, fuel cells could become competitive if they reach an installed cost of $1,500 or less per kilowatt. Currently, the cost is in the $4,000+ range per kilowatt. In the automobile sector, a competitive cost is on the order of $60 - $100 per kilowatt, a much more stringent criterion.

The high capital cost (on a $/kW basis) today has led to a significant effort focused cost reduction. Specific areas in which cost reductions are being investigated include:

1. Material reduction and exploration of lower-cost material alternatives

2. Reducing the complexity of an integrated system

3. Minimizing temperature constraints (which add complexity and cost to the system)

4. Streamlining manufacturing processes

5. Increasing power density (footprint reduction)

6. Scaling up production to gain the benefit of economies of scale (volume) through increased market penetration.

It is diffucult to obtain informations on the actual cost of fuel cells. Probably the must realiable data are coming Institut fur Kraft-Fahr-Zeuge of Aachen University (Germany) [42] (Table **2**).

The Department of Energy (DOE) in USA claims to have reduced the cost of automotive fuel cells from $275/kW in 2002 to $47/kW in 2012 and is targeting a cost of $30/kW by 2017 [43].

These cost reductions reflect numerous individual advances in key areas, including the development of durable membrane electrode assemblies (MEAs) with low platinum group metal (PGM) content.

Table 2.   Cost for Fuel Cell Systems

Type		10 kW	100 kW	200 kW	2000 kW
PEFC	Package costs ($/kW)	4700		3120	
	Total installed cost ($/kW)	5500		3800	
	Operating and maintenance cost ($/kW)	0.033		0.023	
PAFC	Package costs ($/kW)			4500	
	Total installed cost ($/kW)			5200	
	Operating and maintenance cost ($/kW)			0.029	
MCFC	Package costs ($/kW)				2830
	Total installed cost ($/kW)				3250
	Operating and maintenance cost ($/kW)				0.033
SOFC	Package costs ($/kW)		2850		
	Total installed cost ($/kW)		3620		
	Operating and maintenance cost ($/kW)		0.024		

Demonstrated more than 2,500-hour (75,000 miles) durability of fuel cell systems in vehicles operating under real-world conditions, with less than 10% degradation. This is more than double the maximum durability of 950 hours demonstrated in 2006.

Improved the performance of stationary fuel cells, including development of a solid-oxide fuel cell for micro-combined heat and power applications with an almost 25% increase in system power density, which has enabled a more than 30% reduction in stack volume and a 15% reduction in stack weight.

Developed advanced manufacturing methods and materials that enabled a 50% decrease in the cost of gas diffusion layers since 2008.

9. HYDROGEN AND FUEL CELLS

Hydrogen can be produced using diverse, domestic resources including fossil fuels, such as natural gas and coal (with carbon sequestration); nuclear; biomass; and other renewable energy technologies, such as wind, solar, geothermal, and hydro-electric power [41].

The overall challenge to hydrogen production is cost reduction. For cost-competitive transportation, a key driver for energy independence, hydrogen must be comparable to conventional fuels and technologies on a per-mile basis in order to succeed in the commercial marketplace.

Hydrogen can be produced via various process technologies, including thermal (natural gas reforming, renewable liquid and bio-oil processing, and biomass and coal gasification), electrolytic (water splitting using a variety of energy resources), and photolytic (splitting water using sunlight via biological and electrochemical materials). Hydrogen can be produced in large, central facilities (80–500 kms from point of use), smaller semi-central (located within 40–160 km of use) and distributed (near or at point of use).

In order for hydrogen to be successful in the market place, it must be cost-competitive with the available alternatives. In the light-duty vehicle transportation market, this competitive requirement means that hydrogen needs to be available untaxed at $2-$3/gge (gasoline gallon equivalent). This price would result in hydrogen fuel cell vehicles having the same cost to the consumer on a cost-per-mile-driven basis as a comparable conventional internal-combustion engine or hybrid vehicle.

A viable hydrogen infrastructure requires that hydrogen be able to be delivered from where it's produced to the point of end-use, such as a dispenser at a refueling station or stationary power site. Infrastructure includes the pipelines, trucks, storage facilities, compressors, and dispensers involved in the process of delivering fuel.

The high cost of hydrogen production, low availability of the hydrogen production systems, and the challenge of providing safe production and delivery systems are all early penetration barriers. There are few data on the cost, efficiencies, and availabilities of integrated coal-to-hydrogen/power plants with sequestration options. Data on the high-temperature production of hydrogen from nuclear power are limited. Likewise, there is little operational, durability, and efficiency information for renewable hydrogen production systems. Hydrogen delivery options need to be determined and assessed as part of system demonstrations for every potential production technology. Validation of integrated systems is required to optimize component development.

10. FUTURE DIRECTIONS OF FUEL CELL SCIENCE AND TECHNOLOGY

Future development and implementation of fuel cell technology would depend on upward trend in global oil price, depletion of oil wells, fall in oil well discovery and the improvement of hydrogen energy infrastructure. The concern for environmental pollution and damage from the emission of automobile, thermal power plant, petroleum-crude refinery would catalyze the process of development unless financial benefits in terms of lowering of pollution damage cost are perceived by users and the manufacturers. Infrastructure development of the hydrogen energy encompasses production, distribution, dispensing and safety regulations of fuels (e.g., hydrogen, alcohol, esters and natural gases, naphtha and synthesis gases), which is directly fed to the fuel cells or to the fuel processor. Out of these hydrogen and alcohols can be generated from renewable sources (wind, solar power in water electrolysis, biomass gasification and fermentation) and others including hydrogen and alcohol can also be generated from fossil fuel. In the former case, green house gas emission is much lower and almost negligible. One can dream of zero emission of air pollutant and green house gases from automobiles and stationary power plants except for the case of biomass gasification. In the latter case, the air pollutant will be generated in a centralized location and cities will be free of pollution, which is otherwise generated from automobile using internal combustion engine. It should be noted that the hydrogen fuel cell vehicle (H2FCV) and H2FCV-hybrid electric vehicle offers least environmental damage among all the advanced options. When fuelled with hydrogen derived from natural gas, pollution damage costs are 1/8 as large as for today's gasoline internal combustion engine vehicles without CO_2 sequestration and 1/15 as large with CO_2 sequestration [44]. Although economics does not work out at present for PEMFC (Proton Exchange Membrane Fuel Cell) based automobile or SOFC (Solid Oxide Fuel cell) based stationary power plant with present inadequate hydrogen infrastructure but it is hoped that with the increase in crude price, no new crude or gas reserve findings, increase in fuel cell stack efficiency and decrease in cost of the fuel cell and improvement of hydrogen energy infrastructure facility, the Fuel Cell Vehicle (FCV) and distributed power generation from fuel cell will become more profitable leaving aside the cost benefits due to less environmental pollution.

Optimists are looking at 20% use of FCV in worldwide, 10% share of the domestic power generation from fuel cell source and 50% share of portable electronic equipment powered by fuel cell by 2020.

11. ENGINEERING ISSUES

Stack engineering and control is the next biggest hurdle once the above things are taken care of. The biggest challenge is in the computer controlling of fuel cell stack for load

variation with minimum response time, better stack design (improve in heat integration, less fuel flow resistance, by-products removal), lowering of stack mass per unit volume and cyclic endurance.

Other challenges related to successful implementation of fuel cell technology are: DC to DC conversion through electronic transformer which increases current density by compensating through drop in voltage and power conditioner i.e. DC to AC conversion for utility services and domestic appliances.

Finally, the fuel cell vehicle or fuel cell for stationary power have to be mass produced and the development of automated mass production technology is very important in terms of bulk production, cost reduction and reproducibility of fuel cell performance. Most of the development work on MEA preparation is through hands-on experience and hand held technology and it is very difficult to reproduce MEA with similar performance as some amount of manual error always creeps in. Thus automation and development of mass production technology of MEA preparation and assembly line for stack production should be looked into very seriously especially for FCVs.

12. CONCLUSIONS

As it can be read from the previous chapters many technologies of fuel cells do exist and each one of those technologies has its own strengths and weakness. Each technology is well suited for certain environments of applications and has many issues which actually prevents them to be fully commercialized. However there are four technologies which, both due to the wide interest into the benefits they could bring and the development level of the fuel cell type, are probably the most suited technologies to be fully commercialized into the market in the nearest future. Those technologies are the Phosphoric Acid Fuel Cells (PAFCs), Solid Oxide Fuel Cells (SOFCs), Polymer Electrolyte Membrane Fuel Cells (PEMFCs) and Direct Methanol Fuel Cells (DMFCs).

The first two, among all the technologies are probably the most suited for applications regarding static power generation. The technology detains in fact the greatest advantages in terms of: efficiency, fuel cell life cycle, flexibility regarding the fuel used, simplicity of the design and contained costs.

The second and third one are the technologies in which most of the world hold the greatest interest regarding all the other types of applications like: distributed power generation, portable applications and all the applications concerning the automotive and transportation sector. However this will only be possible with the development of a suitable hydrogen network which concerns effective production and efficient distribution (which involves finding effective solutions regarding the hydrogen storing safety issues).

This article, comparing the fuel cells technologies, want to be a good instrument for all researchers and technicians interested to work in a field extremely important for environment and for electrical energy.

CONFLICT OF INTEREST

ACKNOWLEDGEMENT

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