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Proton Exchange Membrane Fuel Cell Systems – A Techno Economic Analysis

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Summary

The problems of toxic emission and resource depletion caused by economic activity are leading to technology changes which will affect the industry energetically and logistically. The power industry has efficiently lowered the dependence from oil by diversifying its fuels : nuclear energy and renewable sources. Traditionally a public industry, utilities are today undergoing structural changes, enhanced by legislative de-regulation but also by stringent emissions and efficiency targets. The car industry is much more oil-captive. Efforts to reduce the emissions are the major driver of research for alternative vehicles – e.g. gas, hybrid and electric. National, regional and municipal emission monitoring are leading to the establishment of programs for pollution reduction, an exemple is the California Air Resource Board (CARB) mandate requiring Zero Emission Vehicles (ZEV) in the coming years. Besides the possibility of powering electric vehicles, the Fuel Cell (FC) technology is also relevant for the energy sector, whereas the commercialisation of silent, high-efficiency packaged power stations (below the MW_{el} size) has begun. The FC are Ultra Low Emission electrochemical engines when they operate on fossil fuels and Zero Emission when pure hydrogen is fed, so that in the case of hydrogen produced through renewable energy sources, i.e. solar, hydroelectric, biomass, there is no emission on the whole fuel cycle. The particular features of the Proton Exchance Membrane Fuel Cell (PEMFC), reported in the study, are likely to enable this FC technology to enter both the electricity and transportation markets. This requires industrial synergies to overcome technological and economical (mostly logistical) bottlenecks. There are three tasks of the present study : a) literature review about hydrogen energy development and more specifically assess the PEMFC status, this is the primary objective of the present work ; b) technical analysis of PEMFC systems to identify the commercialisation pre-requisites, which demanded an interdisciplinary approach to englobe the different domains of the FC technology and solve the major problem : system integration ; c) economic estimates for the subsystem components (fuel processor, H_2 purifier, FC, inverter) : while some are at the laboratory stage, needing to be perfected, others, even if reliable, are practically hand-made. These characteristics of a technology in a pre-commercialisation stage are quantified to expected capital investment and electricity cost for two PEMFC systems. The study results indicate that although the cost of electricity is still too high to compete with conventional systems, i.e. motors and turbines, in the small Combined Heath and Power (CHP) market segment, the PEMFC are expected to advance very fastly on their learning courve and the world's major companies involvement in the technology - reported in detail – is proof of it.

Chapter 1 - Introduction

Growing concerns over global environmental issues such as global warming, casts in doubt whether the growing need for energy services can be met with conventional energy technologies even if the basic energy ressources to do so are available. To meet the needs of societies worldwide, to improve their standards of living consistent with environmental constraints will require revolutionary changes in both energy conversion and end use technologies. Fuel cells could be one of the key technologies allowing for the expanded scope of human activities whilst being consistent with the environmental integrity of the planet.[1]

Definition of a Fuel Cell

Fuel Cells (FC) are electrochemical energy converters made of two electrodes and an electrolyte, fuelled by hydrogen (or an hydrogen-rich substance), with an oxydant (air). The electrolyte and the operating temperature distinguish the different FC technologies, the first, which can be liquid or solid, separates the reactants, isolates electronically the anode and cathode and forms a ionic bridge between the two electrodes. Temperatures range from 80°C to 1000°C. In **acid electrolyte** FC, hydrogen is ionized through the electrolyte, which creates an electron flow, to be subsequently oxidized without combustion with oxygen, or air, to form water. Unlike batteries (energy storage devices) the fuel of the FC is externally stored. The FC is potentially the most efficient electricity generator because FC accomplish the direct conversion of hydrogen to electricity.[2]

Fuel cells have recently been named the Clean Machine and Engines of Change [3] or, more prosaically « clean, efficient power generator, with no moving parts », but little matters : if the fuel cell was invented more than 150 years ago, with early electricity developments, today the industry focuses on combined heat and power (CHP) FC systems and FC vehicles (FCV) with on-board reformers. This paper analyses, from a techno-economic point of view, how this « gaseous battery » has evolved, compared to traditional power systems – batteries, internal combustion engines (ICE) and gas turbines (GT) - by the cost and reliability figures, when available, of the gas chemistry schemes to produce the fuel (hydrogen), including the balance of plant (BOP), to assess the present challenges for commercialisation.

1.1 - Energy trends after World War II

It is conventional for clarity reasons to split the time frame into two main periods - before and after 1973 - and the energy market in OECD and non-OECD countries.

In the period 1945-1973 energy demand rose at rates of 4 % per year in U.S, Northern Europe and Japan, and the oil demand grew at higher rates (8%)[4]; oil supply was abundant and fuel prices were low. The competitive forms of energy, *e.g.* coal, had to re-structure since they required considerably more manpower than oil per equivalent ton and labour costs were rising faster than coal production efficiency. Moreover oil had a fast penetration in the transportation sector, where the private car market was booming.

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[1] Brian M. Barnett and W. Peter Teagan : « The role of Fuel Cells in our Energy Future ». Journal of Power Sources 37 (1992) page 15.

[2] The electrochemical (direct) conversion of fuels into electricity, detailed in Ch.3, is not limited by Carnot Law, valid for combustion engines.

[3] See R. Williams « The Clean Machine » and G.E.H. Ballard contribution (« Engines of Change ») at the XI Hydrogen Energy Conference (HEC), Stuttgart, October 1996.

[4] K. Swart : « Trends in the energy market after World War II », Journal of Power Sources 37 (1992).

During the period 1945-1973 oil prices dropped in real terms, and compared to coal, as a consequence of industry and power generating companies switch from coal to oil. This had an important effect on the upstream sector since it became profitable to install « skimmer » refineries to distill heavy fuel oil into its components : naphtha, middle distillates and fuel oil, provided that a sulphur content as low as 2 ½ % was good enough. The engineering was simple and the idea corresponded to an increased need of supply security and also to provide fuel for the newly-created airlines. The early environmental issues concerned precisely the oil sulphur content, which was lowered to 1.5% in the late sixties. Such « ecological » step accelerated the use of new Middle-East oil fields, which had low sulphur, thus increasing the dependance on that region of the world (OPEC).

The 1973 events, when the Arab countries decided to increase the price per barrel from three to eleven $/bl,[5] are considered as a turnover : energy can be scarce. The man of the street realised that something had gone wrong and the oil companies started an active program of exploration in non-OPEC areas. Since then the share of OPEC oil fell rapidly from 60 to 35% in ten years. In power generation an increasing share was being taken by natural gas and nuclear fuel, leaving very little for coal. Energy saving in cars, buildings and industries started to be considered more seriously. Consequently, the demand for oil has been following a flat trend in OECD countries where cooking and heating in houses and industrial processes is increasingly accomplished by natural gas. Besides, Europe started to reduce dependancy on OPEC countries by exploiting off-shore reserves in the North Sea.

Inversely, the emerging countries in Southern Asia increase oil demand for electricity and transportation and, as in Europe, it is reasonable to think that when the infrastructure for the industrialisation is advanced, environmental concern emerges. This transition to a more mature energy system leads to cleaner fuels and a more efficient energy use.

1.2 - Emerging issues

The power generation industry is changing rapidly in Europe. The traditionally state-owned companies are now moving toward liberalisation together with an increasing competition. Utilities have long practiced centralised electricity production to benefit from the economies of scale (and efficiencies) of GW-size plants, but today we witness a trend toward decentralized electricity production, driven by cost and environmental considerations. This trend arises from the recent development of energy carriers (natural gas), competing now with the electricity carrier (transmission lines).

Stringent regulations for pollution control are increasing the cost and the complexity of power plants with the addition of clean-up devices, *e.g.* desulfurisation and De-NOX. Power industry faces the dilemma to provide low-cost electricity (short term perspective), while also considering the life-cycle balance of all the technologies employed (long term). Will pollution-free fuel cells with their high-efficiency and modularity, be a solution ? An historical change would take place : the energy system would then address long term issues and taking into account the *whole* energy chain, from fuel production to electricity delivery.

The concepts behind the need for cleaner economic activity and more efficient energy use are distinguishing features of this end of century. Ecology can be summarized in two key concepts : Externality Control and Resource Depletion. If the first is a fight-like action

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[5] Prices are given in U.S. currency, as it is used in international oil trade.

against the various forms of global and local pollution, the second is more frequently quiet monitoring of the underground, affected by mining, pumping and other irreversible activities.

There are two drivers for this study on FC : sustainable development and the forthcoming technologies to make it happen.

1.2.1 - Sustainable development

Reflecting the need for a more complete evaluation of the economic flows, the international standards of the Social Accounting Matrix (SAM) give now values to ground-cover vegetation (forests), sewage water, minerals and other types of natural resources, potential victims of economic activity, taken (now) in a broader sense and substracted from the GDP. Apparent two-figure growth rates of Southern Asian countries were often due to deforestation and quick mining, causing irreversible depletion. Countries in the early capitalism stage are learning fast about ashes in the air, lost amenity and, later on, greenhouse effect.

The damages caused by local pollution and global warming effects are pushing the insurance companies to invest in renewable energies to prevent massive disasters in the future as sea-level rise, health hazards and food security threats with their huge economic costs.[6] In sum, sustainability is turning to be a criterion for international investment funding everywhere.

1.2.1.1 - Access to resources

Access to resources is endangered by human activities resulting in irreversibilities in the « system earth », as the cutting of primary forest or nuclear waste build up.[7] In the energy domain the concept of access to resources means fuel availability for every fossil-based economy.

Hydrogen is a renewable fuel from water splitting or biomass, but, as it will be shown later, it is today more economically produced from fossil fuels like natural gas or liquid hydrocarbons by reforming processes, rather than electrolytically, using electricity.

Besides the higher efficiency, concentrating emissions at the fuel production/reforming stage, allows their easier abatement, with no need of tailpipe control devices, *e.g.* car catalitic converter.

1.2.1.2 - Emissions

When produced from natural gas, alcohols or liquid hydrocarbons, hydrogen causes some pollution (CO_2), but both the hydrogen production processes and the FC have high efficiency, thus the CO_2 emitted per useful kWh is potentially lower than combustion technologies. The use of hydrogen in a FC is non polluting : the only by-product is pure water.

Emissions are local, regional and global. It emerges that :

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[6] See : « Renewable Energy Sources : Market Survey » by Merrill Jones, VTZ, Zurich 1997.

[7] For an impressive analysis of the relation between entropy and economics see N. Georgescu-Roegen : « The Entropy Law and the Economic Process », Cambridge University Press, first ed. 1971.

- FC vehicles meet the most stringent emission standards (California Air Ressource Board) and are Ultra Low Emission Vehicles.[8]

- According to a recent study,[9] the environomic comparison between diesel engines and FC powertrains fails to shift the balance in favour of the fuel cell vehicles : the inclusion of the externalities (price of pollution) does not compensate the taxes in the price of the diesel fuel. However, these kind of analysis are strongly dependent on the assumptions made and the value of the externalities.

- FC in transportation imply some hybrid concepts when conventional fuels are used. The combination of the excellent inherent efficiency of the FC at both peak and part load with batteries can result in a 30% efficiency differential (with equivalent greenhouse emissions reduction) compared to a conventional car.

1.2.2 - New Technologies for FC

The FC technology has received great improvements from the wider advances in science during the last decade. We identified more specifically materials science and catalysis as the core fields of enhancement of the FC technology.

1.2.2.1 - Materials science

New materials like porous electrodes and polymeric membranes for ion-transport have recently found application in advanced electrolysers or FC. The consequent improvements enabled the Proton Exchange Membrane (PEM)[10] fuel cell technology to conquer a widespread interest within less than ten years. The porous electrodes and ion conductive membranes ease the FC reactions at more favourable conditions, engendering lower temperature of operation and easier construction.

In the domain of hydrogen storage, carbon nanotubes (Ch. 4) are probably pioneering the advent of lightweight, low-pressure, non-metallic hydride storage. Carbon 60 is a new material. It consists of a sixty-unit molecular assembly of carbon. The discovery of Buckminsterfullerene - C_{60} - was rewarded with the 1996 Nobel Prize in chemistry. Nanotubes are cylindrical assemblies of carbon with coordination similar to C_{60} and may be used for storing large amounts of hydrogen in little space and light weight.

1.2.2.2 - Catalysis

A catalyst is a component of a process which influences the kinetics of a reaction, without overall change in its own concentration. In oil refining or natural gas processing, new highly active catalysts now give results unattainable few years ago, enabling scaling of hydrogen reformers down to the kW range. These advances are confirmed for the reformation of alcohols.

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[8] J. Bentley *et al.* : « The impact of Electric Vehicles on CO_2 emissions ». Report prepared by A.D. Little with Idaho National Engineering Laboratory for the Departement of Energy 1992.

[9] G. Hörmandiger and N.J.D. Lucas : « Is clean enough ? The influence of environmental externalities on markets for fuel cells in transport », Transportation Research D Vol.1, 1996.

[10] Proton exchange membrane (PEM), polymer electrolyte (PE), and solid polymer (SP) are equivalent.

Evidently, new catalytic processes in fuels chemistry are leading to changes in the economics of hydrogen generation, where, so far, steam reforming has been the leading technology. Compact catalytic reactors of high efficiency can perform the production of hydrogen at lower temperature than the older equipment of refineries, over large transients.

The transient flexibility feature is needed to design a « pedal responsive » reformer to feed hydrogen for FCV. Autothermal reformers and the M.I.T.'s « Plasmatron », described in Ch. 5, are potentially mobile hydrogen generators from alcohols or liquid hydrocarbons.

1.3 - Study goals

This study defines three goals :

I - To perform a literature review about hydrogen energy development and more specifically those activities related to the Polymer Electrolyte Fuel Cells (PEMFC), which is the subject of the present work.

II - To technically analyse PEMFC systems in order to identify the bottlenecks for commercialisation, which required an interdisciplinary approach to include the different domains of the FC technology.

III - To provide economic estimates of PEMFC systems under different production conditions and in relation to technology status.

The relevant cross-linked criteria are :

- FC System definition from both the technical and economic perspectives
- Hydrogen production pathways from fossil fuels
- Market acceptance & requirements

As a subsequent and, I hope, applicable, result of the study, I tried to provide the basis for choice of direct industrial engagements, *i.e.* insights to guide investments on basic components development of a FC system[11], market analysis and penetration strategy in a commercial perspective.

If we look at the market sectors involved with fuel cell commercialization, *e.g.* private transportation and electricity generation, we realize how no element, or variable, is « exogenous » so to say. Proof of this statement is found in the fact that even the petrochemical holdings, refocused on core activities, *i.e* oil upstream sector, after the shocks of the 70's, are today directly or indirectly concerned with FC R&D by searching better reformulation of their fuels or prospecting renewable technologies and hydrogen processes.[12]

Oil and gas companies may contribute to FC introduction by development of synthetic fuels - as reformulated gasoline - easier to convert into hydrogen or chosing sulphur-free gas odorants tolerable by a FC.

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[11] The basic components of a Fuel Cell System will include a Fuel Processing, FC Stack and Electric subsystems having variable components, depending notably on the primary fuel, the type of application, i.e. mobile or stationary and size (kW).

[12] For a « Punctual Equilibrium » approach, *i.e.* non-linear, to the issue of major companies' transition policies to renewable energy and related scenarios see : C.Flavin : « Power Shock : the Next Energy Revolution », Worldwatch publication, 1996.

Chapter 2 - Status quo in fuel cells

2.1 - Overview

Fuel Cells (FC) are electrochemical devices that allow the direct convertion of an oxidisable fuel into electricity, with an electric efficiency - usually calculated from the Lower Heating Value[1] (LHV) of the fuel - ranging from 40 to 60%. The first FC was realised in England (1839) by Sir William Grove, aiming at demonstrating the feasibility of reversing water electrolysis. Grove realised his " gas battery " introducing hydrogen and oxygen into a sulfuric acid solution with platinum electrodes. At that time progress in mechanics had already led to the development of steam engines, at first employed in deep coal mines, then in transport. Electricity generation was not yet an industry, the fuel cell stayed at the lab.

In a quick glance at industrialisation we can realize how, historically, after Watt's steam engine, huge efforts by industries and research have influenced 20th century, and our lives, by thermal engine mass production. Motors and turbines are today the main prime movers for transportation and electricity generation. We just mention that :

In 1894 Ostwald, co-founder of the new science of Physical Chemistry along with Van't Hoff and Arrhenius, delivered a lecture to the Bunsengesellschaft, the German national society dedicated to the new subject (Electrochemistry). In it he looked forward to a future in the next century where machines would operate on the principles of the new science, rather than on laws governing the volume changes of gases under the influences of heating and cooling, which were established in the early days of physics. The new machines would operate without steam boilers, flames, soot and smoke and other forms of pollution. They would convert the chemical energy of fuels directly into work, rather than first converting it into heat via an inefficient thermal cycle. Ostwald clearly hoped that the steam engine, with its 10% efficiency, would be replaced by an efficient and non-polluting machine to directly generate electricity from chemical energy sources, which would open up a new civilisation in the coming century[...]His dream, unfortunately, did not come about. The steam engine was improved until its efficiency ultimately reached 40% and the internal combustion engine became the source of choice for smaller uses. However, the advantages of the fuel cell which he observed are still there to be exploited, and one century later, it now promises to become a clean, efficient source of energy, for use beyond the year 2000.*[2]

*When operated with natural gas and with a bottoming steam cycle, large (MW) gas turbines reach 58% efficiency, with prospects of 60% in the future. In the 200kW power range diesel engines reach 40-44% efficiency and gas engine are between 35-39% (Source LENI).

The different FC technologies, operation temperatures, technology status and respective bottlenecks are synthetically presented in the Table 2.1 below.

Fuel Cell Electrolyte	**Temp (°C)**	**Status**	**Disadvantages**
Polymer membrane (NafionTM, Dow, Asahi, Gore, PSI, Dais)	70	Mobile and stationary applications (0.1 - 300 kW) system assessment	CO< 20 ppm
Alkaline(85 wt% KOH in water)	80-150	Mature technology for air independent applications (1-40 kW)	Pure H2 and O2,
Phosporic Acid	200	Commercial200kW CHP units (300$(kW), portable 200W	η_{el} max 43% (nat. gas), price

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[1] The heating value of an oxidisable substance is equal to the recoverable thermal energy resulting from the complete combustion ; when the the water produced from the hydrogen oxidation is condensed we talk of higher heating value (HHV), otherwise it is the lower one. Efficiencies are often calculated from the LHV, although the PEMFC produces liquid water and the HHV is applicable.

[2] J. Appleby, : " Fuel Cell technology : status and future prospects ". Energy. The International Journal 21, 1996, pag 1.

Molten Carbonate ($Li_2CO_3 + K_2CO_3$)	700	Field testing (1MW)	Corrosion, limited modularity, low η_{el} Need CO recycling
Solid Oxide ($ZrO_2 + YO_3$)	800- 1000	Pre-commercial (3-10kW) 200kW tests	Max 0.25 A/cm^2 at 0.7 Volts Hardware stability
Direct Methanol (Nafion^{TM})	90-130	Laboratory (few W)	High Pt loading, lifetime
Heteroply Acid PWA ($H_3PW_{12}O_{40}$• $29H_2O$)	20-50	Laboratory (few W)	Dissolution of the electrolyte

Table 2.1 - Types of fuel cells and their status.

Although FC research's peculiarity is its extremely evolutionary, discontinuous pattern, we will try in this chapter to " picture " its status quo at present by a survey of programs, companies reports and more informal information taken from sector's experts. We focus on the Proton Exchange Membrane Fuel Cell technology.

2.2 - Fuel Cells programs

FC are regarded with interest by many energy agencies[3], because of their high efficiency and extremely low emissions, if operated with conventional fuels - i.e. other than hydrogen. There are several programs and many companies involved in the development of different fuel cell technologies. We will only mention the most important.

2.2.1 - European Community

Europe represents an important market for FC. The European Parliament's Commitee on Transport has adopted a draft report for a 10 year program to increase the use of alternative fuels and electric vehicles[4]. The European Union has established a fuel cell commercialisation program, where EU takes in charge funding for all marginal costs (e.g. services, capital equipment) associated with the production of the FC, if at least two European countries provide 50% of the direct financing required for industrial development. The Joule, Brite-Euram and Thermie programmes deal, within the EU Framework Program, with the issues of research and development, manufacturing processes and demonstration projects of FC respectively. In total, funding from 1992-1995 amounted to 32 million ECU. The EU strategy document puts emphasis on the PEMFC technology - low temperature and low cost - to achieve commercialisation of a CHP system before 2000.

2.2.2 - Switzerland (OFEN)

The Swiss Fuel Cell program is led by the Federal Office of Energy (OFEN) in co-operation with research institutes (EPFL, ETHZ, Paul Scherrer Institute) and private companies (Sulzer). Former Swiss FC research focussed on the development of Solid Oxide Fuel Cells (SOFC) with Asea Brown Boveri (ABB), but the Swiss-Swedish company abandoned FC development in 1991 as part of a business decision not to manufacture small generation equipment. Sulzer has recently founded Sulzer Hexis Ltd. a company devoted to the commercialisation of the HEXIS^{TM} planar SOFC stack. The Paul Scherrer Institute (PSI) leads research in PEMFC on membrane developments and, more

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[3] Armies, with the space industry, are an inportant sector involved because of the specific features of FC, e.g. part load performance, low noise/vibration levels and low off-gas temperature (for infra-red signature), which well comply with the recent shift to a higher electric/propulsion equipment ratio. See : D. Schmal, and B. Barendrecht " FC on-board of naval ships, activities in the Netherland ". European Fuel Cell News, August 1996.

[4] See: European Commission " Joule Program " and " Ten years of Fuel Cell Research " 1995.

recently, on Membrane Electrode Assemblies (MEA) and stacks[5]. Work is under way, in co-operation with EPFL for the development of a FC reformer to process liquid fuels to hydrogen in a drivetrain[6].

2.2.3 - U.S.A[7].

The United States have adopted several legislative measures in the 1990's to support the development and commercialisation of low emission technologies. The federal government passed the National Energy Strategy and the Clean Air Act in 1990. President Clinton has sponsored in 1993 an agreement between the government and the Big Three - " Partnership for a new generation of vehicles " - to develop technlogies for a new, super-clean car for the next century. The federal government also introduced in 1993 the Environment Technology Act to develop demand for environmental technologies. The California Air Resource Board adopted in 1990, the world's most stringent Low Emission Vehicle program, establishing a set of vehicle emission standards and classes. Car manufacturers have to meet the average fleet emission standards by combining four types of vehicles. For exemple as soon as 1998 2% of all new vehicles were to have been Zero Emission Vehicles, 10% in 2003. This target has been recently postponed for five years because of the strong opposition of the California Manufacturer's Association (CMA), representing around 800 companies. A report of the U.S. General Accounting Office warns : " Batteries are far from being perfected, the production cost are excessively high and the market potential is highly uncertain. Ultra-Low-Emission Vehicle, cleaner gasoline and programs to substitute the most polluting vehicles on the roads are more promising at far less cost "[8]

Ballard[9], world leader in PEMFC, suggests that it gives the time for PEMFC vehicle infrastructure to be implemented, thus recognising FCV as the only alternative to the ICEV.

2.2.4 - International Energy Agency[10]

The International Energy Agency (IEA) is been actively engaged in improving the state of fuel cell technologies with a co-ordinated programme of research, technology development and system analysis on Molten Carbonate, Solid Oxide and Polymer Electrolyte fuel cells systems. An Implementing Agreement for a programme of research, development and demonstration on advanced fuel cells was signed by seven countries in April 1990. A strong emphasis is given to information exchange between participants. Programs are subdivided in Annexes, each including its specific research Tasks. In 1995 the Implementing Agreement has been extended for three years and a new programme for 1996-1998 was developed, including:

Annex VI	Molten Carbonate Fuel Cells under Real Operating Conditions
Annex VII	Solid Oxide Fuel Cells under Real Operating Conditions
Annex VIII	Polymer Electrolyte Fuel Cells
Annex IX	Fuel Cells Systems for Stationary Applications
Annex X	Fuel Cells Systems for Transport Applications.

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[5] At the PSI a 60W Electrochem stack has been adapted to work with their membrane, replacing the Nafion 117 of the original design with a remarkable increase in current density (from 0.3 to 0.7 A/cm2).

[6] Autothermal reformers are treated in Ch.5.

[7] Web page http:\\www.eren.doe.gov/hydrogen/hydrprod.htm. Padro, C.E.G.: "The hydrogen program of U.S."

[8] Note fom K. Kordesch:"Fuel Cells and their applications". VCH Ed. 1996, page 356.

[9] Ballard Annual Report 1996.

[10] See: IEA Advanced Fuel Cells Annual Reports, 1995 and 1996.

2.2.5 - Japan

The Japanese government, aware of country's energy dependance, has been actively working to reduce hydrocarbon consumption by long-term initiatives. Through the Moonlight Project, started in 1981, government support was provided for the development of energy efficient conversion systems, including Alkaline and Phosphoric Acid FC. Since 1992, under the Sunshine Project, Japan is providing support for the development and commercialisation of renewable energy sources, e.g. solar, wind and geothermal. Co-ordinated by the New Energy and Industrial Technology Development Organisation (NEDO), research for high-efficiency technology switched to Molten Carbonate, Solid Oxide and Proton Exchange Membrane FC. Under these initiatives the government has made a sound effort to create synergies with the gas industry and electric power utilities. The World Energy Network program (WE-NET) of Japan[11] considers energy security and sustainability with an all-round perspective, by implementation of a worldwide energy network for effective supply, transportation and utilisation of renewable energy, using hydrogen as clean, secondary energy vector. WE-NET extends over 28 years from 1993 to 2020.

2.3 - Some active companies in PEM fuel cell technology

2.3.1 - Arthur D. Little

Arthur D. Little is an American consulting company adressing future energy markets, providing reports for the World Bank and the US Departement of Energy in early 90's. A.D. Little is now technically contributing to PEMFC technology, with projects on ethanol[12] and hydrocarbon reformers for mobile applications, through development of a fuel-flexible processing system for on-board hydrogen generation, to fuel a PEMFC. The possibility of converting gasoline into hydrogen would allow a " no-infrastructure-change " market penetration strategy to fit the FC vehicle to the existing refilling network. Estimates of costs of A.D. Little technology are 16-26 $/kWel for the 50 kWel autothermal reformer in high production volume (10,000 units/yr.). Besides the reformer, the system will include a fuel purification reactor to selectively oxidize the CO contained in the reformate gas from the reformer (PROX) whose catalyst is likely to cost < 100 $ for a 50 kWel unit[13].

2.3.2 - Ballard Power Systems

Ballard, the world leader in development and production of PEM fuel cell technology, was founded in 1979 by Dr. G.E.H. Ballard in Vancouver, British Columbia, Canada, to conduct research on lithium batteries. In 1983, Ballard began developing PEMFC through contracts with the Canadian government, to improve for military applications, the performance of the General Electric PEMFC - air instead of oxygen as oxidant and graphite to replace the expensive niobium plates. In 1989, it changed its name to Ballard Power Systems, which is the parent company of the Ballard Group

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[11] M. Chiba, H. Arai, K. Fukuda, : " Hydrogen Energy Technology Development in Japan : New Sunshine Program ". Proc. XI HEC 1996.

[12] G. Block and W. Mitchell : " Evaluation of Hydrated Ethanol in an Advanced Fuel Processor for Fuel Cell Vehicles ", SAE Technical paper 971646.

[13] For more information on AD Little concept see European Fuel Cell News volume 4, March 1997. Cost estimates are taken from W.L. Mitchell et al. : " Development of fuel processors for transportation and stationary fuel cell systems ", November 20 1996 Fuel Cell Seminar and W.L. Mitchell et al. : " Development of multi-fuel hybrid partial oxidation fuel processors for fuel cell vehicles and hydrogen re-fueling stations ", 30th Annual ISATA Conference, Florence, Italy, June 16-19 1997.

including Ballard Advanced Materials Corporation and Ballard Battery Systems Corporation. The first developed a propietary, low-cost electrolyte membrane, the second was sold in 1995.[14]

Both the federal and the provincial Canadian government have played a main role in financing the development of Ballard FC technology, together with venture capital financing. Ballard has a defined strategy for market penetration, in three phases, which include heavy vehicle, stationary power and Zero Emission cars.[15] The company is preparing for mass production of PEFC systems for heavy-duty vehicles at the turn of the century.

In 1995 Ballard Power Systems has ended co-operation for the membranes with Dow Chemicals and are now employing their own. The company has an exclusive agreement with Johnson Matthey (UK) for the production of platinum-coated graphite electrodes, but industrial sources indicate that JM might start soon selling the electrodes to other purchasers.[16]

Ballard Power Systems has created Ballard Generation Systems in December 1996 for stationary systems. This company has licencees in America (GPU International) and Europe (AEG and GEC-Alsthom) for the commercialisation of their products. The transportation market is also very active: besides the major car manufaturers, it will deliver three buses to the Chicago Transit Authority and British Columbia Transit of Vancouver. A special mention needs to be made about cars : Daimler-Benz has provided 300 million US$ funding for a joint company which will design, produce and commercialise FC powertrains for buses, trucks and automobiles, with methanol as fuel. This might be the final, long-awaited step to commercialisation. The 250kWel power plant prototype fuelled by natural gas started operation in August 1997.

2.3.3 - De Nora

The Oronzio De Nora group is an electrochemical industrial company based in Milan. The core activity has been the development of industrial electrolysers : mercury technology and more recently membrane-electrolysers for the chlorine-alkali industry. In 1990 De Nora constructed a 1 kW PEFC stack, which is still working on discontinuous tests, with proprietary technology, based on metallic hardware and carbon gas diffusion electrodes.

In 1995 De Nora bought E-Tek, an American company producing ELAT^{TM}, a carbon-based electrode for PEMFC, in order to integrate the stack components. De Nora FC have often Du Pont membranes.

De Nora has major commitments in the frame of Euro-Quebec Hydro Hydrogen Project for the realisation of the stack for the fuel cell bus. This project was led with the participation of Ansaldo Ricerche for the fuel cell system. Other De Nora customers are TNO (NL), Ecole des Mines (F), DLR (D), ENEA (I) and Renault for the FEVER car project of the European Union Task Force " Car of Tomorrow ". In most of their projects DeNora is a supplier and not a partner for reasons of confidentiality.

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[14] The Ballard membrane is based upon a trifluorostyrene polymer, less fluorinated than commercial electrolytes. Ref in K. Prater : " SPFC for transport and stationary applications ", Journal of Power Sources 61, 1996.

[15] Http ://www.env.gov.bc.ca.dpa/ar/eeiampaw.html#1.5 " Estimated Economic Impacts and Market Potentials Associated with the Development and Production od Fuel Cells in British Columbia ". By KPGM March 1996.

[16] R. Evans, Johnson Matthey, Precious Metals, Catalysts and Materials, personal communication.

The Italian company has developed a low-cost metallic bipolar plate derived from membrane electrolysis experience[17] which matches the cost targets of the European FC project and it appears suited for mass production.

2.3.4 - International Fuel Cells

IFC has produced over 70 phosphoric acid power plants, employing the proprietary ONSI PC25^{TM} 200 kW unit - 40% electric efficiency - and is the only company actively commercialising a fuel cell system[18]. IFC has developed an advanced production process able to produce nearly 100 units per year. In PEM technology IFC holds a patent, since 1980, covering bipolar plates made of moulded graphite-fluoropolymer composite, which simplify the stack functioning by a wicking action[19]. IFC delivered a 50 kW PEM hydrogen-fed power plant operating at ambient air pressure and it is working on a 50 kW multi-fuel PEM for FCV.

2.3.5 - Mitsubishi

Mitsubishi Heavy Industries announced in 1994 the development of a 5 kW PEM fuel cell system incorporating a natural gas reformer. This project was jointly pursued with Tokyo Gas. MHI has also developed a 15 kW stack. Eventhough in the past MHI reported that fuel cell technologies and activities are not a high priority, probably based upon their mandate to develop pressuried, fluidized-bed coal burners, for the Asian market, the company has developpped a novel compact methanol reformer for a 10 kW stack.

2.3.6 - Sanyo[20]

Sanyo, involved with FC since 1960 with methanol-air and hydrazine-air prototypes, actually develops SOFC, PAFC, PEMFC and MCFC technologies. The company has developed and commercialized a 250 W portable PAFC unit of 25 kg, which uses pure hydrogen stored in a metal hydride as fuel with one hour autonomy.

In PEMFC development the effect of platinum catalyst loading and liquid electrolyte content was studied. During 4000 hours test a 1%/1000 h voltage degradation rate was considered satisfactory ; two stacks of 500 W and 1 kW worked at 0.5 A/cm2 and 0.6 V(3 atm).

Sanyo has built a 1 kW planar SOFC under contract with NEDO in the New Sunshine project. This module has 160x30 cell with a power density of 0.22 W/cm2 ; the endurance was tested for more than 1800 h and decay rate was 4.4%/1000 h. Concerning MCFC, Sanyo was testing a 30 kW internal reforming system for petroleum-fueled co-generation applications including a Ru-ZrO2 catalyst for LPG.

2.3.7 - Siemens

Around 1984, Siemens licenced PEM fuel cell technology from General Electric. Since that time, Siemens has been actively involved in this area by developing air independent (*i.e.* with pure oxygen) PEMFC systems. Siemens developed PEMFC systems for electric submarines - 212 class - for the German Navy. A 300 kW PEM system was recently delivered to Howaldtstwerke-Deutsche Werf shipyards in Kiel, Germany. This system, once re-engineered, could then be useful for buses.

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[17] See U.S. Patent No. 4,340,452

[18] See CLC-Ansaldo: "Papers presented at congress and seminars in 1995".

[19] A.J. Lawrence, U.S. Patent No. 4 214 969 (July 29, 1980)

[20] Y. Mikaye et al. : " Status of fuel cells R&D activities at Sanyo ", Journal of Power Sources 61 (1996).

Most of Siemens patents and applications relate to high temperature fuel cells systems and subsystems[21], although recently an internally-humidified H2/air 10kW PEM fuel cell system for a fork lift truck has been introduced for Solar-Wasserstoff-Bayern. One important partner is the Hoechst group. In the frame of European project BRITE, Siemens has developed a technique for compact low-cost membrane-electrode-assemblies[22] (MEA) with corrugated metallic bipolar plates; moreover, the group has presented a commercialisation strategy for FC to begin in 1998-2000. The FC stacks work at 1.5 bar (abs. pressure) and have a power density of 350 mW/cm2 at 0.75 V ; cost target are 200 DM/kW for the whole system assuming 100.000 pieces per year[23].

2.4 - Stationary applications

The electricity generation industry is mainly interested in overall system efficiency and lifetime although in the last years emissions abatement became a major concern as well. FC systems generating hydrogen from fossil fuels - as the ONSI 200kW PAFC - are noiseless and have practically no air polluting emissions (particulate, NO_X , SO_2). The greenhouse gases (CH4, CO2) emitted, determined by the overall system efficiency (40%), place the FC system above small gas turbines (< MW units). On the other hand, the comparison with engines is less favourable, since diesel and gas unit have electrical efficiencies of 44% and 39% respectively. Saying this, FC systems do have comparative advantages : they are noise and air pollution-free without clean-up devices, which reduces operation & maintenance costs, while the absence of moving parts increases the lifetime to about 40.000 hrs. These features allow FC to be user-sited even in densely-populated areas, thus avoiding T&D lines cost and (increasingly important!) visual impact.

This section offers a brief review of recent mobile and stationary applications for FC systems by the type of FC technology[24].

2.4.1 - PAFC

The phosphoric acid fuel cell technology was developed in the 70's by ONSI, a company of International Fuel Cells (IFC), division of United Technology, and Fuji. Industrial production started in 1990. In most commercial PAFC systems natural gas is used as fuel.

In the commercial PC25TM, the methane stream undergoes a steam reforming process to get a hydrogen-rich gas - previously having cleaned up the sulfur content by a zinc sacrificial reagent[25]. Fuji completed, in 1989 a 11 MW PAFC power plant in Goi, Japan. After this experimental unit the company did not intend to start commercial production, maybe because of the performance degradation of the stack. IFC has become world leader of this technology with the PC25TM model (200kWel), commercial since 1992. In Europe the licensee is Celle a Combustibile (CLC), a jointly-held company of Ansaldo-Finmeccanica and ONSI (see section 2.3.4).

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[21] Siemens is also actively involved in SOFC development (tubular technology from Westinghouse) and in the Direct Methanol FC (DMFC), which are catalyst-adapted PEMFC, but DMFC will not be fully discussed in this paper since research is still at a basic stage and current density, as far as we know has not gone further than 200 mA/cm3.

[22] MEA's are detailed in chapter 3.

[23] E. Grecksch et al. : " PEM Fuel Cells : Development and Commercialisation ", paper presented at Intertech Conference : " Commercialising FC vehicles ", Sep.17-19, 1996, Chicago.

[24] See also S. Penner and al. : " Fuel Cell commercialisation ", Pergamon University Press 1995.

[25] This unit is the hydrodesulphurator, the reaction is ZnO2 + H2S (ZnS + H2O. Reformer reaction is CH4 + H2O (3H2 + CO.

Investment costs are around 3000 $/kW, but the American Department of Energy (DOE) has set a grant - 1000 US$/kW for the first 25 units sold - in 1996. The stack costs 750 $/kW. Industry reports affirm that major niche market exist for PAFC to be competitive with conventional power plants in oil refining and clorine-alkali industry, where high quality by-product hydrogen can be used almost for free[26]. In the first half of 1995 a 1.3 MW PAFC plant was completed for AEM, the electric utility of Milan, by Ansaldo, using European components for gas reforming and electric inverter. The PAFC technology has reached a maturity of more than 500.000 cumulated hours, in real-environment grid-connected units, which confirmed high reliability and efficiency, although a small, constant degradation of the stack performance (0.5%/y), due to catalyst poisoning, is observed. In Switzerland it is estimated that 10% of the electricity could be produced by FC for premium power or with by-product hydrogen from the chemical industry. A PC 25 is on field testing at Services Industriels de Genève, with a cost of electricity between 10/15 Sct./kWh (0.06/0.09 $/kWh)[27].

2.4.1.1 - An Italian Paradox : The Assemini Project.

In the industrial area of Assemini, Sardinia, Enichem, of the ENI Group - major world petrochemical company - has a chlorine-alkali industry, producing, with De Nora membrane electrolysers, soda and chlorine, with pure hydrogen, as a by-product. Estimations made by CLC-Ansaldo have found that with the flow of hydrogen it is possible to generate 9/10 MWel by employing 10x900 kW d.c. hydrogen modules at 50% electrical efficiency - since no reformer would be required. This is a perfect example of " niche " for FC : hydrogen in Assemini is burnt at present and fuel cells could be sold at marginal cost. However, payback time (6 years) due to "political " electricity costs ($0.03/kWh) for the 50 MW of the electrolysis, plus the subventions for coal mines in the close Sulcis region - where an all-purpose IGCC plant will be constructed - have won out so far. Moreover, industrial sources indicate that hydrogen might be sold to the close Sarroch refinery for petroleum cracking. Enichem is a major chemical group and Ansaldo a power plants supplier and a FC developer and licencee, through CLC : it is sometimes sad not to see some evident synergies at national level coming about faster.

2.4.2 - Molten Carbonate Fuel Cell

In high temperature systems the shortcomings of gas purity can be avoided since elevated temperatures accelerate the chemical processes, avoiding the need of a noble metal catalyst as platinum. There are two types of MCFC: the external reforming and the internal reforming. In the first, more conventional MCFC, the fuel is desulphurised and undergoes a reforming process before being fed to the anode. The internal reforming, also called direct fuel cell (DFC) simplifies the procedure thanks to a reforming catalyst in the anode chamber of the cell. The electrochemical reactions occuring in MCFC are[28] :

$$H2 + CO3-- \Rightarrow H2O + CO2 + 2 e- \qquad \text{(anode)}$$

$$1/2\ O2 + CO2 + 2 e- \Rightarrow CO3^{--} \qquad \text{(cathode)}$$

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[26] See C.R. Bentley (ERC): "Vendor development for commercialisation of fuel cells" EFC News, december 1996, special issue and B.R. Gilbert, M.Nawaz and T.P.Chen (Bechtel): "Fuel cells make their chemical process industry moves". Chemical Engineering, August 1995.

[27] See : D. Lan Nguyen : " GAZEL - SIG, Pile à Combustible au Gaz Naturel ", OFEN Annual Report 1996.

[28] From : " Fuel Cells - A Handbook ", (Revision 3) by J.H. Hirshenofer, D.B. Stauffer and R.R. Engleman. U.S. Department of Energy, Office of Fossil Energy, Mogantown Energy Technology Center, January 1994, p.4-1.

The overall reaction is:

$$H2 + 1/2\ O2 + CO2 \Rightarrow H2O + CO2$$

In some way, the MCFC technology goes beyond PAFC limitations and it involves similar commercial interests : fuel distributors and electricity producers. In addressing the competitive environment of energy production the research has been oriented towards a fuel cell which can directly convert conventional fuels, as methanol, gasoline, natural gas and ethanol. The MC technology simplifies the gas purification process, reduces electrode degradation and raises temperature for a topping cycle with a turbine. In the MCFC systems the high temperature (650°C) allows the direct processing of the fossil fuel into hydrogen for conversion into electricity. Nevertheless, CO_2 is required by the electrolyte in the process, which requires the fuel processor to be closely matched with the FC stack, thus necessitating dedicated reformer engineering for each size of the system. Applications are expected to get economies of scale and standardisation advantages in the range of few MW. One of the MCFC problems is that the power density of the cell is almost saturated, offering little perspectives of volume inprovements in the future. MCFC are direct concurrent to PAFC technology, which has low tolerance for CO and still suffers of quite high investment costs (also due to the precious metal catalyst).

2.4.2.1 - The MCFC proof : The Santa Clara Demonstration Project (SCDP)[29]

The 2.1 MW power plant construction started in April 1994 with the participation of the Fuel Cell Commercialisation Group (FCCG), a consortium of municipal, rural and investor-owned utilities in U.S. and Canada. The SCDP start-up activities began in March 1996, electricity generation began in April, but the plant had to be stopped in September because of insulation problems which affected 2 stacks. This was due to the high temperature of the fuel cell.

The MCFC is at the edge of commercialisation, since all the stack and BOP components are commercial, although series production has not started. The current weaknesses (which may increase operation & maintenance [O&M] costs in early commercialisation) are :

- Hardware corrosion by the electrolyte at high temperature (lifetime is expected to be 25.000 hours, eventually improved to 40.000).

- Dissolution of the nickel oxide cathode in the electrolyte creates a precipitate which causes short circuits in the system.

2.4.3 - Solid Oxide Fuel Cell

The solid oxide fuel cell (SOFC) technology is the one at the earliest stage of development, although its origins go back at the beginning of electrochemistry history. At the earlier days of electrochemistry research on conductivity was directed to try to replace the carbon filament, then used in the light bulb. Nernst realised a high performance Zirconia light source around 1893[30]. Because of its high operating temperature (1000°C), recent studies have considered lower temperatures for SOFC (600°C) and mobile applications feasibility, although the slow start-up is a major problem. The main advantage consists in the ability to oxidise the CO produced in the natural gas reforming.

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[29] See: European Fuel Cell Group 1996 Autumn Workshop: "MCFC needs" by Peterhans, S. and Santa Clara Demonstration Project web page: http://www.ttcorp.com/fccg/scdpnew1.htm.

[30] An interesting, detailed brochure is published by H. Möbius, : " On the History of Solid Oxide Fuel Cells.", J. of Solid State Electrochemistry 1 (1997).

There are three main configuration for a SOFC stack :

- The **Tubular** developped by Westinghouse, now licenced to Siemens (pre-commercial stage)
- The **Planar** conception of Sulzer Hexis^{TM} (pre-commercial)
- The **Monolithic** " Honeycomb " structure of Argonne National Laboratories (laboratory stage)

Overall expected efficiency of a MW-size SOFC power plant is up to 70%, though smaller systems without cogeneration would seldom exceed 40% efficiency. SOFC have problems of power stability when the FC is under load, but the multi-fuel possibilities, combined with the high grade heat for CHP make SOFC the ideal candidate for small scale units to shape a distributed power generation system in the future, if materials reliability is satisfactory.

2.4.4 - PEMFC

Ballard Power Systems is testing natural gas and methanol PEMFC stationary sytems and it has planned to start pre-commercial production of its 250 kW unit in 1998. The prototype started operation, grid-connected in August[31]. At present, European agents of Ballard products, AEG and GEC-Alsthom hope to install 250 kW units for electric utilities in Europe. These FC systems are designed to run on natural gas, but the fuel can be methanol or - of course - hydrogen. The system features a steam reformer, a water/gas shift and a more innovative selective oxidation unit, which is believed to include a precious metal catalyst[32]. Unfortunately, no operating data are available and cost is not fully disclosed yet, but it could be around 3 million US$ for pre-commercial units. The aimed strategy is to start full commercialisation after one year of tests in real condtions.

De Nora is at an earlier stage of development in stationary systems, its " new design " 30 kW-stack, is planned for 1998 ; such unit can be scaled to 50kW. The Italian company intends to start joint projects with utilities and it has active research on a CO purifier and on a CO-tolerant catalyst[33].

2.5 - Mobile Applications

As it is clearly explained by a car manufacturer expert, different domains and sciences are taken into consideration for mobile FC systems:

> " When a FC is used to propel a vehicle it shares several attributes with battery-powered vehicles (low or even zero-tailpipe emissions, low noise, modularity and reasonable shape flexibility, perhaps similar manufacturing processes, need for electric drivetrain, etc.) while its fuel/air intake and exaust pipes, the available waste heat for cabin warming, and the relatively high energy density/low cost/rapid refuelling of fuel storage system evoke comparison with conventional [ICE] vehicles and may help to overcome the main obstacles of batteries ".[34]

A special attention in the field of mobile FC systems has to be given to the all-round storage/stack optimisation[35]. If efficiency and lifetime are parameters to be relaxed - for a mobile FC system

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[31] Ballard Press release, September 1997.

[32] Selective oxidation, synonimous of Preferential oxidation, is treated in Ch. 5 - Hydrogen purification.

[33] See : C. Mantegazza, A. Maggiore : " PEMFC Activities at De Nora ", Proc. XI HEC, Stuttgart, October 1996.

[34] C.E. Borroni-Bird, Chrysler Corporation : " Fuel Cell commercialisation issues for light-duty applications ". J. of Power Sources 61 (1996) p 34.

[35] D. Schmal, and P.J. Van Duin, : " A method for the calculation of the minimum Fuel Cell system volume ". Proc XI Electric Vehicle Symposium Florence Italy. Vol. 2 pp. 1-9.

lifetimes of 5000 hours are acceptable - the cost of the FC powertrain has to compete with car engines.

2.5.1 - PEMFC

The economic and technical targets of mobile systems can only be fulfilled by the PEM technology; these are an investment cost of approx. 30$/kW (stack) and power density of 0.4kW/kg[36].

Recently, research has shifted from the stack power density to the fuel system definition and integration. The present goal of PEMFC industry is to create the conditions - e.g. system assessment, infrastructure, public acceptance - and set mass-manufacturing equipment to compete with conventional vehicles.

Besides the aspects of volume, weight and vehicle range, weight distribution, transient response and security in accident or fault situations are of major relevance for customer acceptance.

2.5.1.1 - Exemples of Fuel Cell Vehicles (FCV)

- Arthur D. Little is developing a gasoline reformer for a FC vehicle, the system featuring on-board partial oxidiser (POX), water-gas shift, and a preferential oxidizer (PROX) for fine-cleaning of hydrogen[37]. The gasoline reformer is jointly developed by A.D. Little with Chrysler ; the concept had an official presentation at the Detroit Motor Show in January 1997[38].

- Ballard has realised a pre-commercial 300 kW Bus and has developped the 60 kW Necar II with Daimler-Benz which is the state-of-the-art in FC vehicles for system weight, dimension and performances of speed and autonomy. The costs have been huge and only hydrogen is used, although the foreseen extra investment cost (compared to a diesel bus) for a FC bus - to come in 1998 - is expected to be 30 %.

- Daimler Benz is the first car manufacturer involved in FCV. The German company has unveiled the Necar III at the 57th International Motor Show, September 11-12, 1997 in Frankfurt. This FCV is " a long-awaited fuel cell version of Mercedes brand-new subcompact A-class model "[39] powered by a 50kW Ballard FC system featuring an on-board methanol reformer.

- De Nora is very active in the Joule and Brite European Programs by close co-operation with Ansaldo. The Italian company has supplied *standard* design FC stacks for the Euro Quebec Hydro-Hydrogen Pilot Project (EQHHPP) bus and it is co-operating with Renault, Volvo, Ansaldo Ricerche, Ecole des Mines and Air Liquide in the Fuel Cell Electric Vehicle for Efficiency and Range (FEVER) project. FEVER features 3x10kW improved design PEMFC to power in-wheel motors in a Laguna station wagon with 120 lt. (8 kg) liquid hydrogen tank and nickel-hydride for energy buffer and start up. The Hydro-Gen boat project, led by Ansaldo Ricerche (FC system, DC/AC converter), includes a 30 kW De Nora advanced design stack for the power generation[40] and liquid hydrogen system by Messer Griesheim.

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[36] These are the targets of the U.S. program Partnership for a New Generation of Vehicle (PNGV) in ref 35 above page 36.

[37] The CO clean-up - the most strategic research issue for FC system introduction - is discussed in Ch. 5.

[38] See web page : http ://www.arthurdlittle.com/tpd/fuel.htlm

[39] The Hydrogen & FC Letter, October 1997. Edited by Peter Hoffmann. Http ://www.mhw.net/~ hfcletter/.

[40] M. Tettamanti, A. Maggiore, : " De Nora informative brochure ", Milan, 1996.

- Siemens[41] has contracts with Solar-Wasserstoff-Bayern GmbH for a 10 kW fork-lift truck in the frame of the Bavarian government project for solar hydrogen technology development, in association with Bayernwerk AG, Linde and BMW. Hydrogen in the truck is stored in Metal Hydrides (MH).

- Toyota presented a hybrid RAV 4L FCV Jeep at the Tokyo Motor Show in October 1996, marking a record in metal hydride hydrogen storage[42]. The vehicle is powered by a 25 kW proprietary PEMFC stack with a nickel-hydride battery buffer for peak load and start up. Toyota has also unveiled a new version of the RAV 4L at the 1997 Frankfurt motor show : on-board methanol steam reformer, 500 km range and regenerative braking.[43]

It has to be noted that hydrogen is not a commercial fuel and suffers low energy density in its gaseous form (besides safety concerns). Liquid hydrogen sponsors include BMW which has proposed the concept of a " 1000 km FC car "[44], but the fuel cycle efficiency is heavily affected by the energy requirements for cryogenic storage (30 % of initial energy), and engineering costs are still prohibitive. It is so unlikely that in early commercialisation FC systems will use pure hydrogen as fuel except in the case of metal hydride storage, intensively pursued in Japan.

At present the crucial issue for viable mobile FC systems is the development of a compact unit generating CO-free hydrogen from a more friendly, *i.e.* liquid, fuel.

2.5.2 - Automaker interest in PEMFC

The Polymer Electrolyte technology has the best chances to reach both major performance targets and cost reductions (100/200 $/kW), some of the reasons being :

High Power density	up to 1 kW/lt.
Low temperature operation	70-90° C
Low cost materials	polymers, aluminium
Fast start up for intermittent operation	seconds.

Drive cycles studies[45] have shown that in light-load conditions and/or in an urban environment - the most common - FC have a net efficiency advantage compared to spark-ignition engines : 50% and 10% respectively. The FCV performances on the highway cycle are slighly above an ICE .

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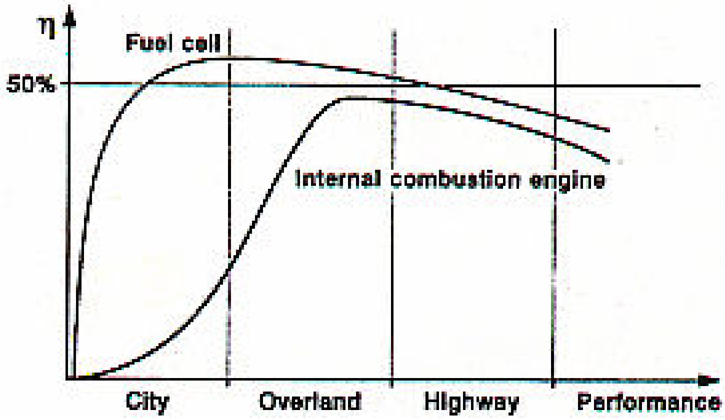
[41] W. Strobl : " Hydrogen as a road fuel for the future ; conditions and prerequisites " Proc. XI HEC, Stuttgart, 1996.
[42] See 4.3.1 for details on storage.
[43] More can be found in Hydrogen & Fuel Cell Letter, October 1997.
[44] J. Tachtler, C. Bourne : " Fuel Cell Systems for Passenger Cars - Opportunities and Requirements ". Fuel Cell Seminar, 1996, Orlando.
[45] Ref 35, page 34.



Graph. 2.1 - Efficiency of FC vs. ICE (Ref.35)

In the Graph 2.1 it should be noted that the comparison is between two different types of systems :

- An on-board FC system, where a FC produces electricity for a later conversion, via electric motors, to drive the wheels. If hydrogen it is stored into hydrides or produced in a reformer, then this system might include batteries for load variation.

- A non hybrid conventional systems with an internal combustion engine driving directly the wheels, the efficiency of the engine being particularly high.

A more rational comparison should be carried out between FC vehicular systems and hybrid internal combustion engine systems, which start to appear on the market. However this analysis goes beyond the scope of this report.

NOTE : Concepts for SOFC are being developped, by Dr U. Bossel and K. Yamada, because of the simpler fuel processor in a SOFC system (pre-reformer only). Nevertheless, the announced 2 minutes start up of a low temperature SOFC has yet to be demonstrated in real conditions[46].

2.6 - Conclusions

The FC technlogy is characterised by strong competition and interdisciplinarity, both where the power generation market and the vehicle industry are concerned. The FC system depends on the type of stack used, because balance of plant (BOP), or more precisely, engineering of the fuel processing, is very different.

It owns notice that higher temperatures allow a progressive " internalisation " of fuel reforming : in the low temperature FC all fuel processing is external. In PAFC there is some tolerance for CO up to some hundreds (2) ppm, avoiding the need for a fine purification step. In the case of MCFC the water/gas shift is eliminated, whilst in the case of SOFC the only gas processing is the pre-reforming of raw fuel.

Current trends in research find mobile applications of PEMFC as the most interesting, because PEMFC shock resistance, low temperature and impressive power density make them a credible solution to conciliate environment and mobility.

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[46] See Ulf G. Bossel : " SOFC in Transportation " EFC news December 1996.

Storage safety is considered as a major barrier for commercialisation of hydrogen-fuelled FC. Nevertheless, the promising improvements of hydrides storage, like the carbon nanotubes, offer chances of greater safety - and favorable cost projections, to compete with gasoline, provided customers do not need a vehicle range of more than 250 km.

The technical competition is therefore between hydrogen fuel with its storage and infrastructure problems, and the validation of concepts of preparing hydrogen on-board the vehicle, using logistic fuels.

Chapter 3 - PEMFC : Details, Issues & Improvements

In this chapter we describe the PEMFC stack and the relevant research issues, as the platinum loading on the electrode or the different stack approaches and related manufacturing techniques, *e.g.* machined bipolar plates vs. woven metal collector.

3.1 - Operating Principles

The basic element of a fuel cell is the membrane-electrode assembly (MEA), it consists of an electolyte phase in contact with a porous anode and cathode on either side. In a polymer electrolyte MEA the fuel - pure hydrogen or CO-free hydrogen-rich gas derived from another gaseous hydrocarbon - and the oxidant - oxygen or air - enter the anode and cathode respectively and generate electricity by the electrochemical oxidation of hydrogen and electrochemical reduction of oxygen.[1] A fuel cell stack consists of many individual cells connected in electrical series by bipolar separator plates. The different fuel cells reactions and MEA thiknesses are shown below [2] :

FC	Anode Reaction	Cathode Reaction	Current Density A/cm^2	Thickness mm
PEMFC	$H_2 \rightarrow 2H^+ + 2\,e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1 (4 on O_2)	0.5
AFC	$H_2 + 2OH^- \rightarrow 2H_2O + 2\,e^-$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	1 (O_2 only)	5
PAFC	$H_2 \rightarrow 2H^+ + 2\,e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	0.7	2
MCFC	$H_2 + CO^{=}_3 \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^{=} \rightarrow 2CO_2 + 2e^-$	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO^{=}_3$	0.15	2
SOFC	$H_2 + O^{=} \rightarrow H_2O + 2e^-$ $CO + O^{=} \rightarrow CO_2 + 2e^-$ $CH_4 + 4O^{=} \rightarrow 2H_2O + CO_2 + 8e^-$	$O_2 + 4e^- \rightarrow 2O^{=}$	1	0.7

Table 3.1 - FC Reactions and Current Densities

3.2 - PEMFC Module

The membrane-electrode assembly (MEA) is the heart of a FC. In every type of FC the MEA is « sandwitched » between two bipolar plates to « stack » together many individual modules, ensuring electrical contact between the electrodes. The FC stack is an electric series of modules. It is interesting to reach a full understanding of the elementary unit by decomposing its functions : we will try to describe the PEFC in a simple, accessible way, by the description, with the help of illustrations, of the basic components of a fuel cell stack, *i.e.* Membrane, Catalyst, Electrode, Bipolar and End Plates.

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[1] This reaction is also called « electrochemical combustion ».

[2] For completness I recall that Alkaline FC are still regarded by someone as a very promising technology - with high power density (up to 2 W/cm^2) - although little industrial interest has raised in recent years. For a good defence of AFC, and precious informations see K. Kordesch : « FC & their applications », VCH 1996.

A commonly used technique to prepare the membrane electrode assembly (MEA) is by hot pressing of catalyst-coated electrodes on the membrane.[3] An alternative procedure consists in spraying the catalysed electrode, on the membrane, with an electrolyte solution, such as liquid Nafion. During the manufacturing of MEA's, it is critical to ensure a good contact between the electrode, the catalyst and the electrolyte to create a three-phase boundary between gas, electrode and electrolyte, with fine gas diffusion, water removal at the cathode and heat transfer.

As experts clearly explain : « The secret of using PEM-film electrolytes lies in the method of bonding of electrodes to the surface, to give the most effective, three-phase electrolyte, electrocatalyst, gas-phase boundary, thereby making the best use of the electrocatalyst »[4].

The energy of electrochemical engines is derived from the free Gibbs energy (ΔG) of the electrochemical reactions taking place. To allow convenient comparison with heat engines the efficiency is expressed in terms of the heat of combustion of the fuel. For a hydrogen/oxygen FC we have :

$$H_2 \text{ (gas)} + \tfrac{1}{2} O_2 \text{ (gas)} = H_2O \text{ (liquid)}$$

The free energy change in normal conditions (25°C, 1 atm.) is :

$$\Delta G = 237.25 \text{ kJ/mol ,}$$

the higher heating value (HHV) of hydrogen is :

$$\Delta H = 285.91 \text{ kJ/mol ,}$$

the theoretical maximum efficiency of the FC is :

$$\Delta G/\Delta H = 237.25/285.91 = 83\ \% \text{ (98.1\% taking LHV).}$$

3.2.1 - The Membrane.

Electrolyte membranes used in FC and electrolysers have the distinctive feature to block molecular species to let pass ions. The early PEMFC, conceived by Grubb[5] were using hydrocarbon-type polymer membranes such as cross-linked polystyrene-divinylbenzene-sulfonic acid and sulfonated phenolformaldehyde. The Gemini Space Program 1 kW PEMFC - 30 kg weight and operating at 1.5/2 bars on pure hydrogen and oxygen - also employed polystyrene-divinylbenzene-sulfonic acid, but crosslinked with an inert fluorocarbon film. It was observed that hydrocarbon-based polymers suffered an oxidative degradation, due to the cleavage of the C : H bonds, affecting in particular the α-H where the functional sulfonic group is attached, thus limiting the cell life. In the eighties a much more stable perfluorinated membrane was developed by DuPont de Nemour - Nafion^{TM} - which is still the reference in Electrochemical PEM research. In 1992 a further development was achieved with a DOW membrane - XUS - which has allowed Ballard's stacks to almost double the current density

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[3] U.S. Patent No. 3,134,697

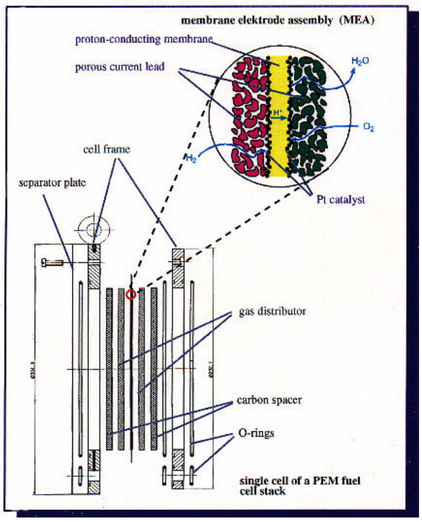
[4] Professor Giuseppe Faita *et al.* DeNora Parmelec, U.S. Patent N°5,482,792.

[5] W.T. Grubb : « Proceedings of the 11th Annual Battery Research and Development Conference », PSC Publications Commitee, Red Bank, NJ (1957) ; U.S. Patent No. 2,913,511 (1959).

from the earlier ones[6]. The membrane appears like a thin sheet of plastic, it has good mechanical strength and ideally has to ensure good ionic conduction while blocking electric current. The PEM has a very hydrophobic component - the (co) polymer - chemically bound to hydrophilic sulfonic groups (SO_3). Today the most used membranes are produced by Asahi and DuPont.[7] Their cost varies from 500 to 900 US$/m^2.

3.2.2 - Electrode

The current densities available from smooth electrodes are usually in the range of a few mA/cm^2 because of rate limiting processes such as the available area of reaction sites. The availability of porous electrodes has changed the specific conditions of current collection within the fuel cell and current densities up to 4A/cm^2 are today possible in laboratory experiments driven at optimal conditions, *i.e.* oxygen feed. The porous electrode has a high specific surface area enabling « dense » electron flow and the physical structure allows good mass-transport of reactants and products to and from the electrolyte interface. Porous electrodes, used in low temperature FC, *i.e.* alkaline and PEM, consist of a high surface area carbon black and a polytetrafluorethylene (PTFE) binder which acts as wet-proofing agent, with dispersed catalyst to increase the reaction rate.[8] The composite structure of PTFE and carbon establishes an extensive adsorption surface within the porous electrode. The membrane-electrode assembly with gas-insulator plates is called FC module.



Graph 3.1 - FC stack and M&A (source KFA, Jülich).

3.3 - Module Key Parameters

Some specific measurements of electrochemistry are taken in the PEMFC research. Besides the electric current, voltage, temperature and ohmic losses, we find more specific T and p, membrane hydration and water transport.

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[6] K. Prater : « The Renaissance of the Solid Polymer Fuel Cell », Journal of Power Sources No. 29, 1990.

[7] A variety of articles is offered in : J. of Electrochemistry, Electrochimica Acta and PSI General Energy volume and Dais web-page. One of the main goals of this latest years research has been the development of a membrane with same stability as DuPont's Nafions (112, 115, 117) at lower costs and with less or without the toxic fluorine *e.g.* hydrocarbon cross linkers in Dais (styréne-butyléne) and PSI (styrene-grafted) membranes. Other are produced by 3M and Gore.

[8] Specific PEM electrode are produced, for exemple, by Johnson Matthey (UK) and E-Tek (USA).

3.3.1 - Current density

The CD depends on gas-diffusion, membrane transportation capacity and catalyst efficiency. It gives, at the laboratory scale, in A/cm^2, a good indication of individual cell performance. Current densities of low-temperature FC are higher than other FC technologies : 1-2 A/cm^2, (air operation),[9] whilst MCFC perform 0.15 A/cm^2 and SOFC reach 1 A/cm^2, these values may assume a working voltage of each cell of 0.65 volts.

3.3.2 - Overvoltage

The theoretical maximum voltage, called open circuit voltage (OCV), of a hydrogen/oxygen reversible cell, operating at 1atm and water product (HHV) will be numerically equal to the hydrogen Gibbs energy of reaction :

$$\Delta G = 237.25 \text{ kJ/mol},$$

since 1 mol = 6.023×10^{23} molecules (Avogadro's number), for each molecule of product this reaction has an electric charge equal to that on two hydrogen ions transfered from the anode to the cathode. The charge of a hydrogen ion is 1.602×10^{-19} coulombs, hence $2 \times 6.23 \times 10^{23} \times 1.602 \times 10^{-19}$ units of electrical charge per mole cross the potential gradient created by the cell voltage (E). The product of the charge on the hydrogen ion and Avogadro's number is the Faraday (F = 96489 Coulomb/Volt) or, because the highest possible work of this reaction is ΔG, the OCV of a perfectly reversible FC is :

$$E_{rev} = - \Delta G/2F = 237.25 \times 10^3/2 \times 96489 = 1.23 \text{ volts.}$$

This theoretical voltage cannot be reached because irreversible losses occur when gases are not in the standard state and net current flows. Irreversible losses occur as well due to slowness of reaction, concentration changes due to diffusion, and finally for internal resistance. In low temperature FC - like PEM - the largest losses occur due to the cathodic (oxygen reduction) kinetics ; these can be heavily affected if too much water is flooding the cathode at high current densities.[10]

The overvoltage is the difference between the Open Circuit Voltage, V_0 (idle state) and the Terminal Voltage under operating conditions. The overvoltage is an indicator of the losses in a galvanic element under the conditions of delivering current. The ohmic resistance R is derived from current i ; R is determined by the kinetics of electrode reactions, by the physical structure (geometry) of the cell and the materials used. The relation is described by the equation :

$$V = V_0 - iR$$

The internal resistance R arises from :

- **Activation polarisation** present at low current is due to the limited surface area and activity of the catalyst,

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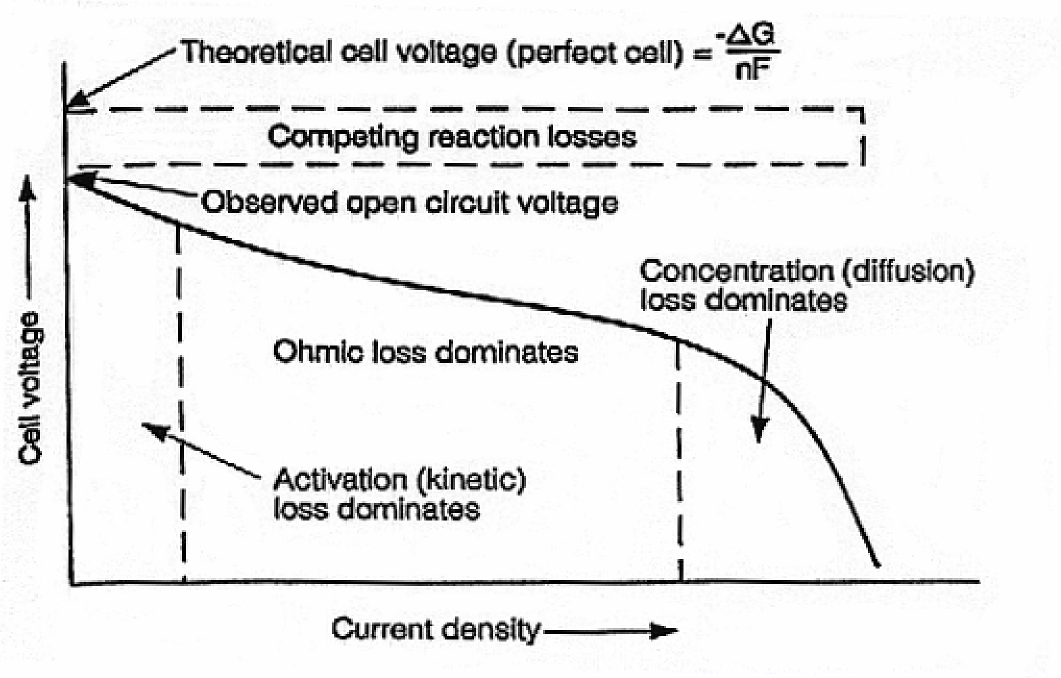
[9] European Commission : « A 10 Year Fuel Cell Research, Development and Demonstration Strategy for Europe ».

[10] See Ch.3.4.3.3 Water Removal.

- **Ohmic resistance** arising from the resistance of the electron and ion flow through the electrode and electrolyte

- **Concentration polarisation** begins at high currents and results from depletion of reagents at the three-phase boundary.



Graph 3.2 - Volts vs. A/cm^2

3.3.3 - Platinum loading

The amount of precious metal catalyst is a key parameter in FC economics since platinum, the ideal catalyst, costs approximately US$ 20/gm. In PEMFC the content of Pt is measured in milligrams.cm^{-2} deposited on the electrode on a carbon black support. Crucial issue has been the development of manufacturing techniques for obtaining finer distribution of active metal particles to increase catalyst dispersion, thus minimising the noble metal content. From a reference value of 4 mg/cm^2 of the General Electric/Hamilton Standard-United Technology stack, the Gemini space flight model[11], the platinum loading is now between 1 and 0.5 on the anode and 0.5 at the cathode.

3.4 - PEMFC Stacks

A FC stack includes MEA sandwiched between bipolar plates, an humidification section (if the stack is internally humidified), cooling plates, end plates, water removal system, tie rods and possibly sealing.

3.4.1 - The Principle : Useful Voltage Output

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[11] U.S. Patent No.3,134,697

A FC stack consists of many modules in electrical series. In such a configuration the electric current delivered will be that produced by each element, but the total voltage will be the sum of the voltages of each module.

3.4.2 - Bipolar Plates

Bipolar Plates (BP) are the interconnection element between MEA's ; they realize a more compact stack because the anode of one cell is in electrical contact with the cathode of the following one, while maintaining separation of reactants. In the field of stack engineering, for many years the main problem has been ensuring a series of FC modules in a compact frame by means of cheaply-produced BP.

The BP ensure electrical connectivity, gas distribution and separation, heat removal and management of the liquid water produced.

The stacks of the different FC companies can be distinguished by the design of the bipolar plates :

- Ballard started with graphite-machined bipolar plates but produces now metallic-grooved units. The design of grooves along the surface of the bipolar plate is of major importance for cell efficiency and durability : while at the anode a fine gas distribution, current collection, membrane humidification and heat transfer have to be preserved, at the cathode water removal and air delivery add complexity. It has been proven that a cross flow geometry in gas distribution improves reaction speed, but to ease water removal vertical grooves are more suited.

- De Nora has chosen to follow a metallic approach which is claimed to be best suited for mass production. Their design is characterised by a gasket matrix where electrode and collector are fitted. The collector, derived from electrolysis technology, is metallic - preferably aluminium - sheet and it can be produced with inexpensive techniques. The BP of De Nora FC is a flat metal frame, which accomplishes the functions of transmission of the electric current through the cell elements, the release of heat to the external environment, and gas separation.[12]

- Siemens' design involves corrugated metal sheets with an internal cooling fluid. The manufacturing is done by stamping techniques.[13]

3.4.3 - Stack Key Parameters

3.4.3.1 - Specific Weight (Power Density in kW/kg)

Ballard accomplished major progresses by replacing the DuPont membrane with a new, high conductive membrane from Dow Chemicals (XUS), but costs pushed the company to develop its own partially-fluorinated polymer. Power density (W/kg) improved of a factor 25

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[12] U.S. Patent N°5,482,792.

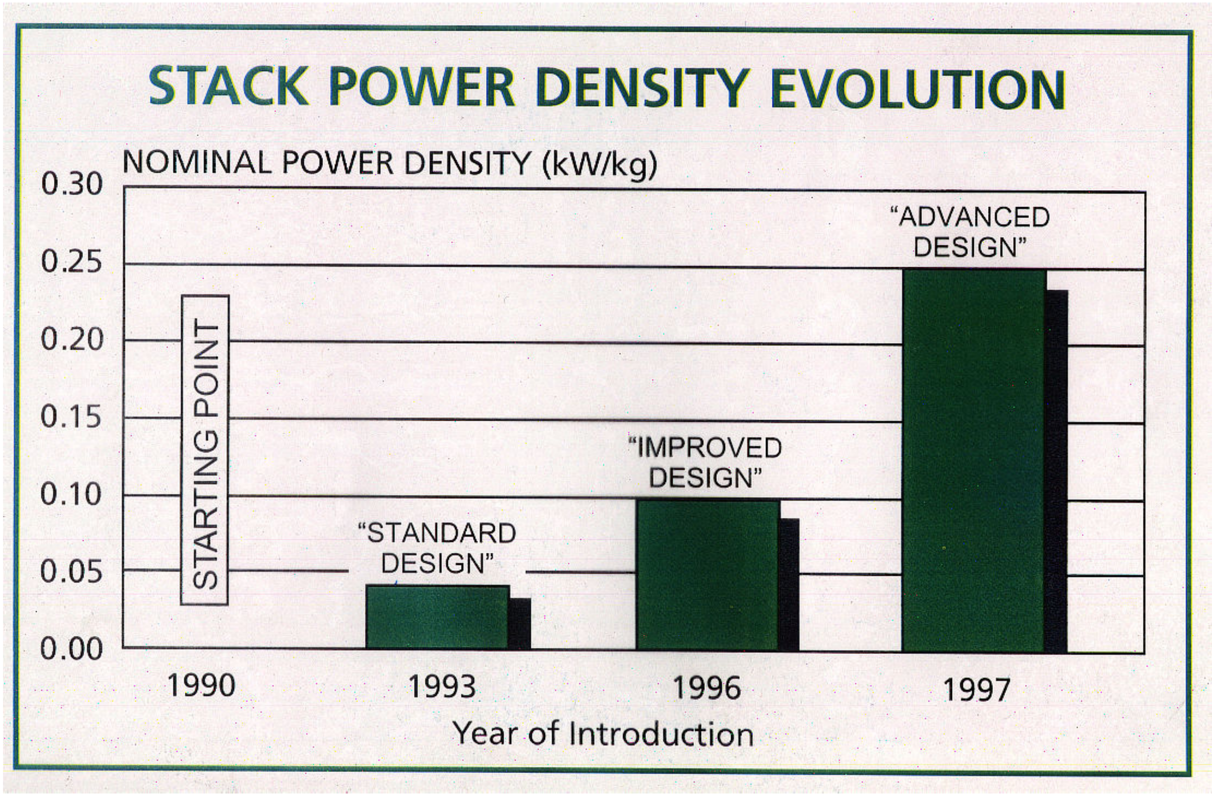
[13] E. Grecksch & T. Moser : « PEM Fuel Cells : Development and Commercialisation », Intertech Conference, Chicago, september 1996.

(>1kW/lt), *i.e.* the same « box » which used to produce 1 kW now is rated to 25/30 kW.[14] Moreover, the perspectives of cost reduction on all the FC components - *i.e.* catalyst diffusion,[15] membrane, bipolar plates - make the Proton Exchange Membrane Fuel Cell the only alternative to ICE for transportation. Fresh assessments of this statement are found in hybrid car projects or battery substitution for full FC power.[16] De Nora stacks have gone from 0.1 to 0.27 kW/kg ; air-cooled and air-breathing stacks are expected to increase these values.

3.4.3.2 - Specific volume (kW/lt)

Improvements in this domain reflect those registered above : Ballard's stacks have passed from 0.3 to 1 kW/1t (peak power). DeNora's have attained the threshold of 0.13 kW/lt requested by the European Community program to finance mobile applications. In the course of 1997 DeNora will present its new design stack, with 0.43 kW/lt to be employed in the HYDRO-GEN vehicle project.

In the Graph 3.3 below we can see the improvements in power density of De Nora stacks. The FC in 1993 delivered 0.05kW/kg doubled in 1996, while in 1997 this value has risen to 0.25kW/kg (0.32 peak). This 5-fold improvement was realized with thinner electrodes, but especially by advances in bipolar plate technology.



Graph 3.3 - Stack improvements - De Nora.

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[14] See : K. Prater : « SPFC for Transport and Stationary applications », Journal of Power Sources 61 (1996).

[15] See Ch. 3.3.3 - Platinum loading.

[16] Ballard developped the first generation bus with unoptimized stack at this pourpose. See K. Prater, Journal of Power Sources, 1992,1994, 1996. See also A. Brunia, C.E. Kluiters, D. Schmal: « Battery selection and testing for a fuel cell/battery hybrid electric cars » TNO - Environmental Sciences, in 27th ISATA, 1994 Aachen, Gemany.

3.4.3.3 - Water Removal

One peculiarity of PEFC is that water is produced in the liquid state and not as steam, hence the need of good hydration of the membrane to provide ionic conductivity is balanced by the risk of electrode flooding. Normally the water is removed from the back diffusion at the cathode by an excess of air flow, typically twice what is required for oxidation in the stack. An original method of water management was introduced by Ballard,[17] - « Anode Water Removal » - where excess air and a concentration gradient bring back the water to the anode to humidify the membrane and keep dry the cathode. In this way fuel and oxidant do not need to be water-saturated to humidify the membrane, whilst allowing low air pressure, high and stable peak current and water removal by the fuel stream.

3.4.3.4 - Heat removal

The stack needs to be cooled to 80°C. The management of heat can be performed by air or gas circulation within holes in the bipolar plates. In the case of liquid coolant, required for large systems, the water exaust can be cooled down and re-cycled by mean of a water circulating system. This function can be optimised by an appropriate heat exchanger, to release heat at the fuel gas processing stage or for space heating.

3.4.3.5 - Anode and Cathode Pressure

The FC power increases with the operating pressure but systems become complicated ; it is therefore normal to operate the cell at near-atmospheric pressure. The most recent stacks developed by Ballard, Siemens and De Nora work between 1 and 3 bars. It is believed that vehicular FC systems will operate at a slightly higher (4 bars) pressure to obtain a higher current. Even if operation at high current has consequences on the voltage efficiency, the dynamic behaviour and the possibility of recovery from the gas exhausts are believed to be more suited for mobile applications.[18]

3.5 - Conclusions

We can see a feature of FC technology : it consists in the inherent interdependency of every element involved in the system. So, for exemple, research for an hydrogen/air FC to improve on the Alkaline technology (Hydrogen/Oxygen only) by a stable solid electrolyte - the membrane - converged with efforts to lower the platinum content in the catalyst by means of better dispersion of Pt particles on electrically conductive Carbon Black.

The improvements in the engineering of the stack and module have been impressive, considering the small amount of funds and the time frame to pass from lab scale innovations to pre-commercial testing of a bus having has a goal to be commercially operated on the roads of Chicago and Vancouver : Ballard's « Coldstream » or the NEBUS by DB and car-makers involvement confirms it.

It is reasonable to think that the unique peculiarities of the PEMFC technology, after having frozen budgets for AFC and PAFC mobile projects, will be increasingly supported from

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[17] K.B.Prater : « PEFC : a review of recent development », Journal of Power Sources, 51 (1994), pag.138.

[18] Fuel processor for FCV might include a scroll expander recovering 10.2 kW on a 50 kW_{el} system at 70% efficiency (A.D.Little, Multi Fuel Reformers for FC in Transportation, May 1994) in Ch. 5.

national programs and private industry funds, for both transportation and power generation. The PEMFC has high energy efficiencies as well as environmental advantages and research is now devoted to achieve large cost reductions for fuel processor and system integration : compact and cheap alcohol and hydrocarbon reformers. Advanced Fuel Cell systems studies are providing the balance of plant (BOP) components for PEFC operation on commercially available fuels.

Direct Methanol Fuel Cells[19] are being developped because no fuel processing system is required and methanol is a renewable fuel. However, DMFC suffer low current density (0.3A/cm^2) and reformer emissions can include formic acid and formaldeyde, which are hazardous to health.

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[19] M.P. Hogarth *et al.* Johnson Matthey : « Direct Methanol FC Technological Advances and further Requirements », in EFC News, March 1997, copyright « Platinum Metals Review ».

Chapter 4 - PEMFC - The Choice of the System

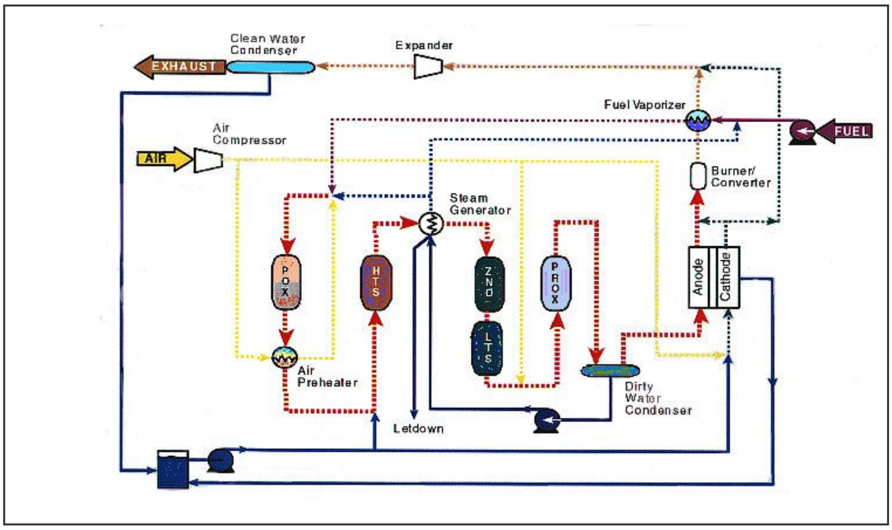
4.1 - PEMFC Systems

We have so far described what a Fuel Cell is, how it works and who develops FC, but in order to suppress any undue impression of idealist environmentalism, it is recalled that FC are not batteries, *i.e.* the fuel has to be stored outside the cell. This is an advantage since neither the fuel, nor the reaction products are confined - thus limited - by the FC volume and very high power densities are attained without suffering long recharging times and low part-load efficiency. Nevertheless, hydrogen (PEMFC fuel) is the lightest of elements, harder to store than liquid fuels and mostly confined to large-scale, albeit varied, industrial processes like ammonia production and oil refining.

The hydrogen literature offers the image of a *chicken and egg* dilemma to approach the complexity of choices to introduce a widespread use of hydrogen for FC : the system needs to be mass-produced to advance its learning courve, but to be mass produced it needs a reliable infrastructure, worth making if mass consumption takes place.

Breaking this circular logic is a crucial issue for every (power generating) technology. PEMFC need very pure hydrogen; it is compulsory to analyse the issue of gas production, storage and distribution, which characterizes the FC system: we enter the fuel-strategy debate.

The general PEMFC system is :



Graph 4.1 - A FC system

The BOP (electric equipment) can differ largely depending on the FC application taken into consideration, *e.g.* neighborhood power supply, vehicle powertrain etc. There are three basic markets for polymer FC considered in the literature[1] :

- Mobile systems or drivetrains - The ZEV market offers huge possibilities for PEMFC since it is unlikely that batteries will provide driving range and recharge times acceptable for

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[1] A more detailed segments definition is possible within each market (Ch.6), here we mean to point out the wide range of applications for PEMFC, while underlying the economics of scale potential of FC car mass-production.

customers' requirements. Cost and security thresholds are particularly hard, but they will be overcome, reaching 20-50 $\$/kW_{el}$, during the next decade.

- Semi-mobile or portable - This application can go from a few watts to few kW. It is likely that « premium » off-grid location application will benefit from the unique features of the FC. Concepts in this domain include marine (or mountain) leisure generators, toys, lap-top computers and communication or metering devices.

- Combined Heat and Power (CHP) packages for decentralized power supply - The power range is between 10 and 250 kW, these systems have a fuel processor, unless located near a hydrogen stream. The main fuels considered to date are natural gas and methanol although R&D is under way to develop processes for conversion of LPG and gasoline-type fuels.[2]

4.2 - Storage Solutions.

There are many ways to store hydrogen. Compared to hydrocarbons, hydrogen has a high specific heat but a low energy density. Hydrogen is most concentrated in its liquid form at -253°C, but cryogenic storage is an energy-intensive process, losing 30 % of the initial heating value.[3] Nevertheless, Ford, BMW and Siemens are developing a concept for a 1000 km range FC vehicle, and major FC projects, like the EQHHP bus and the Joule hydrogen boat, both led by Ansaldo, are employing liquid hydrogen.[4] Older mobile FC prototypes have employed non-carbon-containing carriers like ammonia and hydrazine, but this is history.

Besides the liquid hydrogen option, FC vehicle fuel systems will either include an on-board reformer to « extract » hydrogen from fossil fuels (or alcohols), or pure hydrogen in metal hydride, which might be the favorite choice of the Japanese car industry.

Stationary FC systems are not limited by volume constraints and the main issue is the reliability of the gas reforming process ; favourite fuels are natural gas, alcohols and LPG.

4.2.1 - Safety

The common perception of hydrogen is highly negative. The flammability range, when mixed with air, at ambient pressure goes from 4 to 75% and it has been associated with highly-advertised accidents, *e.g.* Zeppelin Hindenburg and Space Shuttle.[5]

Serious and complete tests led by NASA have shown that hydrogen it is not more dangerous than natural gas, or gasoline, since in real-life applications low concentrations are the most common and in such case all fuel gases form explosive mixtures with air. Moreover, a hydrogen flame radiates almost no heat. Detonation concentration limit is 1% for gasoline and 4 % for hydrogen. NASA has being handling hydrogen since the 60's and have recorded no fatal accident caused by the hydrogen fuel itself. Flame speed is very high, which makes it

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[2] A broader analysis of gas reforming is on Cp.5.

[3] J. Odgen et al. « Hydrogen Energy System Studies », in Proceedings of the Coral Gables Meeting, International Hydrogen Energy Association 1995.

[4] Ansaldo has also developed a brassboard methanol reformer, but to date no demonstration project was reported.

[5] Details are given by « The Hindenburg Incident : cause and effect ». Addison Bain, NASA, 8th Annual U.S. Hydrogen Meeting, 11-13 March 1997, Alexandria, Virginia.

burn fast rather than spread out, this is unlikely to occur with other fuels having vapours heavier than air, as gasoline.

The ease of dispersion should be considered in commercial products by proper designs taking advantage of hydrogen buoyancy compared to air. FC systems could have a catalytic burner for hydrogen detection - *e.g.* platinum - without the need for odorants or colorants, which detract from fuel quality and will add complexity in the clean up.[6]

Hydrogen storage in hydrides is very promising in small scale hydrogen storage units, because of their extremely high safety (well above gasoline) and low compression-energy requirements (approx. 10 bars). In case of accident a broken hydride tank would pour granular material - the metal hydride or, when available, carbon nanotubes - without releasing hydrogen unless a heat source is close, and even in that case it would not explode but burn smoothly. One of the advantages of hydride storage is that the tank can be shaped into available free spaces as today car fuel tanks, with no geometrical restriction.

4.2.2 - Hydrogen energy cost, density and energy requirements

Hydrogen distribution costs are mainly determined by two parameters of the storage technologies : 1) The Energy Density of the storage system by weight and volume. 2) The Energy Requirements for the hydrogen storage-release cycle.

In the Table 4.1 below the energy requirements and costs of three different hydrogen storage systems are given. Liquid hydrogen has very high densities and energy requirements, while metal hydride storage requires less energy to store but system weight (not shown) is unfavourable.

Storage System	Liquid	Criogenic	Microspheres	Hydrides
Temperature	20K	80K	250°C	250°C
Pressure (bar)	<6	240	620	13
Density (kg H_2/m^3system)	50	40	20	50
Storage energy penalty (% of stored H for storage cycle)	35	25	10	waste heat
Capital Cost ($/GJ)	1000	4000	3000	3333
$ per kg of H_2 stored	112	480	360	400

Table 4.1 - Storage systems.[7]

Liquid hydrogen is certainly the most dense form of hydrogen for delivery ; it has excellent purity for a PEMFC and it can be economically produced and delivered from a large reforming plant.

Gaseous hydrogen is the cheapest option for a vehicle fleet with a medium-size refuelling station ; it is less energy-hungry and requires inexpensive material. Reinforced plastic tanks allow a pressure of 250 bars and FC vehicle can reach ranges of 400 km.

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[6] J. Gieshoff, K.Ledjeff-Hey : « Safety Device for Hydrogen Appliances ». Proc. XI HEC, Stuttgart 1996, pp 2355-2360.

[7] Source : G.D. Berry : « Hydrogen as a Transportation Fuel : Costs and Benefits », Lawrence Livermore National Laboratories, March 1996 page 25.

4.2.3 - Relevant Projects' Storage Solutions

On-board improved-storage exemples are :

- LH_2 (-253°C) to improve at most the vehicle's range in the BMW approach [8]

- Methanol (CH_3OH), as suggested by Mercedes [9] after the presentation of the NeCar III, is safely storable but polluting in the processing since aldehydes can be formed.

- Improved high-density metal hydrides (MH) in the Toyota RAV 4L vehicle.[10]

- Compressed gaseous H_2 in light alloy tanks (300bars) in the Ballard-Daimler Benz commercial prototype bus.

In approaching the fuel storage issue from a different direction than the natural gas/hydrogen path, Siemens and others are engaged in the research for a Direct Methanol Fuel Cell (DMFC). The advantages of methanol, renewable and liquid fuel as hydrogen carrier have led Daimler-Benz to choose on-board methanol reforming for their PEMFC transport systems.

4.2.4 - New Frontiers : Nanotubes

The search for a non-metallic hydride for storing hydrogen have considered Glass Microspheres (GM), but they have the disadvantage that low temperature and/or high pressure are required. GM are lighter and cheaper than metal hydrides.

The discovery of fullerenes, base of carbon nanotubes, has rewarded Prof. Richard E. Smalley with the Nobel Prize in Chemistry 1996. The base of carbon nanotubes is C_{60} a molecular aggregate of 60 carbon atoms which forms a sphere. Nanotubes are larger (C_{76} , C_{82}) carbon assemblies, extended to form an elliptic structure becoming, at theoretical limit, a tube. The substance can contain a great amount of hydrogen, does not have the heavy weight of metal hydrides and it is potentially inexpensive. Work under way at National Renewable Energy Laboratory[11] has shown that single-walled nanotubes (SWNTs) have better storage performance on both gravimetric (4%wt) and volumetric ($50kgH_2/m^3$) energy density compared to metal hydrides and activated carbons. The claimed achievement of 7 liters of molecular hydrogen adsorbed per gram of carbon (70%wt) by Dr. N. Rodriguez and T. Baker of Northeastern University has recently fired up interest for the technology.[12] Besides the hydrogen storage, carbon nanotubes might be utilized for electrically conductive plastics, filler material for plastics and bipolar plates, being harder and thinner than graphite. Daimler-Benz is testing nanotubes for hydrogen storage and the American company Hyperion foresee a cost of \$2 per pound.[13] A simplified view of C_{60} is given below.

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[8] Hettiger, W. and others: "Refueling equipment for liquid hydrogen vehicles". In XI Hydrogen Energy Conngress, Stuttgart 1996. BMW has proposed a 1000 km range FC car, see J. Tachtler : « Fuel Cells Systems For Passenger Cars - Opportunities and requirements », Fuel cell Seminar, Orlando Florida, 1996

[9] http:\\www.daimlerbenz.com/spotlite/necar/necar_e.h

[10] Hydrogen and Fuel Cell Letter October 1996.

[11] A.C. Dillon et al. « Storage of hydrogen in single-walled nanotubes ». Nature Vol.386, 1997.

[12] Hydrogen & Fuel Cell Letter, Editor Peter Hoffmann, March 1997.

[13] *Ibid*, June 97.

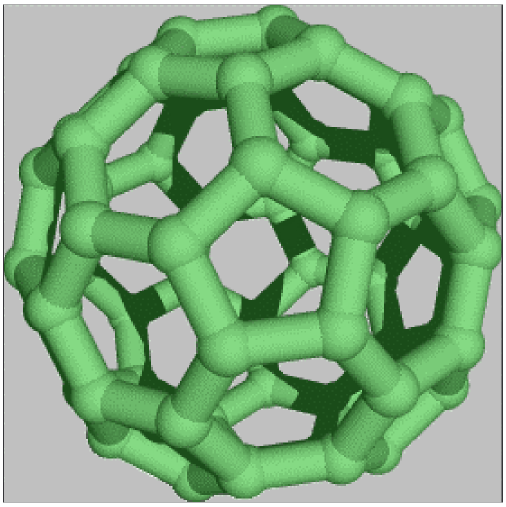

Figure 4.1 – Buckminsterfullerene (source : LANL).

4.3 - Fuel Feed Pump

Hydrogen - or the raw fuel feed - is delivered to the stack - or the reformer - by a customized high-safety gas regulator able to provide fine flow-metering for stoichiometric optimisation with air delivery and the water removal pump. In the case of an on-board reformer the fuel feed has to tune the gas/air (Partial Oxidation) or the gas/water (Steam Reforming) composition in order to provide optimal hydrogen generation, *i.e.* substoichiometric (0.5) air : fuel ratio for partial oxidation and excess (3) steam : fuel ratio for steam reforming.

4.4 - Air Compressor

In hydrogen/air FC the nitrogen contained in the ambient air remains inert at the cathode and is usually removed with excess air. Thus, the air blower can be responsible of more than a half of parasitic power consumption[14], although other sources[15] indicate that 15-20% of the FC output is lost to drive electrical compressors. The availability of low-pressure cathodes can reduce the size of the fan motor, with an increase of system efficiency.

Another important issue to be adressed is compressor efficiency decrease at part load. Since the PEFC is more efficient at part load it would be interesting to valorize this feature by development of air compressors which maintain a constant efficiency over the wide load range. Air is at 1.5 bar pressure in DeNora (advanced design) and Siemens stack, *i.e.* 0.5 bar overpressure. Cost for an unoptimized air delivery system is between 75-120 $\$/kW_{el}$.

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[14] K. Prater : « PEFC: a Review of Recent Developments », Journal of Power Sources 51 (1994).

[15] ETSU Report No.131.

A recent work[16] of Energy Partners Inc. defined a control strategy to drive the air compressor in a FCV. The FC performance was simulated in a dynamic stress cycle[17] (DSC), which reproduces vehicle requirements, under three strategies :

1) Constant pressure (ratio 3), constant flow rate (stoichiometry 2.5 at maximum power),
2) Constant pressure and variable flow rate (stoichiometry 2.5 througout the power range),
3) Variable pressure (ratio 1 to 3) variable flow rate (stoichiometry 2.5 througout the power range).

The flow rate is controllable in a variable speed compressor. The operating pressure can be regulated by a back pressure regulator at the exaust. Results indicate that the FC operates better when pressure and air flow rates are proportional to the power output : strategy 3 ; although strategy 2 shows very little difference in energy consumption and efficiency. The biggest savings of controlled operation are achieved at low power levels and at idle state.

4.4.1 - Oxygen Enrichment

The combination of an air separator with the fan can increase the efficiency of the FC by a greater proportion of oxygen in the oxidant stream. An exergy analysis of the option should be used for optimisation. A study to asses the energetic performance of a pressure swing absorption (PSA) unit to provide enriched air to the FC cathode is currently being pursued at the Institut Français du Petrole.[18]

4.5 - Power Conditioning and Process Control Unit

Cost for the complete electric system in the commercial PC 25 200kW PAFC is one third of the total FC system : 1000$/kW, but economies of mass production should lower the cost to 20$/kW. Efficiencies of the Electronic Control, Inverter and Transformer range around 70-95 % at full load. In most applications high-voltage DC output is more suited to maximise inverter efficiency: a stack with many modules and low area MEA's (≈100 V DC). Model and simulation studies[19] are useful to simulate cell operation under different regimes, *i.e.* stationary, transient and unstable, regarding cell, electric grid and system exploitation contraints.

4.5.1 - DC - AC Inverter

The efficiencies of different inverter technologies are quoted below. Mosfet and GTO technology efficiencies decrease at part-load, the software-controlled Insulated Gate Bi-polar Transistor technology can maintain > 90% over the load range. The table 4.2 summarizes the technology status.[20]

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[16] F. Barbir : « Control Strategy of a Vehicular Fuel Cell Power System », Hydrogen Energy Congress Proceedings, 1996.

[17] USABC Electric Vehicle Battery Test Manual : Revision 1, Report DOE/ID-10479, Idaho National Engineering Laboratory, July 1994.

[18] PhD Thesis : « Etude théorique et expérimentale de dispositifs d'enrichissement d'air en oxigène et de leur impact sur le fonctionnement des piles à combustibles », IFP, Centre d'Energétique, Sofia Antipolis.

[19] See J. Domergue, LEI - EPFL : « Modélisation et Simulation d'un système pile SOFC et convertisseurs de puissance associés », in co-operation with Direction des Etudes et Recherches of Eléctricité de France.

[20] Source : Prof. A. Rufer, LEI, EPFL.

TECHNOLOGY	*CURRENT STATUS*	*TARGET*	*Cost($/kW)*
MOSFET Efficiency	82-86%	95%	N/A
GTO Efficiency	86-90%	95%	N/A
IGBT Efficiency	95%	-	30

Table 4.2 - Inverter technologies

4.6 - Water Pump and Options

The reactants, hydrogen and air, being previously cleaned from impurities, mainly CO, are delivered to the FC stack, but a third element - water - is needed for two main functions :

- Stack cooling ; it is often accomplished by air or water circulating through a circuit, grooved within thicker plates or individual cooling plates.

- Membrane Electrolytes need to be hydrated to perform ion transport. Since the hydrogen ion is not mobile as a free proton it is surrounded by a hydration shell of one or more water molecules. PEMFC need humid hydrogen - at least 60% water - for fine water management through the membrane. Most FC stacks have an *internal* water management system.

DeNora's stack is internally humidified by appropriate modules sited close to the gas entry.[21] The cooling of water can be performed with a plastic, inexpensive heat exchanger, as proposed by Siemens.[22]

At the water exit site an optional hot water storage unit is often suited for washing and space heating (cogeneration use). In mobile reforming systems the water is fed back to the reformer and water/gas shift reactor.

A catalytic afterburner for anode off-gas can be employed for heating or adsorption cooling in cars and houses, besides eliminating safety concerns of residual volatile combustibles.

FC vehicles will probably need a battery buffer for start up and peak load shaving, because of slow reforming equipment response.

4.7 - Rationale & Paths

We can distinguish three main strategies for fuelling PEMFC stack. They all feature distinct advantages, either on an established technology or infrastructure implementation, or economics of the engineering, *i.e.* steam reformer, gasoline availability, methanol catalysis, but they also « bet » on some innovative devices enhanced by catalysis and material science to reach acceptable costs : friendly hydrogen cartridges (nanotubes), compact multi-fuel reformer and CO tolerance or removal (valid for path two and three).

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[21] See De Nora *Informative Brochure* and related pictures.

[22] See : E. Grecksch & T. Moser : « PEM Fuel Cells : Development and Commercialisation ». Intertech Conference, Commercialising Fuel Cells Vehicles, Chicago, september 1996.

The first path involves a hydrogen plant : from a large (>1MW) hydrogen plant to a 400 Nm^3/hr station, where reformed NG, coal, biomass or electrolytic, liquid or compressed H_2 is conditioned in bottles or hydrides for decentralized FC systems. Pipelines are considered to be economical only when a large hydrogen demand is established.[23] Reliability of steam reformers and environmental benefits are the advantages. This concept involves utilities and medium-sized industries and it is more suitable for Independent Power Producers (IPP) to enter both power generation and the transport applications of FC, lowering financial risk both in fuel production and FC system commercialisation. This path could benefit from improvements in low-pressure hydrides, as the aforementioned Nanotubes, because low-pressure storage increases the feasibility of small size electrolytic production facilities.

The second approach envisages a centralized synthetic fuel production and de-centralised reforming and electricity. In this case the option of methanol - the easiest to reform by the car processor – is the most probable. The car reformer can work at low temperatures (300°C), alcohols are convenient to store, renewable and their production is well known by chemists. The large-scale methanol strategy might be encouraged by expectations of research on Direct Methanol Fuel Cells and easy public acceptance. Technically, the methanol steam reformers produce some CO (1%vol.), which has to be removed before entering PEMFC anode (Ch.5).

Gasoline reforming can be seen as the « ecologically conservative » approach in the R&D of fuels for FC, avoiding risky changes in the existing fuel infrastructure.[24]. Fuel chemistry is oriented toward partial oxidation and autothermal reactors, fast-responding and able to treat gasoline, diesel, Jet-fuel or alcohols like ethanol. The target of fast response (max 10 sec.) already mentioned is a major bottleneck for reactors reaching 1000°C, while the issue of reforming hydrocarbons is more complex than for alcohols. This solution needs also validation for the CO removal system.

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[23] J.M. Odgen : « Hydrogen Energy Systems Studies », Proc. 1995 U.S. DOE Hydrogen Program Review, p 4.

[24] A.D.Little (web page : http://www.arthurdlittle.com/tpd/fuel.html) has presented a multi fuel reformer concept at the Detroit motor show January 1997. Intensive research on gasoline reforming processes is ongoing in the U.S.

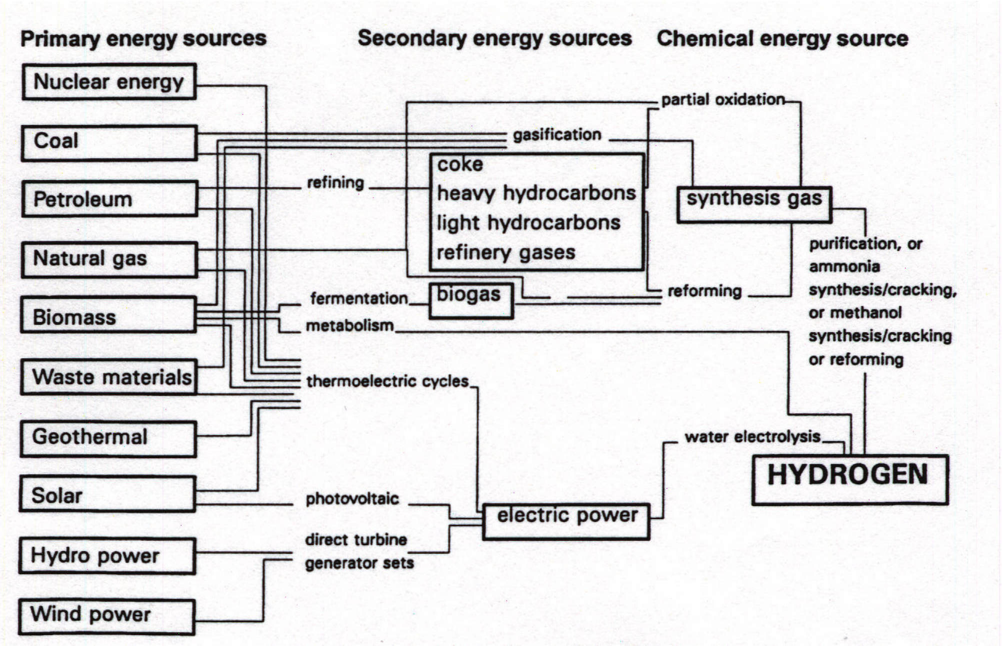
Chapter 5 - Fuels Chemistry

5.1 - Hydrogen carriers

The all-round optimisation of the energy conversion system takes broader significance when we look at the issue of fuel production and quality. Hydrogen can be produced from many different sources. For this reason hydrogen-related processes extract hydrogen from a « carrier » to minimise production factors outlays in producing and storing it.

One of the main lessons so far taken in FC research, is that FC systems engage a complex combination between economy of scale for fuel processing components - *e.g.* a reformer - with modular FC stacks, unlikely to be scaled-up to multi-MW size[1].

It is usual to refer to hydrogen as a energy vector because it is an intermediate product from fossil fuels or electrolysis (not an energy source or primary renewable) to be converted to electricity, mechanical or thermal energy after storage and on demand.



Graph 5.1 - Hydrogen carriers (Source : Dicks).

5.2 - Economics of Hydrogen production

The most economical hydrogen generating process for medium and large plants is Methane Steam Reforming (MSR). This statement is assumed to remain valid for the next 20 years.[2] Small production units can use Partial Oxidation (POX) or Autothermal processors (ATR), the last being considered suited for « pedal responsive » applications in automobiles. Renewable processes include electrolysis of water and pyrolysis of biomass to produce methanol. Renewable hydrogen production techniques might be profitably integrated and,

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[1] This is sharply affirmed in the European Commission Report : « Ten years of fuel cell research, development and demonstration strategy in Europe ». Directorate XII & XVII, Version 1995.

[2] A.L. Dicks : « Hydrogen generation from natural gas for the fuel cell systems of tomorrow ». J. of Power Sources 61 (1996) page 114.

having no CO_2 release on the whole fuel cycle if electricity is provided from renewable sources, have an advantage in the long-term perspective of a non-fossil based economy with possible applications in the electrification of developing countries.

A list of comparative hydrogen production costs is given below. Costs are given in 1990 US$. Some of the processes are not commercially avaiable (biomass), while others are undergoing quick development : partial oxidation can be scaled down to 10 kW_{el}. We detail further steam reforming and partial oxidation including their combination (ATR).

PROCESS	**READINESS**	**COST ($/GJ)**	**EFFICIENCY (%)**	
			ENERGY	**EXERGY**
Methane Steam Reforming	mature	5	86	78
Partial Oxydation of oil	mature	9		
Coal Gasification	mature	10	59	49
Hydroelectric electrolysis	mature	10-12	85	
Wind electrolysis	R&D/mature	30	NA	
Thermochem. Water Decomp.	early R&D	30-50	21	19
Solar PV Electrolysis	R&D/mature	30-50	8 (from state-of-the-art)	
Biomass gasification	R&D/mature	12	NA	
New...photoelectrolysis etc.	Laboratory	NA	NA	

Table 5.1 - Hydrogen generating processes.[3]

5.3 - Fuels Processing

Three different hydrogen generating processes are analysed : the steam reforming (SR), the partial oxydation (POX) and the catalytic partial oxidation (CPO) or autothermal reforming (ATR). We mention novel techniques of plasma cracking as the carbon black and hydrogen process (CB&H) and the « Plasmatron » ; the « Unmixed Combustion » process is also described.

Many studies have been done on hydrogen production technologies and its use in fuel cell systems. Our approach is to revisit the technical possibilities, with a new set of environmental, economical and systems questions in mind.

The analysis concentrates mainly on methane conversion to hydrogen, natural gas being a market of increasing competition, in order to assess the feasibility of a stationary system for decentralised electricity production, but we review progress on methanol and hydrocarbon reforming processes, since use in FC vehicles is becoming realistic and many projects are under way at the time of the writing.

We include models and operating results, when available with reformulated gasoline or ethanol.

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[3] Sources : H. Audus et al. : « Decarbonisation of Fossil Fuels : Hydrogen as an Energy Carrier », Proc. XI HEC, Stuttgart 1996. Cited from U.S. DOE : « Hydrogen programme implementation plan » (1990). M.A. Rosen for the efficiencies (XI HEC proceedings, 1996).

5.3.1 - Unwanted reactions

There are three reactions in the SR and POX which are unwanted :

Boudouard Carbon Formation (CO disproportionation)

$2CO \longleftrightarrow C + CO_2$

CO Reduction (Steam carbon)

$CO + H_2 \longleftrightarrow H_2O + C$

Thermal Cracking

$CH_4 \longleftrightarrow C + 2H_2$

5.4 - Steam Reforming (SR)

The major part of the world's hydrogen production (≈ 45 MT/y) is accomplished by the methane steam reforming (MSR) process. In a generally tubular reactor (Figure 5.1) a pressurized mix of sulphur-free methane and super-heated steam react over a nickel-based catalyst. This is generally followed by two - high and low temperature - adiabatic water/gas shift reactors to convert CO to CO_2 with extra steam and subsequently produce more hydrogen. The first stage HTS operates at 350-450°C and uses chromium promoted iron-oxide catalysts. The second stage (Low Temperature Shift) has a copper-zinc on alumina catalyst, operates at 150-250°C and can reduce CO concentration to about 0.5-2 % of dry gas. The LTS catalyst can be damaged by steam condensation, sulphur poisoning and sintering due to thermal excursions. Some of the hydrogen is first consumed for the catalytic (ZnO_2) hydro-desulphurator located upstream of the process.

This scheme is the base case since it is a standard, employed in the commecial PC 25^{TM} FC system.[4]

The steam reforming reaction is:

$$CH_4 + H_2O \quad \Rightarrow \quad CO + 3H_2 \qquad (\Delta H_{R\ (T=473K)} = +214\ \text{kJ/mol})$$

followed by the water-gas shift reaction (≈ 400°C):

$$CO + H_2O \quad \Rightarrow \quad CO_2 + H_2 \qquad (\Delta H_{R\ (T=473K)} = -39.4\ \text{kJ/mol})$$

The total reaction is:

$$CH_4 + H_2O \quad \Rightarrow \quad CO_2 + 4H_2$$

Half of the hydrogen is produced from the water. The steam reforming reaction is highly endothermic (T = 900°C at metal tube) and tubular metallic heat exchangers provide the heat

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[4] See Ch. 1.3.1.

for the reaction by burning off gas from the purification unit and/or FC anode. The SR process can have a high yield with a high steam to carbon ratio, *e.g.* 3 or 4, but it has a poor transient response since whenever a higher flow of hydrogen is demanded, the resulting higher reformer heat demand comes before extra anode off gas is available. Small (200kW) FC reformers have a start up time of 2 to 4 hours. The temperature has to be maintained uniform along the reformer stainless steel tubes.[5] The simplicity of operation and good yield are sometimes offset by the maintenance cost of the heat-exchange tubes and a general bulkyness of the system.

5.4.1 - Thermodynamic Efficiency

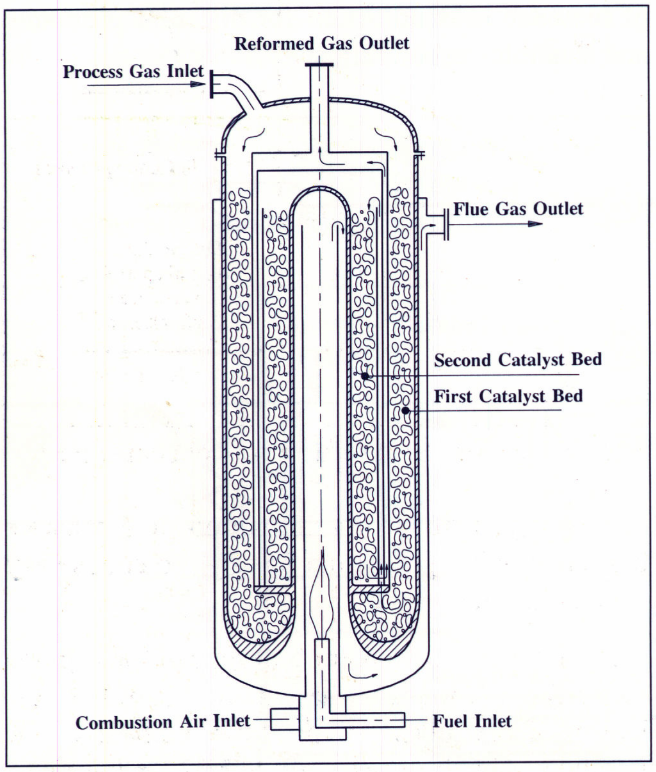

Figure 5.1 - Haldor Topsoe HER Design Steam Reformer

At reformer outlet the average gas composition is : 75% H_2, 13% CO, 10% CO_2, 2% CH_4. After the water-gas shift, 1Nm^3 of CO reacting with H_2O gives 1 Nm^3 of H_2, the proportions at the outlet are : 78/80% H_2, 20% CO_2 and between 2 and 0.5 % CO.

Having the following tables :

Molecule	ΔH_o LHV(kJ/Kmol)	Molecular weight (kg/kmol)	Cp (kJ/kg.K)
H_2	241.800	2	14.050
CH_4	802.300	16	2.165
CO	283.000	20	1.038

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[5] This is done with propietary convection control system in the Haldor Topsoe Concept-3 model.

Knowing that :

Kcal ⇒k J	1 kcal = 4.18 kJ
m^3 ⇒ kmol	22.3 m^3 = 1 kmol

The efficiency can be calculated as follows :

A reformer fed with 79 m^3 CH_4, of which 4 m^3 CH_4 are burnt, with a gas MIX of 155 m^3 with 1850 kcal/m^3 has an outlet of 320 m^3 of syngas (75% H_2, 13% CO, 10% CO_2, 2% CH_4). This output has an enthalpy equal to :

$\frac{320\ Nm^3/h}{22.3\ m^3/kmol}$ = 14.5 kmol/h ⇒ 75 % H_2 = 10.76 kmol/h
13 % CO = 1.86
10 % CO_2= 1.43 (no HV)
2 % CH_4 = 0.287 kmol/h

The outlet enthalpy is :

- H_2 = 10.76 * 241.800 = 2.601.798 kJ/h
- CO = 1.86 * 283.00 = 526.380
- CH_4 = 0.287 * 802.300 = 230.260

TOTAL = 3.358.408 kJ/h

The inlet enthalpy is :

- $\frac{75\ Nm^3\ CH_4/h}{22.3m^3/kmol}$ * 802.300 = 2.698.318 kJ/h
- 1850 kcal MIX/m^3 * 4.18 kJ/kcal * 155 m^3/h = 1.198.615
- 4/22.3 * 802.300 = 143.910

TOTAL = 4.040.864 kJ/h

η = 83.1 %

The leading companies for small scale (50-200 kW) steam reforming engineering are International Fuel Cells, Haldor Topsoe and Kinetics Technology International (KTI). Since estimated costs for a 50 kW reformer - delivering approximately 50 Nm^3H_2/h - are between 6000 and 8000 DM/kW[6] (without the water-gas shift), the pure MSR is found to be economical for powers higher than 100kW.

In an alternative design proposed by Medalert[7] the disadvantages of high alloy steel tubes of conventional reformers are (claimed to be) overcome by a porous ceramic tube made with alpha and gamma alumina, treated with nickel promoted with alkali metal salts. The tube functions as a membrane allowing hydrogen to flow through to promote an internal water-gas shift reaction of CO with steam. The advantages are lower operating temperatures (300°-600°) and a higher conversion, more than 90%, at lower steam to carbon ratios, *i.e.* 1:3-1:5. It is believed that further study will help to determine if state of the art permselective ceramics could improve the CO separation so that little or no further gas treatment would be necessary in the fuel processing system.[8]

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[6] J.B. Hansen, Haldor Topsoe, personal communication.

[7] U.S. patent No. 5.229.102

[8] A. Mc Evoy, Physical Chemistry, Chemistry Department, EPFL, personal communication. CO removal is treated in Ch. 5.5.

5.4.2 - Elements on Methanol Steam Reforming

Methanol is a liquid fuel which can be produced from renewable sources (biomass) and can be reformed at temperatures as low as 250°C. For a catalytic (copper zinc oxide) methanol reformer the reaction is :

$$CH_3OH + H_2O \quad \Rightarrow \quad CO_2 + 3H_2 \qquad (\Delta H_{R\,(T=298K)} = +131\ \text{kJ/mol})$$

The reaction product can consist of 75 % hydrogen and 25 % carbon dioxide ; 63 % of 131 kJ/mol (82) are required to vaporize the reactants. A steam-to-carbon ratio of 1.2 is assumed, 80 % of the hydrogen is consumed at the FC anode. The system uses FC off-gases to supply heat to the reformer and no high temperature shift is required.

The methanol steam reformer can be a very efficient hydrogen generator : 81 % based on the LHV of methanol. This results in projects concerning on-board methanol reformers for FC vehicles ongoing in Europe, Japan and in the U.S.[9]

5.5 - The Partial Oxidation process (POX)

The POX process oxidizes a hydrocarbon or an alcohol with oxygen - or air - in substoichiometric conditions. When air is used and nitrogen dilution in the product stream is not a disadvantage, the POX process may produce trace quantities (< 1%) of ammonia. The methane reaction is :

$$CH_4 + \tfrac{1}{2}\,O_2 = CO + 2\,H_2 \qquad (\Delta H_{298K} = -35.68\ \text{kJ/mol})$$

« The steam reforming of methane, though it has the advantage that it does not require expensive feed components, requires expensive, hard-to-maintain equipment to transfer the necessary heat to the reaction zone at a high temperature level. Due to the presence of catalysts, if the feedstock contains sulphur-bearing impurities, the reforming step must be preceded by a desulphurizing step to avoid poisoning of sulphur-sensitive reformer catalyst (Cox and Williamson, 1977) »[10].

The above-mentioned characteristics of the MSR reaction make it unsuited for the production of hydrogen in small or mobile FC systems, which are actually the most favorable application for PEFC technology. The catalytic partial oxidation for the production of hydrogen is under intensive development throughout the world. Since the exothermic nature of the reaction allows a decrease in size, costs and maintenance of the equipment, POX is probably the favourite process for on-board fuel conversion of FC vehicles.

The POX process can be high-temperature non catalytic (POX), catalytic (CPO) or integrated with a steam reforming reaction or autothermal (ATR).

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[9] At Foruschungzentrum Jülich GmbH (Ref. Journal of Power Sources 61 (1996), in Necar3 (DB), RAV4 (Toyota) and GM program (also including gasoline). The exemple is taken from R.Kumar : « Fuel Processing for Transportation Fuel Cell System », Argonne National Laboratories, First International Symposium of the New Materials for Fuel Cell Systems, Montreal, Canada, 1995.

[10] G.A. Karim, G. Zhou : « The Uncatalyzed Partial Oxidation of Methane for the Production of Hydrogen with Recirculation », J. of Energy Resources Technology, Vol 115, December 1993, page 307.

5.5.1 - Uncatalyzed Partial Oxidation

The partial oxidation requires high temperatures of the order of 1700K to ensure good conversion rates, the high temperature favors high conversion rates from both reaction rate and equilibrium standpoint. Possible oxidants for the conversion of methane are pure oxygen, oxygenated-air, a steam-oxygen mixture or a steam oxygenated-air mixture. The methane to oxygen ratio directly influences the reaction temperature. The problem is that the increasing in oxygen consumption will reduce the yield of hydrogen and carbon monoxide, thus producing more water and carbon dioxide. The production of hydrogen from hydrocarbon is anyway greater than in the MSR, where one half comes from the water, but the non catalytic POX can tolerate variations in the quality of the feedstock and does not require sulphur removal.The reaction is :

$$\underset{(1.5\ \text{vol})}{CH_4 + \tfrac{1}{2} O_2} \quad \Rightarrow \quad \underset{(3\ \text{vol})}{CO + 2H_2} \qquad (\Delta H_{R\,(T=473K)} = -283.6\ \text{kJ/mol})$$

Pressurized operation tends to increase the reaction speed, decrease the size of the equipment and improve gas separation, but it poses mechanical problems and reduces conversion as expected from equilibrium, since, as it can be seen from the equation, the product gas has larger volume than initial feed.

The temperature is often maintained constant by cooling with a steam recovery boiler the heat generated and approach an adiabatic process. The option of a heat exchanger between product gases and feedstock raises reactor insulation and operating temperature. Equilibrium is also approached by recirculation of reactive radicals, *e.g.* CH_3 , in the early stages of the process (1% by volume at 800K inlet).

Because of the high preheat required (material issues) and low efficiency of the POX process it is often preferred to use catalysts in order to speed the reaction at lower temperatures.[11]

5.5.2 - The Catalytic Partial Oxidation and Autothermal reformers

The Catalytic Partial Oxidation (CPO) has the same reaction as the POX but the use of catalysts eases the process at lower temperatures. CPO being an exothermic reaction, releases heat by a sub-stochiometric combustion. Research is oriented toward an internally heat-balanced reforming process : the autothermal reformer (ATR).

In the ATR the *in situ* oxidation zone of the reactor supplies the heat needed by the endothermic steam reforming reaction, which takes place in the same chamber. Autothermal reformers (ATR) are then an hybrid process between steam reforming and partial oxidation with high hydrogen yield and catalyst clean up by steam .

If SR high yield raises the efficiency, POX reactors advantages come also into consideration : better suited for conventional hydrocarbons such as LPG, straight run naphtha, gasoline.

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[11] Arthur D. Little « Development of a Catalytic Partial Oxidation Ethanol Reformer for Fuel Cell Applications », The Society of Automotive Engineers, Alternative Fuels Conference and Exposition, December 7, 1995.

ATR have a good transient response and are more compact than the traditional SR.[12] It is however worth mentioning that progresses are being made also in SR, in particular with methanol plate fin catalytic SR, developed by Gastech/Degussa and British Gas.[13]

A.D. Little has developped an ATR reactor which can run on ethanol or gasoline, employing a conventional nickel-based catalyst. The fuel-air ratio is 2 and optimal operation is achieved through fine mixing of reactants by evaporator and reactor design, thus avoiding carbon formation from poor dispersion. One of the advantages of the ATR is that the sulphur compounds do not damage the catalyst at temperatures above 800°C, while no undesired ammonia is produced. Operating results are given in the Table 5.2 below.

	Ethanol	Gasoline
Stack efficiency (LHV)[1]	51.2%	51.2
Fuel processor Efficiency (LHV)[2]	**84.2**	**78.3**
Pumps and Compressors (kW_{el})	- 4.1	- 4.2
Expander (kW_{el})	4.4	4.6
Fuel Input (kW_{th} LHV)	54.9	68.5
Gross FC DC power (kW_{el})	23.7	27.0
Net power (kW_{el})	23.9	27.4
LHV Gross system efficiency	43.0	40.2
LHV Net system efficiency	**43.3**	**40.8**

1) Fuel cell DC power out/total hydrogen to anode
2) Total H_2 to anode/total fuel input to system

Table 5.2 - A.D. Little Multi-fuel processor performance

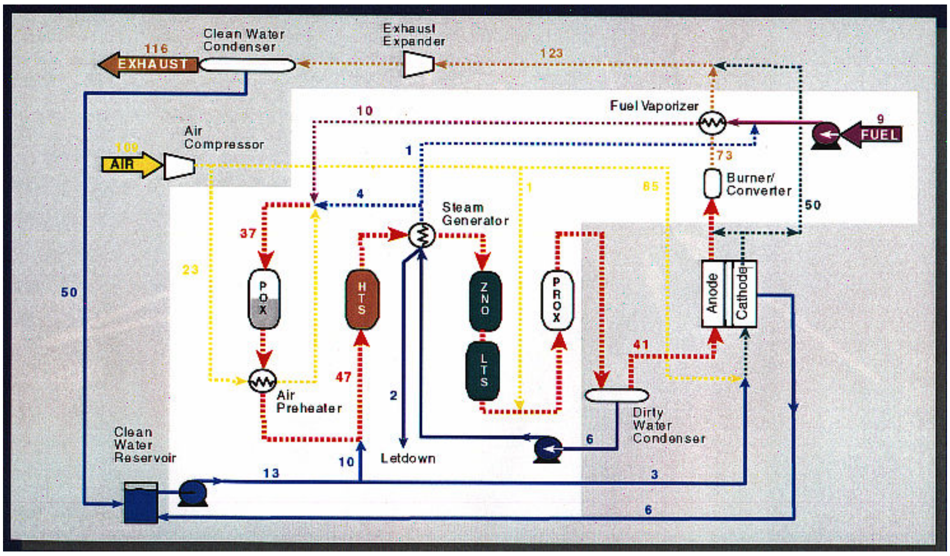

Figure 5.2 - AD Little PEMFC System Flow Diagram

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[12] A complete simulation of SR, POX and autothermal reformers is given by ETSU, report No.02/00097 for Diesel, Kerosene, Reformulated gasoline, Unleaded gasoline, LPG and Leaded gasoline. We base some of our discussion on the results of this report.

[13] E.A. Polman et al. : « Novel Compact Steam Reformer for Fuel Cells with Heat Generation augmented by Induction Heating », European Fuel Cell News, March 1997. B.H. Cooke : « Compact Reformer for the SPFC », ETSU Report F/02/00021/REP.

5.5.2.1 - The Hot Spot^{TM}reactor

The Hot Spot[14] is an autothermal reformation process developped by the English company Johnson Matthey. The reactor can be used to generate hydrogen from methanol in FC vehicles. The process starts with a POX reaction, rapid and self-sustaining, then it exchanges heat for the following reforming reaction. The addition of steam, when sufficient heat is available, increases the hydrogen yield to 50 %. Johnson Matthey has made considerable advances from the original design : it starts in less than 1 minute and is a third of the original volume (0.5kW/lt).

The Hot-Spot catalyst is also tested in a tubular reactor at EPFL (IGC-DC) with liquid hydrocarbons to be optimised for a car system in a joint project with Paul Scherrer Institute.

5.5.3 - Efficiencies

The efficiencies are defined as follows :

- **Fuel Cell Efficiency** : η_{FC} = DC Power produced/Heating Value of Anode Gas
- **Fuel Processor Efficiency** : η_{FP} = Heating Value of Anode Gas/Heating Value of Fuel to Processor
- **Gross System Efficiency** = $\eta_{FC}\eta_{FP}$.
- **Net System Efficiency** = DC Power produced - Parasitic power/ Heating Value of Fuel to Processor

In the table 5.3 below the efficiencies of SR, ATR and POX for methane, methanol and ethanol processing are given. Operating parameters are taken from manufacturers.[15]

CASE	1	2	3	4	5
Reformer	**SR**	**ATR**	**POX**	**SR**	**SR**
Fuel	CH4	CH4	CH4	Methanol	Ethanol
Gross Power Output (kW)	24.9	25.1	24.9	25.0	25.0
Net DC Power (kW)	23	22.6	23	22.1	22.7
Total inlet (kmol/h)	0.98	1.5	1.36	0.73	0.81
Fuel Processor Eff. (%)	94.2	84.2	79.5	109.3	87.9
Gross System efficiency(%)	33.3	32.9	30.9	42.3	32.6
Net System Efficiency (%)	**30.7**	**29.6**	**28.6**	**37.5**	**29.7**

Table 5.3 - Efficiency of ST, ATR, and POX reforming systems (source A.D. Little)

The most efficient fuel processor is the methanol SR (109.3%), with methane and ethanol SR following, while ATR and POX have lower values (84.2% and 79.5%). This is expected since methanol has significantly lower reforming temperatures - 260°C in this model - than methane and ethanol, considered « refractory » fuels (difficult to reform and requiring higher reforming temperatures).

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[14] U.S. patent No. 4,897,253

[15] Kinetics Technology International for methane SR ; General Motors/Los Alamos National Laboratories for methanol SR ; Arthur D. Little for methane POX &ATR and Ethanol SR.

The comparison of fuel processor efficiencies may be confusing because it does not account for the energy inputs other than the fuel input, as the heat recovery from the anode exhaust gas. It is thus recommended to look the overall system efficiency, mainly determined by the FC efficiency, which comparatively shows similar values. The FC efficiency depends of anode gas conditions and system operating pressure. The overall fuel processing efficiency reflects not only the reformer technology, but, mostly, the effectiveness of thermal integration of the system.

In the Table 5.4 we report model results of gasoline-type fuel processing with their respective efficiencies.

CASE	6	7	8	9
Reformer	**ATR**	**Hot Spot**	**POX**	**ATR**
Fuel	Gasoline	Gasoline	Gasoline	Naphtha
Gross Power Output (kW)	59.03	58.48	60.38	59.02
Total Parasitic Power (kW)	9.03	8.47	10.37	9.02
Net DC Power (kW)	50.00	50.006	50.10	50.00
Fuel Feed Flow (kmol/h)	0.116	0.104	0.144	0.119
Net System Efficiency (%)	**33.27**	**37.26**	**26.96**	**33.65**

Table 5.4 - Efficiencies of reforming schemes for hydrocarbon fuels (Source : ETSU).

If the autothermal process can be demonstrated to work with conventional (logistic) fuels such as LPG (propane and butane), NG or reformulated gasoline it may become an essential element for mobile applications of PEMFC.

5.6 - Novel Reforming Processes

The carbon black and hydrogen process,[16] although voracious of electricity, releases no side gases, but abandons the enthalpy of the carbon component. It works with a reactor where a plasma torch pyrolyses the feedstock. The plasma gas is hydrogen, recirculating from the process. A heat-exchange system conducts the heat-transfer from the high-temperature products to the feedstock and plasma gas, which are pre-heated to set values. Excess heat is used to produce steam for external use. The reaction is :

$$CH_4 + \text{electricity} \Rightarrow C + 2H_2$$

The Kvaerner Company is the developer of the process, and it is running a pilot project to further assess global viability of this technology, which, if using base-load renewable electricity, would release no emissons. The overall energy balance and fuel efficiency needs to be closely examined. The CB&H system will be a stationary one.

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[16] B. Gaudernack et al. : « Hydrogen production from Natural Gas without Release of CO_2 to the Atmosphere », XI Hydrogen Energy Conference Proceedings, 1996.

The « Plasmatron », developed at the Massachusetts Institute of Technology (MIT), is a plasma reformer able to generate temperatures as high as 10.000°C (average 1200°C), which make it suited to reform biogas, diesel and gasoline with no need for a catalyst. The Plasmatron features cheap carbon electrodes (durability 1000hrs), it is compact (fast reaction) and can operate over a wide range of feed rates at 80 % efficiency in the 1-1000kW range, while ensuring reduced CO_2 emissions by highly controllable electric heating of ionized gasoline-air mixtures to produce hydrogen rich gas. The electric power requirement is reported to be about 3% of the delivered hydrogen rich gas.[17]

Unmixed Combustion is an original concept joining the unmixed combustion catalyst, which delivers uniform heat through the reactor, with a nickel-calcium-based reforming catalyst. The system uses two reactors : in the first fuel and steam at 700°C and 8 atm produce H_2 , CO and CO_2 , whilst oxidised nickel and calcium are reduced to remove CO and CO_2. The gas subsequently enters the second vessel at 500°C to further reduce CO and CO_2 while air is passed into the first reactor to re-oxidise nickel and turn calcium carbonate into calcium oxide in an alternate process. Hydrogen is 90% pure at the reactor outlet.

5.7 - Hydrogen Purification

Standard PEMFC platinum electrocatalysts have a CO tolerance between 10 and 20 parts per million volume (ppmv) of dry gas fed to the anode, while the optimised reformers can at best achieve 0.5% CO content [18]. As a consequence a clean-up system is needed before the reformed gas enters the FC. This field of research belongs to advanced material science and catalysis.

Tests by Johnson Matthey with 50 : 50 Pt/Ru catalyst alloy showed that minimal improvements in CO-tolerance (>30 ppm) required increased catalyst loading (1.6 mg Pt/cm^2), which is uneconomical. CO-tolerance increases with stack temperature but unfortunately today's perfluorosulfonic membranes do not allow temperatures much above 100°C.[19] It is then compulsary, at least as an intermediate phase, to further purify the hydrogen-rich gas.

We distinguish between Separation Processes (Adsorption and Membrane processes) and Chemical Conversion Processes (water/gas shift conversion, selective methanation, selective oxidation). Different processes are applicable following the gas flow considered, but improvements in gas processing make the frontiers for profitability of the different techniques to vary largely. Selective oxidation, also called preferential oxidation (PROX) is being developed by Ballard, General Motors, A.D. Little and Toyota. Membrane technology is proposed by Johnson Matthey among others. The pressure swing absorption (PSA) is in advanced commercialisation stage and it can be scaled down to a few Nm^3 per hour and, eventhough it is not compact, we discuss it because it might be an intermediate solution to purify hydrogen from natural gas in a stationary system.

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[17] D.R. Cohn *et al.* « Near-term possibilities for Extremely Low Emission Vehicles using on-board Plasmatron Generation of Hydrogen » International J. of Hydrogen Energy, July 1997 pp.715-725.

[18] Note : 1% = 10.000 ppm.

[19] For Nafion the maximum allowable temperature is 130°C.

5.7.1 - Separation Processes

5.7.1.1 - Pressure Swing Adsorption (PSA)

The PSA technology is a physical separation method. The separation is operated by carbon molecular sieves, activated carbons or zeolites, thanks to the different kinetic adsorption of the different gases in the porous structure of these materials. The « sieves » retain impurities of the feed gas thanks to their decreasing molecular size in the tank. PSA is not new ; traditionally employed by chemical industry to obtain very pure gases because of the energy advantage compared to cryogenic purification, it has been scaled down to 7 Nm^3/hour from an earlier threshold of 200 Nm^3/h. PSA is widely used in air separation for nitrogen production or oxygen enrichment, or as in our purpose, for hydrogen purification.

In the basic structure a PSA unit employes two or more tanks filled with an adsorbing material with the right porosity working alternately : while one is absorbing the other desorbs. The adsorbing sieves - activated carbons and zeolites - are low-costs due to mass production : between 1000/1200 \$/Nm^3h of pure gas for very small units. PSA is hardly found in PEMFC systems because of volume expenses and discontinuous operation do not suit mobile applications.

5.7.1.2 - Ceramic, metallic and polymeric membranes

The second physical separation technique for CO abatement is the membrane technology. The advantage of a continuous process allows gains in the system volume and continuity during operation. The disadvantage are the fabrication problems and stability in operation.

A diffusion membrane is commonly regarded as a barrier which can be selectively permeated by some components of a mixture. This causes a change in the composition of the fluid flowing through it. The driving force may be a pressure difference, concentration or electrical potential gradient.

The permeability is a measure of a gas flow across a membrane per unit area and pressure difference :

$$Pe = \frac{F_i}{A.\Delta P}$$

where :

Pe = Permeability of component gas i ($mol.s^{-1}.m^{-2}.Pa^{-1}$)
F_i = Flux of component gas i through the membrane ($mol.s^{-1}$)
A = Area of membrane
ΔP= Pressure difference across the membrane

Permselectivity, the ratio of permeabilities to species in the mixture, is considered as the most distinctive property of a membrane, i.e. an ideal membrane is one that separates all of the desired products at the maximum flow required. As a general rule, permselectivity increases as the pores of the membrane become smaller and is virtually infinite for a dense membrane. Also as selectivity or membrane thickness increase then the permeability of the membrane to the gas decreases. Diffusion membranes are used in hydrogen purification.

A porous ceramic is often employed to support a thin-film deposition of selective membrane for CO removal from the gas stream of a reformer. In a project led by British Gas [20] with a Dutch membrane supplier, tests have been carried out to investigate the feasibility of either a separation unit using SiO_2 coating on metal support or the integration of the separation membrane into the steam reformer. The results confirmed insufficient stability in a steam-rich environment, which caused a low selectivity, *i.e.* CO passes through the membrane. The low separation factor is the main disadvantage of ceramic membranes at present ; this is why alternative selective ceramics (ZSi) are likely to be tested in the near future.

In 1964 Johnson Matthey invented palladium diffusion technology which is today the industrial standard for ultrapure (99.999999) hydrogen production. Hydrogen Engineering Applications (HEA) division has reconfigured [21] the traditional (foil and tube) system by development of a thin (0.7 μ), silver-supported membrane to meet the PEMFC requirements in purity and costs. The Pd/Ag is able to purify a reformate gas (70%H_2 ; 28%CO_2 ; 2%CO) to 99.99% medium-purity hydrogen, showing a considerable increase in the flow rate, which passed from 25 to 200 cm^3/cm^2/min at 10 bar pressure and 400°C. An individual membrane can deliver 1.5 m^3/h at a permeation rate of 4 m^3/h m^2 (STP). Estimates of cost for a 60 Nm^3H_2/h unit are UK £ 100.000 or approximately 2000 \$/Nm^3h ; assuming an average FC consumption of 0.7 Nm^3/kW/h this corresponds to 1400 US\$/kW. Durability for a station purifying hydrogen-rich gas with 200ppm of CO is 3 years[22]. This product uses at best the known selectivity of Palladium, a metal characterized by a structure suited for hydrogen permeation and stable over a wide range of temperatures. Tests showed that the membrane suffers mechanical stress at the operating pressure (15-20 bar) mainly due to the solubility of H_2 in the Pd lattice at low temperature. Moreover, Pd cost has overcome gold. It is in the manufacturer interest that the Pd-Ag membrane system is likely to operate together with the Hot Spot reactor as a two-stage hydrogen generation-purification system for PEMFC vehicles running on methanol if economic issues can be adressed.

Hydrogen separation by a polymeric membrane was recently investigated by modelling and experimental tests.[23] The membrane withstands pressure and temperatures of 70 bars and 90°C and it can handle gas streams of up to 15 Nm^3/h in a single shell-and-tube type arrangement. The model offers a good representation of hollow fiber permeator operation with coincident experimental results, although limited to three-component mixtures. Taking into account that permeabilities of hydrogen and carbon monoxide through glassy polymers are very similar to those of helium and nitrogen respectively, the experiment was carried out with these last two (45 % each and 10 % CO_2) for handling and safety reasons. Concentration of He and N in the permeate were 85 and 5 % respectively. These results are encouraging for a single stage separation unit.

Elsewhere,[24] the calculated performance of a non-porous polymer membrane showed unfavourable performance of hydrogen yield in regard to the CO content in the permeate.

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[20] B. Hölein, R. Peters : « Gas-Cleaning of Hydrogen-rich fuel gas », Contribution to Subtask 4, Foruschungzentrum Jülich GmbH. IEA Workshop, ANNEX VII, 21/22.11.96, Orlando, Florida, USA. Also ETSU Report F/02/00025/REP « Ceramic membrane fuel processor for the solid polymer fuel cell »

[21] J.C.M. Booth et al. : « Advanced Hydrogen Separation Via Thin Supported Pd Membranes », Proc. XI HEC, Stuttgart, 1996.

[22] T. Purcell, HEA, Johnson Matthey, personal communication.

[23] G.C.Kapantaidakis et al. : « Hydrogen Separation in Gasification Gas Streams by Asymmetric Polymer Hollow Fiber Membrane », Proc. XI HEC, Stuttgart, 1996.

[24] G.Colsman : « Verfahrenstechnische Optimierung der Brenngaserzeugung Brennstoffzellen in Kraftahrzeugen », KFA, Jülich.

5.7.2 - Chemical Conversion

5.7.2.1 - Low temperature Water/Gas Shift

The water/gas shift option for CO removal in dynamic responsive hydrogen processors is pratically abandoned. In most catalytic (copper/zinc) reformers the optimal operating conditions, *i.e.* methanol to carbon ratio, do not allow the 2% CO produced to be brought to satifatory concentrations (10-20 ppmv) by a low temperature water/gas shift because no extra steam is available. Moreover the reaction kinetics are extremely slow, meaning that practically no useful transient response can be obtained.

5.7.2.2 - Selective Oxidation

The selective - or preferential - carbon monoxide oxidation in presence of H_2 (PROX) reaction is :

$$CO + \frac{1}{2} O_2 \quad \Rightarrow \quad 2CO_2$$

PROX reactors go back to WW1 when gas masks used by the army (to oxidize the poisonous CO) had iodic acid in a sulphuric solution, which impregnated powdered pumice ; the iodine and CO_2 produced were retained by sodium carbonate. Hopcalite, a mix of Mg, Cu, Co oxides and Ag was subsequently preferred, the main problem being that the catalyst functions on a dry gas only.[25]

Early Arthur D. Little work [26] on integrated FC systems was based on the assumption that the Hopcalite catalyst of the selective oxidation reactor is effective for the operating environment. The actual A.D. Little system is an autothermal (ATR) reactor with two water/gas shift stages and an advanced PROX reactor. The high dispertion of the precious catalyst leads to high activity (2mmol CO/sec.gr_{cat} at 120°C) and good economic figures (Table 5-4). Besides the choice of catalyst and support to provide optimum activity and selectivity, there are three key elements :

- Control of operating temperature,
- Control of residence time,
- Control of air addition rate and mixing to match the CO concentration ($\lambda \approx 2$).

The first two affect both catalyst selectivity and conversion rate, whilst the third concerns the selectivity only since excess oxygen leads to hydrogen burn up. Moreover, at temperatures higher than 200° C more CO appears, which is believed to be caused by the reverse water /gas shift reaction :

$$CO_2 + H_2 \Leftrightarrow CO + H_2O$$

At present, each of these issues is covered by patents belonging to car and FC manufacturers and oil companies.[27]

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[25] « Nouveau Traité de Chimie Minérale » page 634, Vol. VII Carbone, Masson et C^{ie} Editeurs.

[26] U.S. Department of Energy, Contract No. DE-AC02-92-CE50343 : « Multi-Fuel Reformers for Fuel Cells used in Transportation », Phase 1, Final Report, pag. 49.

[27] See : US Patent Nb. 5,637,415 (General Motors); 5,604,047 (Exxon) ; 5,482,680 (Ballard); 5,436,086 (Vickers Shipbuilding & CJBD); 5,271,916 (General Motors).

There are two major types of PROX reactors : the isothermal and the adiabatic. Work at Los Alamos National Laboratory resulted in a two-stage, three chamber adiabatic and isothermal PROX reactor, where trimetylbenzene (boiling point 164 °C at 1 atm) is the control fluid. Fine oxygen (air) metering is performed by a mass-flow controller, ensuring that the total amount of oxygen (air) injected is between 1.5 and 2 times the CO concentration by volume. The catalyst is placed at the exit side of the reactor and its temperature is monitored to control the O_2 feed rate (this is not possible in an isothermal PROX).

One of the main problems is the absence of a real time CO sensor to makes system response to CO concentration fast enough. A control strategy developed by Melster [28] enables the amount of O_2 (*i.e.* air) supplied to vary on a real-time basis, in order to continuously maintain the desired oxygen-to-carbon monoxide ratio (2). In this conception the dynamic system assumes the reformate and CO content to the PROX to vary continuously in response to the power demands on the FC system. The strategy is based on the fact that H_2 content will lower if too much O_2 is injected ; so, lacking CO sensors, the difference in H_2 content between inlet and outlet is used to control the amount of injected air. The embodiment employs advanced hydrogen sensors, air meter and an Electronic Control Module (ECM) with the hardware and software for interpreting signals and implement the algorithm.

The following Table 5.4 summarizes the operating performances and economics of the PROX reactor developped at Arthur D. Little and Los Alamos National Laboratory. Work is under way at the time of the writing to test PROX performance with real reformate feed.

Operating temperature	***120°C***
Catalyst activity	**2 mmol CO/sec g_{cat}**
Hydrogen consumption	**< 1%**
Activation energy	**8 kcal/mol**
Estimated volume for 50kW PROX	**5 liters**
Estimated cost of active catalyst for 50KW PROX	**< 100 $**

Table 5.4 - PROX Catalyst Performance (A.D. Little, 1997).

5.7.2.3 - Selective Reduction

The selective CO methanation (reduction) reaction is :

$$CO + 3H_2 \quad \Rightarrow \quad CH_4 + H_2O$$

The major work in this field reported satisfactory results using a Ni-based CRG-F catalyst developed by British Gas.[29] With the catalyst bed temperature around 200° C and Gas Hourly Space Velocity up to 20.000hr^{-1}, the CO content was < 50 ppmv. These results could only be obtained at precise operating conditions : catalyst bed inlet temperature > 250 °C and > 3.5 bar pressure. Toyota methanol FCV employs a methanation reactor with a ruthenium catalyst.

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[28] US Patent Nb. 5,637,415 ; Jun 10, 1997.

[29] Dr. T.A. Smith, ETSU Report F/02/00031/REP : « CO Removal by Methanation for the Solid Polymer Fuel Cell », 1996.

5.9 - Remarks &Conclusions

PEMFC promises to be the cheapest FC technology : metal hardware with plastic membranes and graphite or, more probably, aluminium bipolar plates, shape the silent, non-polluting, ultra-compact energy-generator, which makes water as by-product. Where does THE problem lie ? PEFC are fuelled by hydrogen. This light element needs to be very pure and humidified before its use in the cell. While this last condition is stack-integrated, abatement of CO content down to 20 ppm (≈ 0.002 %) is so far performed in large, separate gas processing units. As the PEMFC doesn't need to be used in multi-MW power plants, in the 1-200 kW power range availabilility of fuel processors will allow FC to enter the generation market, by downscaling of reforming equipment, with small, modular units providing decentralised electricity and heat when and where needed.

In the case of a stationary power generating system the high efficiency of the Methane Steam reforming process, together with its reliability is the option of choice, while the option of CO abatement to 20 ppmv will require an *ad hoc* comparative reliability, availability and maintenability analysis between PSA and PROX.

Whenever a fast (minutes, seconds) load following PEMFC system is suitable, as in the case of a vehicular powertrain, ATR promises comparative advantages in terms of technical and economical efficiency.

Hydrogen cleaning from CO is the most strategic issue in PEMFC systems : selective oxidation is domain of agressive competition.

The turbulence in the fuel processing research for PEMFC systems does not allow either precise conclusions about the final fuel for PEMFC, or relaxation on the issue of the equipment costs. Nevertheless, the significance of the projects and the companies in the game give us the feeling that mobile and stationary PEMFC systems liquid fuelled (HC, alcohol) are realistically stepping close to commercialisation since :

1 - PEMFC stacks have attained the required power density for vehicle applications

2 - Dynamic reformers for hydrocarbons or alcohols are available

3 - Carbon Monoxide clean-up devices are being tested and optimised to be operated with reformate from (2).

Concerning the issue of CO removal, we decided to focus our following economic analysis on two modular purification units : selective oxidation (PROX) and pressure swing absorption (PSA) technologies.[30]

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[30] These technologies are opposed respectively to cryogenic purification and metallic membranes; the first is only suited for very large scale plants, while the second is not expected to advance its learning courve because of the noble metal content.

Chapter 6 - Fuel Cells Economics.

No other single technology has the widespread potential for major impacts across almost all energy generation and consumption sectors.[1]

6.1 – FC Power Systems

Standard scheduling of a power system considers fossil, run-of-river and nuclear plants for base load because they are not efficient at part load, while dam-stored hydropower and gas turbine (GT) technologies are energy limited, meaning that they are more suited to supply high-cost peak demand. Power plants may be energy limited either because of limited total available energy, or because fuel and operation & maintenance (O&M) costs are important in the case of GT. The FC do not belong to either. If the dispatching of an electric system is marginal cost-based only, the FC will supply peak power (at the top of the load curve, above GT), during a few hours per year only. Instead, real environment operation of commercial FC, as the PC25C by ONSI operated, for instance, at *Services Industriels de Genève*, shows that the PAFC system is for base-load operation ; this is the logical consequence of the high investment costs (3000$/kW), but also the very low O&M (3% of the investment cost per year) and fuel costs, due to the absence of moving parts and the high electrical efficiency respectively.

It is expected that in Europe the use of natural gas for power generation will rise from 50MTOE to 100MTOE in 2005.[2] More methane will be available in Europe thanks to the investments under way which will ensure large supplies from Russia, Algeria and Nigeria.[3] Therefore, it is likely that gas availability will continue during the first half of the XXI century. Electricity prices are, of course, more interesting for peak supply and are increasingly being met by GT technology, because of the limited availability of economical hydrogeological sites. Meanwhile, persistance of nuclear and large fossil plants to supply base load power is uncertain, this is mainly due to increased environmental concerns.

In this context, the hypothesis of a FC-network system to provide peak load electricity may become realistic : the FC can match daily variations in demand because it is rapidly responsive from part to full load. In this strategy the fuel cells can generate peak power on demand, while being in continuous operation during the rest of the day because featuring a higher part load efficiency (see Graph 6.1). Further in the future, when autothermal reformers will be available, fast shut-down and start up will be possible for small, off-grid CHP units (5-100kW). Hospitals, heavy users of telecommunications and computer equipment are likely to find FC attractive, because they would otherwise have to invest in a back-up system with no benefit for the time the generator is standing by. The availability of small cogeneration FC sets will open up a new market, because even though engines are competitive on cost and may have good efficiency (diesel 43%, gas 38%) the environmental performance of the FC is a considerable advantage. FC avoid high rotating engines maintenance (up to 3 ct./kWh) and decentralized heat production can be the driving force, enhanced by legislation.

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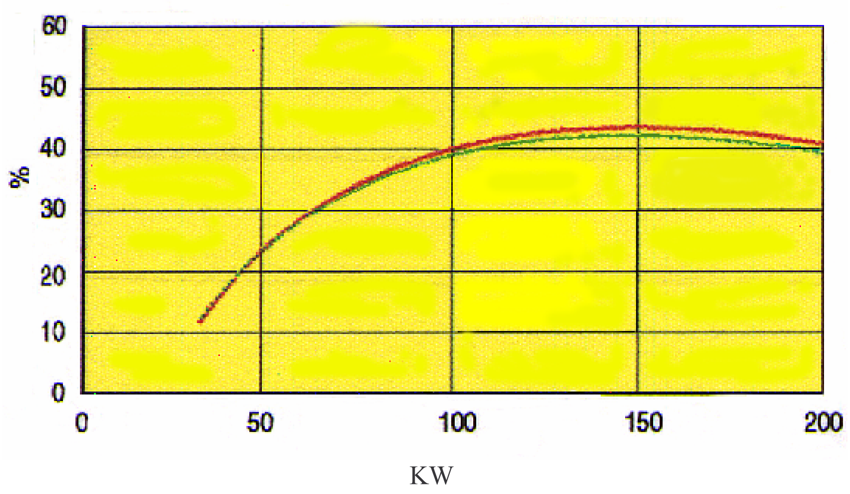
[1] B.M. Barnett, W.P. Teagan, A.D.Little Inc.

[2] P.G. Claus : « L'avenir du secteur gazier en Europe », Secr.Gen EUROGAS. Présentation à la Conférence ASIG, 22 mai 1997, Lausanne.

[3] A relevant exemple is the Jamal Project led by Gasprom and BASF, which will have a capacity supply of $14*10^9$ m^3/y.



Graph 6.1 - Efficiency vs. Load of PAFC (source D.L. Nguyen, SIG)

6.2 - Economies of scale & Learning Courve

The *two thirds rule* of economies of scale is geometry : if one needs to double the volume of gas treated in a reactor, material expense (metal surface) is two-thirds higher (larger). The relation can be written as :

$$\mathbf{C = kxP^{\alpha-1}}$$

C : unit cost (\$/kW, \$/m^3),
P : capacity (kW, m^3),
k : technical constant,
α : scale exponent ($0<\alpha<1$).

This formula is applicable to the fuel processor, in particular for standard methane steam reformers and PSA purifiers, which, as seen in Ch.5, need respectively large surface heat exchangers and molecular sieve tanks.

Compared to the SR/PSA - or SR/membrane - scheme, the ATR/PROX processor scale effect is probably reduced - the α factor is closer to one - and the technical constant might also be lower. In ATR/PROX FC system direct reactions occur on the catalyst surfaces (fuel and CO oxidation by just air and water stoichiometries), rather than through exchange of heat, thus widening flows boundaries for a given size.

Learning curves can be expressed as in the Graph 6.2 below, for PAFC, with the cost per kW as a function of cumulative production in MW. The learning process may vary largely for companies producing similar goods. It has been suggested for the PAFC industry[4] that a 85% cost reduction (per kW) will results for each doubling of cumulative production till commercialisation phase. Estimations for PEMFC do not exist yet, but it is expected to be higher because lower temperature and flexibility of size should allow a faster standardisation.

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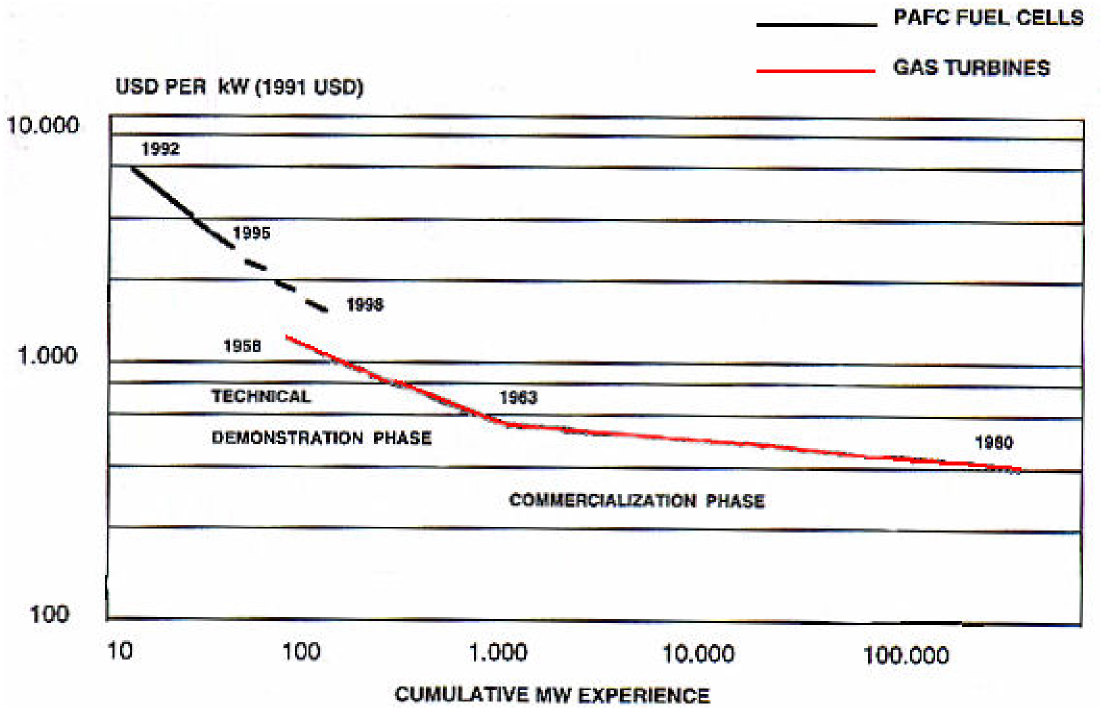
[4] D. Hart : « An Analysis of Fuel Cels and Gas Turbines in Small-Scale Distributed Power Generation », pag.45. Master Thesis, Imperial College of Science, Technology and Medicine, September 1995.

Learning curves are expressed by the power function :

$$y = ax^{-b}$$

where :
y : number of direct labour hours to produce the x^{th} unit
a : number of labour hours to produce the first unit
x : cumulative units produced
b : measure of labour hour reduction rate for cumulative production increase.



Graph. 6.2 - Learning curve of PAFC (source : T. Bozzoni, CLC Ansaldo)

The PEMFC stack costs should decrease to 500 \$/kW in the next five years and special effort is devoted for it by the European Community programme.

6.3 - Markets

Main tools for market analysis are provided by studies on I) stationary and II) mobile FC systems :

I - Scenarios for *vehicle introduction*[5] : the main disadvantages reported for this application are the low investment cost targets (100\$/kW), the fuel (stations implementation, fuel processor spares) and FC (spares) infrastructure and general maintenance (garages etc). The major advantages are the great economies of scale resulting from the vehicle market, which is strategic for individual mobility.

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[5] An exaustive overview is found in : Gene D. Barry « Hydrogen infrastructure for vehicles » Lawrence Livermore National Laboratory, October 1996.

II - Scenarios for *power generation systems* [6] : the reported disadvantages are the overall high efficiency & reliability targets required. PAFC are the reference and have 0.5% efficiency decrease per year ; availability is 90-95%. Moreover, because of the high capital cost FC investments are very sensitive to interest rate. Advantages : existance of niche markets, where either cheap fuel or high emissions value, justify the high investment cost. Dimension targets and fuel infrastructure requirements are relaxed. FC are by far the best technological prospect for small cogeneration in term of efficiency and low pollution.

6.3.1 - Sizes & Types

FC are not expected to take more than one percent of the **large scale** (>30 MW) power generation market, which corresponds to 1.3 GW, in the year 2020.[7] This market will be composed of :

- integrated power systems, where a gas turbine remains the main generating component and a high temperature FC forms a topping cycle,

- large-scale industrial processes, where hydrogen is available as a by-product (chlor-alkali).

The high temperature MCFC and SOFC will take the big share, while PAFC will be following, disadvantaged by the low thermal performance (200°C). The market is rather small because the high temperature FC technology needs proof by field-testing for stack materials and BOP.

The booming **medium size market** (1-30 MW) raises essential interest of FC industry. Distributed Power Generation (DPG) represents the growing need for small plants located near load centers. Gas turbines are the technology to beat because, despite the low cost, in the few MW power ranges they loose some of their efficiency ; FC's silent and clean operation will be appreciated in populated areas. Therefore, economical and environmental criteria will determine the choice, case by case. This market is expected to go from present 15 GW to 55 GW in 2020 ; FC could take 10 GW of it. Either MCFC or SOFC technology will be leader.

In the **10 kW - 1 MW powerband** FC have a strong competitor : diesel engines can attain 43% (38% with gas) electrical efficiency with a flat behaviour from 40 to 80%.[8] Turbines have low (25%) efficiency, but can now lower NO_X to 15 ppm.[9] Thus, FC need to lower their cost and take advantage of air and noise pollution high value since the user is near. The estimations by EscoVale of this market, including standby, cogeneration and site supplies, might rise to 45 GW from the actual 20 GW. FC will take around 7 GW. The most promising application is for cogeneration installations, where cost goal is to go lower than 2000 $/kW. SOFC are expected to be the leading contender followed by PAFC, PEMFC and MCFC. We believe that the share of the power generating market for PEMFC will ultimately be determined by the reliability and cost of the fuel processing and clean up system. The stack

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[6] D. Hart : « An Analysis of Fuel Cells and Gas Turbines in Small-Scale Distributed Power Generation », pag.45. Master Thesis, Imperial College of Science, Technology and Medicine, September 1995.

[7] The market penetration estimates are provided by the three-year study from EscoVale : « Fuel Cells : Applications and opportunities ». Three-volume management report, UK£2,800. Source : Electrical Review Vol 229 No 18.

[8] Source LENI.

[9] E. Benvenuti : « Combined cycles with Advanced Technology GT and their contribution to lowering CO_2 Emissions to the Atmosphere ». Data Nuovo Pignone, August 1997.

will need to operate at high voltage, while size and density relaxation - compared to mobile application - will be an advantage.

The market **below 10 kW** is satisfied by small motor generators and rechargeable-battery sets ; the PEMFC and SOFC are the main contenders in the FC family. Interest comes from the military and aerospace industry ; considering that more than a million small diesel and petrol gensets are sold each year, it is more than a 1000MW market. Uncertainties concern what part of power-only and what CHP will be demanded. By 2020 CHP sales might reach 100.000 units for a combined capacity of 400MW, while electricity generators (1-10kW) will be around 100MW. Strong demand for electricity-only FC may come from the army to replace battery-powered military kit (30-300W), such as night vision systems and communication devices, but the civil customer may emerge from the growing need for reliable power in high value applications : portable computers, home smart metering and communication equipment. 2020 sales estimates for battery replacement vary largely : from 250 to 800 MW.

Vehicles demand represent a possible market of 57 GW by 2020, composed for 42GW of FCV and 15GW of commercial vehicles such as vans, buses, trucks and fork-lift trucks. The commercial vehicles are favoured in early commercialisation because they are intensely used, have central refuelling stations and government might take an active role to enhance their introduction (perceived environmental benefit). Other studies[10] foresee 800 units for commercial vehicles by 2010-2015, while FC cars are mass-produced by 2018-2019. The vehicle market will entirely be taken by PEMFC, some applications, as vans and boats, might also present chances for alkaline technology.

6.4 - Top Down Approach for Electricity Cost

The investment for a FC system is evaluated for two stationary hydrogen production schemes[11] :

A - Hydrogen produced in a neighborhood-scale MSR (100kW min.) with a PSA unit. Electricity is delivered through existing lines to the customers. The utility is the FC owner.

B - A modular 50kW ATR/PROX fuel processor producing hydrogen for a private user from gas or liquid hydrocarbon.

Hydrogen might also be produced in a large-scale reforming plant, to be delivered in high pressure tanks, but this in not a realistic system in our case. The interest rate is 7%, availability is 7500h/y (85.6%) for the MSR and 5000h/y (57%) for the ATR. We compare below capital, operating and variable costs for the two FC systems.

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[10] Robert J.D. Evans, Market Development Manager, Fuel Cells: « The Solid Polymer FC ; Market Prospects & the Challenge for Commecialisation ». Johnson Matthey Plc.

[11] In this case we consider the ADLittle ATR reformer, developped for FCV, as a stationary power plant. This assumption, although objectable, can be justified by the fact that the still-high economic estimates for a drivetrain (400$/kW + stack) compensate the normally higher cost of a stationary FC system.

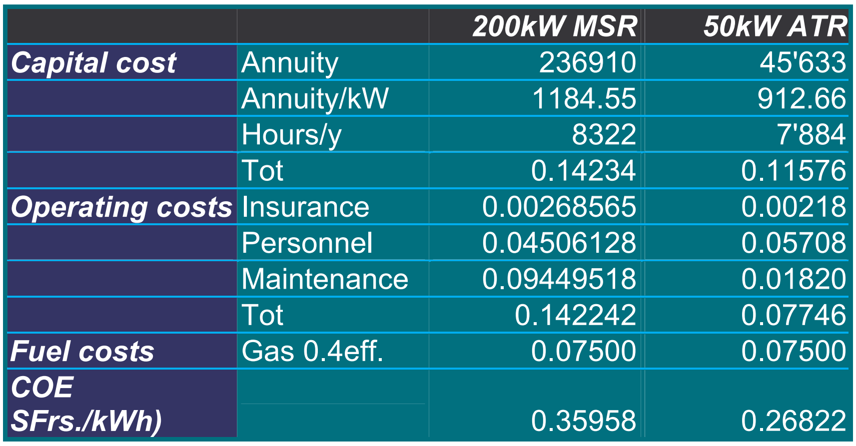
	200kW	**50kW**
MSR	$1000\$/\mathrm{kW}_{el}$	
Stack (present price)	$3000\$/\mathrm{kW}_{el}$	3000\$/kW
PSA[1]	$800\$/\mathrm{kW}_{el}$	
ATR[2]		130\$/kW
PROX[3]		20\$/kW
BOP[4]	$250\$/\mathrm{kW}_{el}$	250\$/kW
Amortization (years)	10	10
Capital cost	**5050\$/kW**	**3400\$/kW**

Table 6.1 - Capital cost assumptions.

1) PSA units above 100kW$_{el}$ are assumed to have linear costs.
2) ATR production conditions of 100 units per year
3) Costs are approx. 100\$ for the catalyst only in a 50kW PROX (source A.D. Little).
4) BOP is assumed to be the same, since state-of-the art equipment is used.

The results of the **electricity cost** below are derived from the following assumptions :

- Insurance cost is 0.3% of investment cost,
- Maintenance cost is 2.5% of investment cost,
- Operation cost (personnel) represents two people at 50% (≈ 75.000 sFr.) for MSR and one operator at 30% for ATR technology (22.500sFr.), which has comparatively a lower reliability.



		200kW MSR	***50kW ATR***
Capital cost	Annuity	236910	45'633
	Annuity/kW	1184.55	912.66
	Hours/y	8322	7'884
	Tot	0.14234	0.11576
Operating costs	Insurance	0.00268565	0.00218
	Personnel	0.04506128	0.05708
	Maintenance	0.09449518	0.01820
	Tot	0.142242	0.07746
Fuel costs	Gas 0.4eff.	0.07500	0.07500
COE SFrs./kWh)		0.35958	0.26822

Table 6.2 - Cost of Electricity for 50 and 200 kW systems.

6.5 - Financial Boost : The Dutch Exemple[12]

The Dutch Government has edicted several measures to support energy conservation and reduce greenhouse emissions by putting ecological energy investments under a low VAT regime (6%). An innovative taxation measure now experienced in the Netherlands, aims at speeding environmental investments by allowing an arbitrary amortization : the « VAMIL depreciation », introduced in 1996 by the Ministry of Housing, Spatial Planning and Environment.

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[12] See : P.H. van Dijkum : « Specific Taxation Measures include Fuel Cells », European Fuel Cell News, Merch 1997.

An even more recent tax initiative of the Ministry of Economic Affairs is the « Energy-investment deduction ». This measure, which includes FC CHP systems and FC electrical drive systems for powers < $1000kW_{el}$, enhances the VAMIL depreciation by setting energy-investment deduction rates spanning from 52 to 40% of the investment. FC projects can save on tax payments by fast amortization and strong deductions.

6.6 - Legislative Enhancement

The energy markets are changing a lot : the principles of efficiency and competition are entering in a traditionally state-owned monopoly by mean of international legislation and long term concerns. If it was economical to achieve economies of scale by GW-size plants in the past, today utilities find it more economical to build decentralized, user-sited plants that will release the energy suppliers from building new central plants and upgrading - or expanding - the grid.

6.6.1 - Unbundling

The principle of Unbundling is likely to advantage small-scale, efficient power generation, because lower investment costs, construction delays and high reliability - *i.e.* low maintenance and operation costs - will favour a packaged product, which can be commercialised by small, highly-specialized companies. The product supplier is licensee of the basic components, *i.e.* reformer, stack, and can mandate for spare parts replacement. Since production, transmission and distribution take place simultaneously there is no need for separate, and heavy accounting, as data transmission via modem is sufficient.

6.6.2 - Third Party Access (TPA)

The principle of TPA is one of the major drivers in the energy policy of the European Union : it simply means that access to the network is possible to the independent producer. In the Electricity sector the discussions on tariffs and frequency regulation responsability are animating the implementation of the TPA. The liberalised market begins on January 1st 1999. TPA is a major advantage for FC commercialisation.

6.7 - FC Commercialisation - Swiss case

Main criteria for FC system development are :

- WHAT is needed for the BOP, e.g. Components, Mass production feasibility
- HOW operation is possible, e.g. O&M, Back-up system.
- WHERE are the weaknesses in the fuel processing, *e.g.* CO removal, integration.

In order to clarify what are the possible **behaviours** of the parties involved in FC system research, it is interesting to specify the more or less vested interests and strategies of potential FC actors. The table below, valid for the Swiss case, where neither a car manufacturer, nor an oil company are present is not applicable elsewhere, but it may be valid for more than the present case.

Actor	Goals	Strategy
FC producer	Test, Pilot plant, strategic licensing, vehicles	Integration of technology, patent protection, mass production techno-economics
Research Institute	Presence in new technologies, data, costs, fundings, tests, patents	System integration Applied research, Technology diffusion, Diffusion of learning, appraisal studies,
IPP	Market segment identification, product evolution, Customers requirements	Interface between developers and applications, In-depht knowledge of local environment.
Utility	Emissions reduction, networks regulation, supply security	Demand side management, price flexibility, pilot projects

Table 6.3 - FC Research Goals and Strategies

None of these agents alone can develop a complete FC system with hydrocarbons or alcohols fuel processing. We believe that even in the absence of a power plant builder, *e.g.* ABB (CH), Ansaldo (I), Siemens (D), it is likely that the need of system integration will be the driving force to establish a co-operation. The technical bottlenecks in the conclusions of Ch. 5, *i.e.* CO clean-up system and system integration, can be worked out by a collaboration electrochemists, thermodynamicists and electricians.

The Table 6.4 below summarizes the interrelated **research priorities**, associated with their applications.

#	Activity	Che.	Mech.	Ele.	IPP	Utilit	Application
1	On-H_2 stack operation		●			●	operational data for ALL other #, H_2 boat
2	ATR catalysis,	●					FCV, CHP station
3	CO-removal : PROX,PSA	●	●		●		CHP station, FCV if dynamic
4	DC-DC Regulator, inverter, ECM			●			higher efficiency
5	Power recovery, heat exchangers, thermal integration		●		●	●	FCV, CHP station design
6	Sensors, meters, pumps	●	●		●		PROX design
7	Spares production				●		lower cost

Table 6.4 - Research activities and applications in Switzerland

The following research shedule might be suggested :

Step	Power (kW)	Mission	Means
1	10	Stack lifetime Gas reforming	Extreme operation, Technology Assessment
2	10	Stack optimisation RAM of H_2 system	Storage implem. Spares production
3	10-200	Overall system optimisation	Industrial synergies Simul. tests results
4	10-100-200	Commercialisation Tests	Marketing, Political engagement

Table 6.5 - 4-Steps Development Schedule

6.8 - Remarks

- The PEMFC technology is entering both the power generation and the transportation sector but the specific features of these two markets - *e.g.* lifetime, infrastructure and cost - do not necessarily allow technology improvements in one to benefit the other.

- The hydrogen production development activity, needed for fuelling the FC, can be more attractive if FC are used for power generation and traction at the same time. Later, an increased share of electricity generated from renewable energy can find application in hydrogen generation.

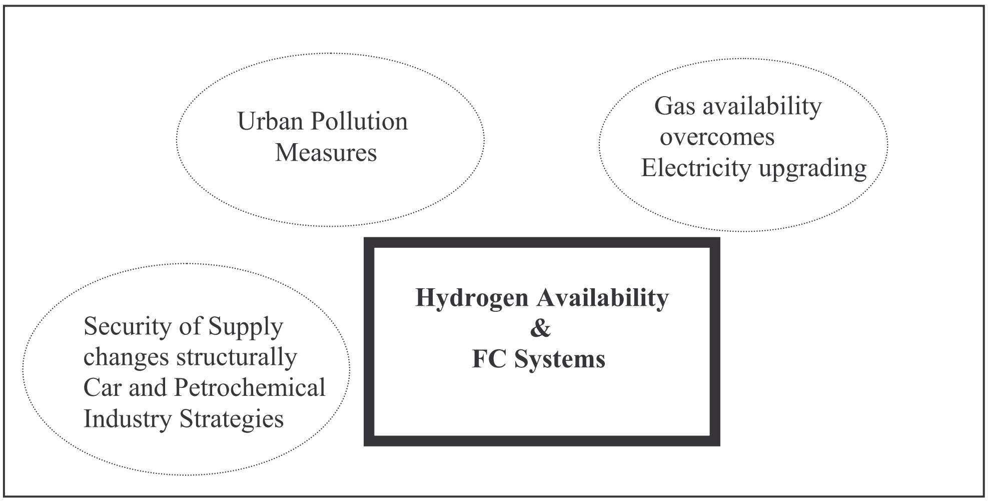

Figure 6.1 - Relevant MacroEconomic Factors for Fuel Cell System Introduction

Utilities and Industries have interest in parallel development of both power and vehicle market since, as it is clearly explained by G. D. Barry :

« The *chicken & egg* dilemma facing vehicle manufacturers and fuel suppliers can be resolved through production of small-scale hydrogen generation and storage equipment, manufactured at rates in coordination with hydrogen vehicle production rates. On-site fuel production can guarantee fuel availability for fleets and perhaps homes ».[13]

We conclude that :

I - Infrastructure for vehicles leads to strong standardisation and rapid economies of scale because integrated mass production conditions create synergies between an alternative fuel and the current energy and industrial infrastructure.

II - Dispersed small-scale reformers, peak-shaving electrolysers and storage equipment for stationary FC systems increase gas demand and optimize electricity production, enabling FCV mass production through hydrogen refuelling station.

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[13] Gene D. Barry : « Hydrogen as a Transportation Fuel : Costs and Benefits », Lawrence Livermore National Laboratory, March 1996 page 6.

Chapter 7 - Feedback of the Study

7.1 - The Debate - Towards hydrogen economy or just technological improvement ?

One of the personal conclusions I have come to through this research concerns the evolution of private transportation : car firms, utilities, electronics, chemical and oil industry *are* concerned by the consequences - meaning geopolitical as well as environmental - of the present oil-based economy. The changes in sight are not only due to inventions which make them possible, they are basically provoked by urgent constraints and willingness to take decisions - more than making inventions - which will generate turnover in sustainable technologies. The switch to fuels like hydrogen and methanol for FC, even if transitionally sourced from natural gas, is a radical change : from petrochemistry to electrochemistry. The use of fuel cell engines might be the major techological feature of the 21th century industry.

7.2 - Engineering

Research on membranes concerns electrolyte performance and cost. Membranes from PSI and DAIS do not need to be fed with 100%-humidified gas, simplifying the hydrogen side of the cell. It is interesting to note that although the membrane-electrolyte is the core component of the PEMFC, the hardest tasks of FC construction are mechanical : reactants and water management, *i.e.* the task of Bipolar Plates.

Ballard has reached an impressive record in power density in the NeCar II : 1kW/liter. This result exceeds the requirements set by the Partnership for a New Generation of Vehicles and the U.S. Department of Energy, but, unfortunately, costs goals are not so close : the NeCar II FC, realized by Ballard (proprietary membranes and graphite bipolar plates) with Daimler-Benz (Johnson Matthey provided the gas diffusion electrodes), is still a very expensive engine. Technically, a graphite BP is weak in case of strong vibration (or crash); that is why metals as titanium, aluminium, niobium or different superalloys are commonly used to improve resistance.

Besides the material cost, minimized using aluminium, a major cost penalty is due to the machining of the raw metal sheet to « cut » grooves in the BP (the flow fields). This accurate work requires heavy-equipment investment and many hours/unit. In the recent years, the most urgent problem of the FC industry was the construction of an efficient, industrially-oriented bipolar plate, which if mass-produced would result in price reduction of the stack from the present situation (10.000$/kW).

DeNora's metallic BP, derived from the electrolysis technology, is made of woven metal wire and it is low cost.[1] The Italian company's improved design has an original solution to reduce volume and weight by an optimisation in the cooling system.[2] It was estimated that stacks up to 2 kW can be air cooled. Moreover, « air-breathing » FC, which eliminate the air blower, are also being developed for < 1kW stacks.

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[1] The mass production of DeNora bipolar plates is one of the objectives of the FC busproject led by Ansaldo Ricerche, Air Liquide, Neoplan, DeNora and others, and it can be seen as the final condition for economical stack production in Europe.

[2] G. Maggio, V. Recupero, C. Mantegazza : « Modelling of temperature distribution in a solid polymer electrolyte fuel cell stack ». Journal of Power Sources No.62, pag.167-174

7.3 - Economy.

As PEMFC are at the pilot-project stage, cost of mass production are limited to cost evaluation of separate components. Hence, only estimates of PEFC systems costs, assuming mass-production conditions are available.

Membranes are now around 10 % of the stack cost. Membrane development has been justified by the hight costs of DuPont's NAFION (US$700 /0.8m^3) : cheaper material with similar, or better performance is available such as PSI's styrene-grafted, DAIS' triblock, Gore's or Ballard's.[3] The main step-up in production is the switch from lamination to extrusion process. Since more producers appear every year it is logical to think that the cost of the membranes will lower to 200/400$/m^2, *i.e.* (100/200$/kW), but, in mass production, a cost of 50$/m^2 is considered possible in the future.

The cost of electrodes is determined by the amount of catalyst, which is considered acceptable between 0.6/1 mg Pt/cm^2. MEA with loadings as low as 0.1 mg Pt have already been realised.

The FC stacks available today are still very expensive and can only be delivered by constructors in joint-project frames under secrecy agreements.[4] Costs might lower soon to 3000$/kW. Ballard plans to charge 35$/kW in 2004, when the company will produce 40.000 units per year.

PEMFC systems are not commercial. Their present status and future targets are summarized in Table 7.1 below. We can see how the stack has a major importance in the cost of a FC system ; this is due to the small production volume and payback of the engineering required to achive the performance.

COMPONENT	Current Cost	CHP Target	Transport Target
Total System cost	14.000 \$/kW$_{el}$	800 \$/kW$_{el}$	150 \$/kW$_{el}$
Stack	10.000	180	45
Fuel processing	1500	180	40
Air delivery system	75	45	15
Humidifier	112.5	52	25
Power conditioner	30	180	-
Buffer system	60	52	-
Control & Instrument.	1200	105	30

Table 7.1 - PEM Fuel Cell System components : present and target costs (source ETSU) [5]

In the European Commission strategy report [6] the 2005 targets are :

200 ECU/kW for stack
1500 ECU/kW for the system

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[3] PSI estimates, in mass-production conditions, are around 200 US$/m^3. Dais membrane is approx. 30% less expensive than Nafion, but it is today only available on 12``X 12`` surface.

[4] De Nora, today's only short-term supplier able to deliver a 10kW unit in two months, proposes a lease/test contract for 2 years.

[5] ETSU Report No.131. New and Renewable Energy Enquiries Bureau, Harwell, Didcot, Oxfordshire, OX11 0RA. We converted values from UK£ using an exchange rate of 1.5.

[6] European Commission, Directorate General XVII : « A Ten Years FuelCell Research, Development and Demonstration Strategy for Europe », Version 1995, pag 15.

7.4 - Ecology

As we have seen, hydrogen can be produced in many ways : emission-free via electrolysis from renewable energy, *e.g.* wind, PV or hydroelectric sources, although it is very energy-expensive. In such schemes PEMFC systems with renewable hydrogen engage a central hydrogen production-storage facility, developed with utilities and distributors. If Authorities are sensitive to the problem of peak-shaving, a possibility is the use of a central electrolyser, in an existing plant, to be operated in off-peak hours, or for frequency regulation in the electric grid.[7]

Although, today's most economic way to produce hydrogen is natural gas reforming at a central facility, the main emission is a fairly-pure CO_2, which can be used direnctly in greenhouses or chemicals.

FC are contemporary with the invention of electricity : as D. Hart sharply puts it « Grove had discovered a way of producing electricity when not even Michael Faraday had found a use for it ! ». It is highly symbolic that electrochemistry was the *berceau* of early electricity works, whilst later progress led to thermomechanical systems, burning high Carbon-to-Hydrogen ratio fuels to generate rotary power to exite the Von Siemens dynamo. Are FC at the threshold of a revenge at the dawn of the 21st century ? Be it as it may, the issues of security of supply and emission concern strengthen this belief : even though resources depletion might not be *the* environmental problem in the energy domain, since it is unlikely that we will be able to burn existing fossil resources at present rates before the greenhouse effect becomes unsustainable, the likelihood of having a diversified oil production decreases while companies pump in deep off-shore oil fields and Gulf countries keep 70% of oil reserves on storage.

In 1996 oil price rose by around \$8/bbl, which represented an increase of ≈ 40%. It is estimatedthat if the US embargo against Lybia, Iran and Iraq is maintained, oil demand may edge the very near supply capacity, causing the price to hit \$40/bbl in 2005.[8]

The option of methanol for FCV has some toxic emissions problems, but they can be overcome by keeping the reaction temperature high enough to prevent aldehyde formation and it is compatible with biomass processing. The drawback is that traditional energy crops, as in Brasil, mainly produce ethanol, only reformable at much higher temperatures (700°C), and so useless in a methanol cycle. Their conversion will be eased by experience gained in alcohols. Methanol is easy to store and vaporize, its reforming process is simpler than any other liquid fuel (250°C), and it is renewable. These reasons, plus the recent agreement between Daimler-Benz and Ballard Power Systems to found a joint company for the production of buses, trucks and private vehicles, boosted the option of methanol-fuel for mobile FC system mass-production. In fact, although critics say that in the whole chain of methanol production 50% of available energy is lost going from methane to methanol to hydrogen, the complete methanol FC system will better fit in a car than any other fuel because of inherent simplicity (storage, processing) and car range can compete with conventional gasoline ICE whilst being (at worst) an ULEV [9].

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[7] Projects are led in Germany, as the 100kW MTU 30 bar electrolyser.

[8] M. G. Salameh : « Crude Oil Prices on an Upward Trend », International Association for Energy Economics Newsletter, Summer 1997.

[9] In the same direction the voluntary 25% CO_2 reduction proposed by German car manufacturers

FC industry recycles used membranes by liquefaction of Nafion, for subsequent mixing with the catalyst in « coating » the electrode. The platinum electrocatalyst is also recycled in used electrodes. These possibilities add profitability in mass manufacturing.

7.5 - Durability & Maintenability.

These fields are of major relevance for PEMFC technology today and very few data are available. DeNora has a small stack which has been running discontinuously for five years now ; it is meant to prove the validity of their design. Stationary FC should reach 40.000 hours lifetimes before stack replacement. The field-tested reference ONSI PC25 PAFC are proven successfully in the field of durability: 5 years. Mobile applications need operation lives of 5000 hours min.

The issue of maintenance and personnel training oughts to be fairly negotiated between FC suppliers, utilities and research institutes. It is believed that the durability limit for most applications will be set, not by the stack as such, but by the performance of CO abatement unit.

7.6 - Conclusions

Within a historical perspective, hydrogen certainly is one of the most fascinating elements : we dare to talk by now of a possible Hydrogen Economy.[10] Only uranium and carbon, as a single elements,[11] have given as much as hydrogen, and engaged science on fertile fields, in visions and applications. The FC had to make improvements over almost two centuries to answer new energy needs and pass the laboratory stage toward commercial takeoff. Saying this, it would be wrong to contemplate the unusually slow development of FC technology, forgetting the massive, vested interests of oil-based industry or mentioning oil price trends and safety aspects of gaseous fuels. Remarkable engagements are undertaken by major chemical groups (Dow, DuPont, Hoechst), car industry (Mercedes, BMW, Toyota, Chrysler, , Honda,GM) and energy industry (RuhrGas, ERC, GPU, British Gas) to develop FC systems, and the most ambitious goal is the private car.

Deregulation in the energy sector might have affected negatively FC technology penetration in the utility market. In the past electric utilities have pioneered new technologies, moderating the risks with the monopoly status, but by now the enhanced competition has rather eased lowest-cost providers, who rely on an assessed maintenance infrastructure. Therefore, it could be harder for energy suppliers to purchase hight-cost, market-entry units without subsidies. Although, the ecological and technical features of the Fuel Cell, associated with proven reliability, can match the marketing goals of efficiency-oriented municipal utilities, which act in a competitive market where an "ecological label" is constantly pursited as an essential element with respect to politicians and consumers.

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[10] J.O'M. Bockris : « Energy. The Solar Hydrogen Alternative », The Architectural Press, London, 1975.

[11] We refer here to elements as seen from the Periodic Table, the aim being to underline the variety of properties (reduction, refining, fuel, lifting agent etc.) and the applications which follow from it.

Ultimately, the PEMFC generator will become economical if either :

- down-scaling of **refining equipment** (as ATR) make the FC system compatible with conventional fuels like natural gas and liquid fuels. The advantage is that no retreatement or end-of-pipe cleaning devices are needed. Or :

- novel (light, high-capacity) **hydride storage** creates the conditions for an hydrogen refuelling infrastructure based on traditional central reforming plants. Or :

- the FC system justifies a price premium compared to conventional motor generators either by appropriate credits for its efficiency, cleanliness and noiselessness, or because of its high-value **flexibility** in case multi-use FC system, as power generator in the house and as powertrain for a vehicle.

PEMFC systems should be investigated for both small (1-20 kW) and medium (100-500 kW) powerband.

7.6.1 - Renewables vs. Hydrogen ?

Since 1973, conscious of oil-dependance for electricity production and transport, the search for an alternative energy system has started. This effort has brought new technologies to the market, *e.g.* nuclear, PV, and led to improve old ones, as the wind generators. The technologies based on renewable sources have since become cheaper but do not yet provide an alternative energy system, be it for electricity demand peak shaving or transport.

The dispersed character of windmills and discontinuity of photovoltaic have restrained a resolute gensets market penetration, because of storage weaknesses. Concerning mobile applications little is feasible without a convenient fuel. Green municipalities finance battery-vehicles to reduce urban pollution, albeit pushing the emissions back to the power plant. The lower overall efficiency, when electricity is generated from fossil fuels should be reason for reflection. Range autonomy and time of recharge of battery vehicles will probably stop their suburban and rural use anyway.[12]

R&D on alternative energies has been focused on details of each renewable energy source without the necessary global assessment of the whole energy system: basically electric and fuel networks and their maintenance. From such a state of things FC, which need fuel and electric subsystems and have as principal advantages high efficiency and no emissions, have been neglected by institutions and medium entreprises. Subventions for re-buying energy produced from PV would have more sense with a clean energy carrier for storage - hydrogen - and an efficient conversion device : the fuel cell.

The transmission & distribution energy sector is typically a natural monopoly in every real case and if one follows economic theory. Decentralized hydrogen production and electricity generation via dispersed FC systems could reverse the situation.

In this sense was planned the most ambitious (unaccomplished) project of the European Community Fuel Cell Programme : the Dispersed Hydrogen Network, which should have

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[12] An interesting experiment is led in Turin, where 20 electric Panda with a 50 km autonomy are rented for 5000 It.£/h.

carried centrally reformed hydrogen through a pipeline to the FC users for cogeneration and in refilling station for city buses.

It is my opinion that hydrogen production could be the distinctive feature of the national energy systems in the future. The We-Net program in Japan and current projects in Iceland [13] are the closest approach to the hydrogen economy concept.

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[13] See : « The Economist » August 16, 1997, where the government plans to convert fisherman's diesel boats (in Iceland there are more boats than cars !) to alkaline FC drive, with hydrogen produced in a former ammonia plant.

Industrial Contacts

Company	**Activity**	**Contact**
Ansaldo (CLC)	PAFC commercialisation	Tullio Bozzoni, Director
Ansaldo Ricerche	MCFC, PEMFC	Angelo Dufour, Vice Director
Arthur D. Little	Fuel processor, market development	J. M. Bentley, Director technology and product development
		Robert S. Weber, Catalysis
BMW	FC systems	Wolfang Strobl, Joachim Tachtler
Carbotech	Pressure Swing absorption	Klaus Giessler, Dep. Management
De Nora	PEMFC stacks	Michele Tettamanti, sales
		Antonio Maggiore PEMFC development
Haldor Topsoe	Steam reformers systems	Ernst Jansen, C. Lau Larsen
Johnson Matthey	Catalysis electrodes, noble metals	Robert Evans, Market development
		Thomas Purcell product manager
Siemens	PEMFC stacks	Johachim Grosse

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