

Chapter 4 - PEMFC - The Choice of the System

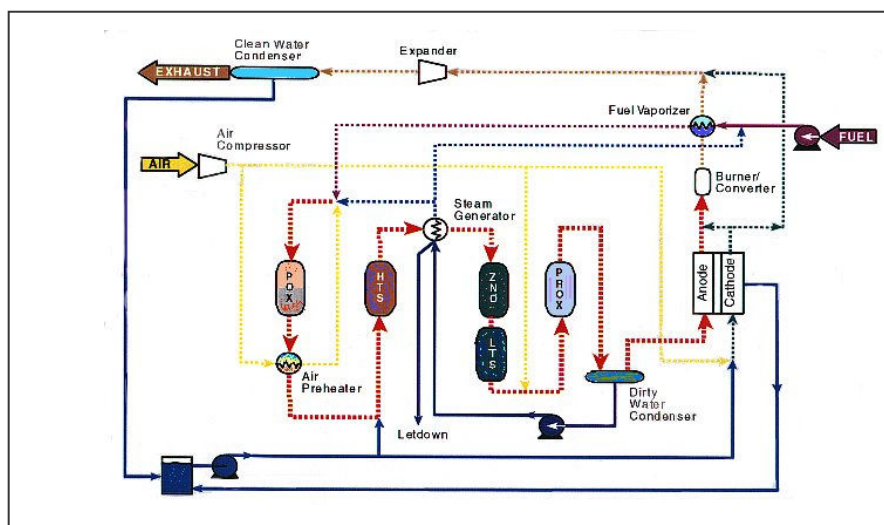
4.1 - PEMFC Systems

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 curve, 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 literature¹ :

- 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

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 been 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

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 ³ system)	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.

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 examples are :

- LH₂ (-253°C) to improve at most the vehicle's range in the BMW approach ⁸
- Methanol (CH₃OH), 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 H₂ 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 C₆₀ a molecular aggregate of 60 carbon atoms which forms a sphere. Nanotubes are larger (C₇₆, C₈₂) 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 Laboratory¹¹ has shown that single-walled nanotubes (SWNTs) have better storage performance on both gravimetric (4%wt) and volumetric (50kgH₂/m³) 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 C₆₀ is given below.

⁸ Hettiger, W. and others: "Refueling equipment for liquid hydrogen vehicles". In XI Hydrogen Energy Congress, 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.

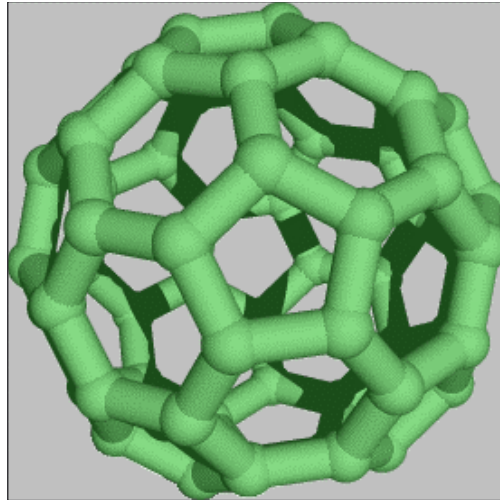


Figure 4.1 – Buckminsterfullerene (source : LANL).

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 consumption¹⁴, although other sources¹⁵ 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 addressed 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}.

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

¹⁵ ETSU Report No.131.

A recent work¹⁶ 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 cycle¹⁷ (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 throughout the power range),
- 3) Variable pressure (ratio 1 to 3) variable flow rate (stoichiometry 2.5 throughout 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 exhaust. 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 assess 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 Pétrole.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 studies¹⁹ are useful to simulate cell operation under different regimes, *i.e.* stationary, transient and unstable, regarding cell, electric grid and system exploitation constraints.

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

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 oxygène 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 Electricité 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).

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 Nm³/hr station, where reformed NG, coal, biomass or electrolytic, liquid or compressed H₂ 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.

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.