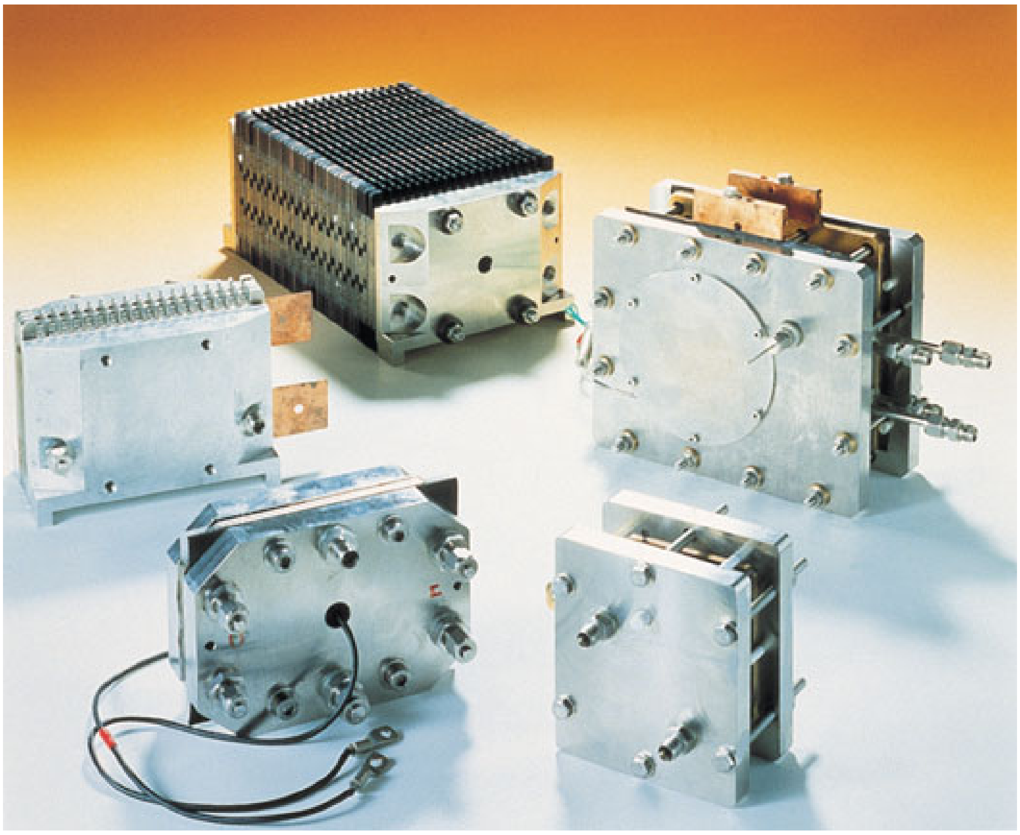
PEMFC LOW TEMPERATURE FUEL CELLS

Scientific and technological barriers

A large proportion of international research and development efforts concerning new energy technologies focuses on proton exchange membrane fuel cell, better known as PEMFC, chosen almost universally to power the fuel cell vehicles of the future. In this area, many barriers have still to be broken down to guarantee the competitiveness of the formula. The CEA is working on several aspects of this problem.



Fuel cell components designed by the CEA for studying mass transfers in the cell core, on the one hand (in the top right corner) and materials, on the other (top left and bottom corners).

Totem de Pierre/CEA

Among the various types of **fuel cell** commonly developed, this is the one known as the "solid **polymer electrolyte** acid" (figure on page 43) fuel cell and it has been chosen by virtually all automotive program developers world-wide. Generally referred to as PEMFC, it also attracts the attention of industrial firms for stationary applications up to one megawatt, for portable devices up to 100 W and for carriable devices less than 5 kW. There are three main reasons for the interest shown in this technology:

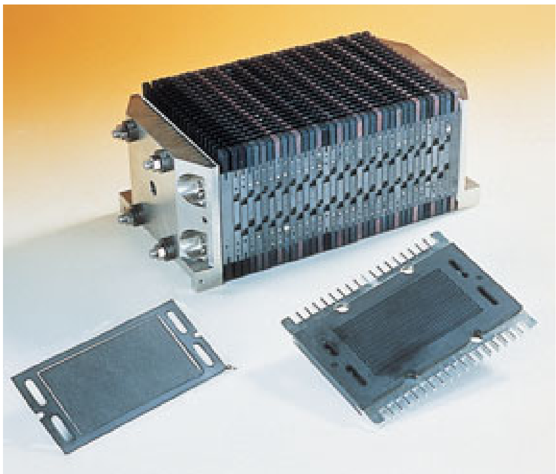
First, its relatively low operating temperature (< 100°C) holds the promise of a simplified technology allowing rapid start-up and easy dissipation of the heat produced at ambient temperature, and this is an essential feature for automotive applications. Secondly, unlike alkaline, it is unaffected by the presence of CO_2 in the **air**. Last but not least, its *100% solid* technology means that it benefits both from a lifetime considerably greater than liquid electrolyte devices (no moving parts inside the converter) and easier industrialisation. As a result, a cost compatible with the target market can be foreseen, particularly as this fuel cell is considerably more compact than those of other applications.

The most important research and development efforts worldwide are currently based on PEMFC technology. The main aim of research is to increase performance (in terms of efficiency, compactness and weight) and reduce cost (by a factor of 5 to 100 according to the type of application). Indeed it is in this area that the CEA has been working since 1996, to prepare a technology that is commercially viable, with a deadline varying according to the type of application, and to present 50 kW demonstrators for stationary and transportation applications.

At the request of French car manufacturers, the CEA is concerned first and foremost with the development of new fuel cell modules and with enhancing their electrochemical response. The proposed solutions relate for the most part to the development of new materials (type, implementation and integration) for the critical components of a PEMFC: bipolar plate (50% costs, 90% weight) and the membrane-**electrode** assembly (50% costs and maximum **conversion efficiency**). Since 1996, this research has led the CEA to file some fifteen patents.

Furthermore, it should be pointed out that a fuel cell module, where the combustion energy of a **fuel** (hydrogen for the PEMFC) is converted into directly usable electrical energy, must, in order to operate, be associated with auxiliary devices supplying the reactants (hydrogen and air), conditioning them (pressure, flow) and managing by-products (water, heat, electricity). These auxiliary devices can account for up to 60% of system weight and volume with an energy consumption of around 20%. One of these devices, fuel storage, forms a major technological barrier as, for certain applications, system autonomy and optimised management is dependent on it. To guarantee industrial application of the solutions proposed, whether concerning materials or their integration, the CEA has thus also acquired digital and experimental means enabling it to continuously evaluate the impact of these solutions on the various components of a fuel cell energy source.

The aim of such action is to define the optimum architecture of the fuel cell and the integrated system in line with specifications drawn up by the company (e.g. private vehicle, bus, submarine exploration machine, standby generator set, etc.). The objective is to reduce the cost of critical components and integrated systems, to increase performance of complete systems and to guarantee reliability of operation while at the same time minimising the impact on the environment.



1 kW PEMFC fuel cell module used for performance testing at the CEA/Grenoble and its components: the membrane-electrode assembly on the left and a graphite bipolar plate on the right.

Totem de Pierre/CEA

While the fuel cell has a history dating back nearly two centuries, it is reasonable to consider that the first industrial applications within the next three years will mainly concern certain "niche" markets (public transport, submarine exploration). To penetrate these markets, the PEMFC must prove its robustness and its capacity to compensate the still high costs of this technology by a marked reduction in operating costs. It should also be noted that fuel supply is not a critical factor for these markets, unlike for general public applications. At the same time, the CEA is working on the technological breakthroughs that could raise the last barriers (mainly cost and fuel) of PEMFC technology and allow its rapid use by car manufacturers.

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The progress made in proton conductive membranes

Proton conductive membranes form the core of PEMFC type fuel cells. Their importance is obvious, as it is their **conduction** properties that will determine electrochemical recombination of hydrogen with oxygen, the cell **fuels**, and thus its performance. **Ohmic drops** limit operation at high current densities and are mainly associated with membranes (ratio of thickness over proton **conductivity**). Furthermore, the latter must exhibit good chemical and mechanical resistance properties in operating conditions, not be permeable to gases and maintain a high water content at high temperatures since this determines conduction properties.

Creation of a membrane for a PEMFC fuel cell by polymer solution casting.

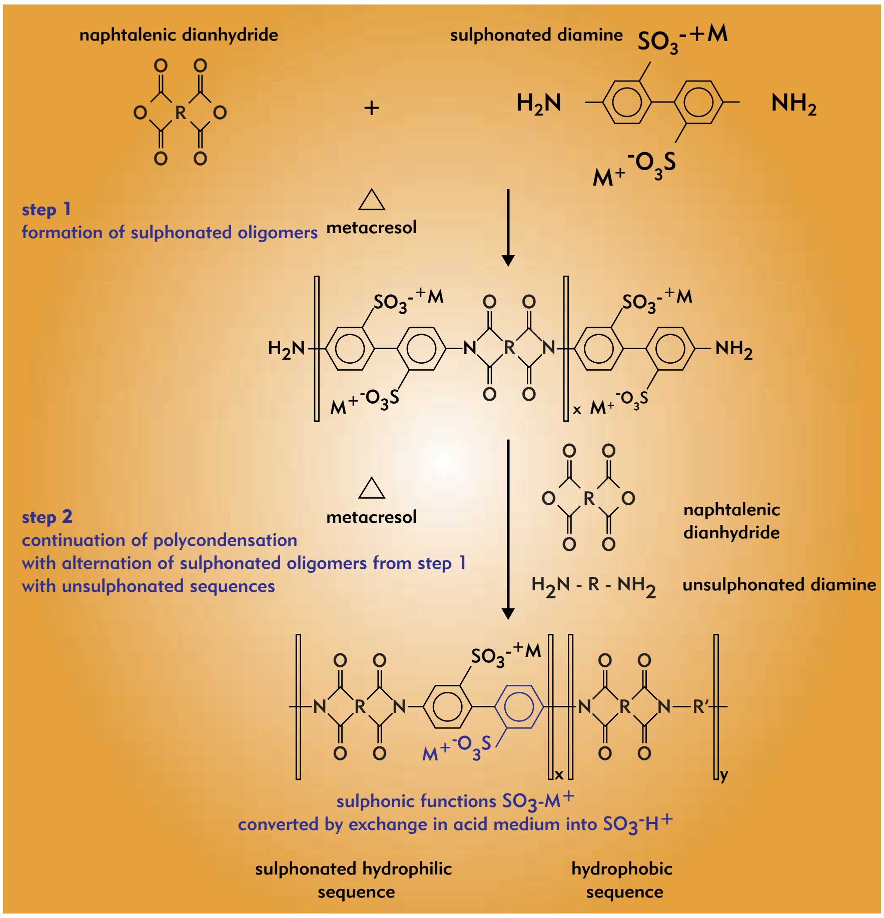
CEA

The need for new membranes

The current reference material is the *Nafion* type **perfluorinated polymer**, marketed by the American firm DuPont de Nemours. However, its excessive cost (approximately 700 Euro/m^2) is not acceptable for this technology, which requires tens of square meters of membranes to make a cell using filter-press type assembly so that the 50 kW necessary for vehicle traction can be obtained.

The lack of selectivity for **methanol** of these membranes, when considering the development of direct methanol cells for example, combined with the problem of recycling fluorinated polymers, particularly when the platinum, which is a **catalyst** closely linked to the membrane, has to be retrieved, are all additional reasons for creating new membranes. This need is all the more crucial since the temperature operating range has had to be raised to 150/200°C to minimise the problem of poisoning of the **catalysts** from the carbon monoxide.

Figure 1: The two steps synthesis: the first line shows the dianhydride and the sulphonated diamine allowing, in a metacresol medium, the sulphonated sequences shown on the second line to be obtained by polycondensation. M^+ corresponds to the triethylammonium used during synthesis and subsequently exchanged by H^+. In the second step, the polycondensation reaction continues by adding unsulphonated diamines and dianhydrides to the previously sulphonated sequences. The exchange capacity of the resulting polymer is defined by the ratio of sulphonated and unsulphonated diamines used.



The sulphonated polyimide method

Their thermal stability and the ease with which **sulphonic** functions can be **grafted** on to the aromatic cycles make thermostable heterocyclic aromatic polymers an excellent choice of material. The originality of the approach adopted by CEA and CNRS research workers is based on the chemical nature of polymers, the use of already sulphonated monomers and on the possibility, by a two-steps synthesis (figure 1) of controlling the distribution of charged monomers along the polymer chains (random copolymers or copolymers consisting of sulphonated blocks of various lengths). The process of creating membranes by polymer solution casting is an easy means of producing composite membranes and membrane-electrode assemblies.

Following validation of this polymer type as part of a CEA-CNRS partnership, a more ambitious programme was set up. This programme, which is part of a campaign backed by the ministry of Research and Technology, combines the resources and expertise of public research and industry. The LMOPS (Laboratory of organic materials with specific properties) at the CNRS is responsible for synthesis, while the CEA is in charge of implementing membranes, physico-chemical characterisation and ageing tests *ex situ* and in the fuel cell. Finally, the company Sorapec is responsible for producing membrane-electrode assemblies and for testing them in the fuel cell.

Modulable properties

Naphtalenic dianhydrides were chosen for the chemical resistance properties that they confer on the resulting polymers. A mixture of **diamines** is used in unsulphonated sequences to optimise solution casting and ionic migration properties as well as the stability of the membranes created.

The process of preparing membranes, either homogeneous or reinforced by fiber

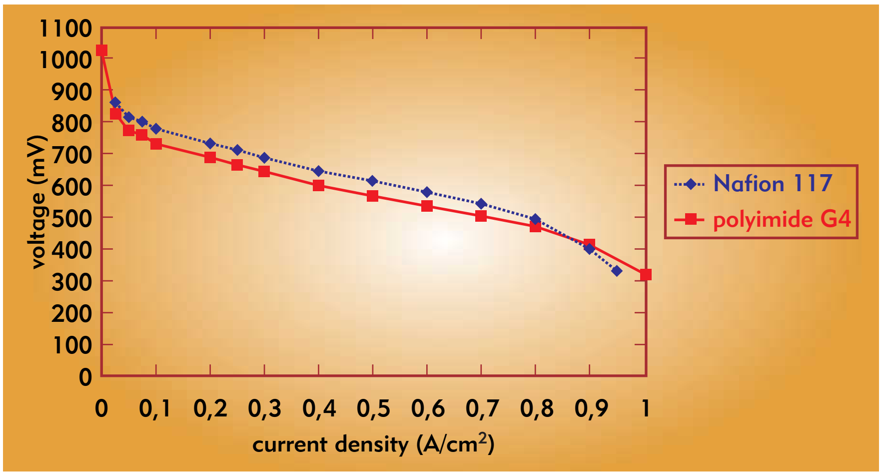


Figure 2: Comparison of polarisation curves for a Nafion 117 (◆) membrane and a polyimide membrane (■). The membrane-volumic electrode assemblies were obtained by cold pressing of membranes between two volume electrodes. The resulting curves correspond to the following test conditions: T = 70°C T (humidifiers) = 75 °C; P(H_2) = P(O_2) = 4 bar.

glass fabric, has been validated at industrial level (several m^2). The conduction properties achieved yield a performance similar to that obtained with *Nafion* type membranes (figure 2). The chemical stability of these membranes has allowed experiments in fuel cells to be conducted over more than 3000 hours. The advantage of these polymers with high glass transition temperatures (greater than 300°C) has been proved by the original microstructures obtained resulting from segregation between the hydrophobic and ionic parts: these microstructures lead to **anisotropic** swelling properties and modulable conduction and ageing properties.

Optimising membrane-electrode assemblies

Creation of composite membranes (polymer mixtures, reinforced or multi-layer membranes, etc.) and the corresponding membrane-electrode assemblies now form part of a *PACo Network* campaign backed by the ministry of Research. The aim of this campaign is to optimise membrane-electrode assemblies by combining a chemical and a physical approach (multi-layer membranes, alloys, asymmetrical membranes).


CEA/CNRS

Reactor used at the CNRS/LMOPS for synthesis of the sulphonated polyimides used for the composition of high performance proton conductive membranes.

An optimisation that also calls for research to understand the migration mechanisms in these materials.

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Cell core: progress in the field of membrane-electrode assemblies

The cell core, or membrane-electrode assembly, has always accounted for a very small part of the cost of proton exchange membrane **fuel cells** (PEMFC), both from the point of view of the **electrolyte** (ion exchange **polymer** membranes), and the **catalyst**. It is usual to consider that the cost of a cell is more or less equally shared by three items: the membrane, the **electrodes** and the bipolar plates. The catalyst used in this type of cell is made of pure platinum or platinum alloyed with a transition element (Cr, Mn, Ni, Co, Fe). Indeed, only this **noble metal** has enough electrocatalytic activity to reduce the oxygen and oxidise the hydrogen while, at the same time, ensure long-lasting resistance to corrosion (dissolution) in this highly acid chemical environment. Research carried out since the beginning of the sixties has thus focussed on cutting down on the quantities of platinum at the electrodes and maintaining or improving performances. The catalyst quantities are expressed in milligrams per cm^2 of electrode surface. Thus, savings worth two orders of magnitude have been made on the amount of noble metals used over the last thirty years, without this having undermined the **power density** (see figure). Moving from metal platinum electrodes to electrodes using very small particles of platinum (2 to 3 nanometers) on a carbon powder base has greatly contributed to this reduction by improving the catalyst's electroactive surface area. Another important contribution is the use of a proton conductor to impregnate the catalytic area over a thickness of several tens of microns thus enabling the reactive species to reach the catalytic sites over a larger volume (geometric surface × active layer thickness), giving the name "volume electrode". This operation results in catalyst surface areas which multiply the geometric surface of the electrode one hundred times.

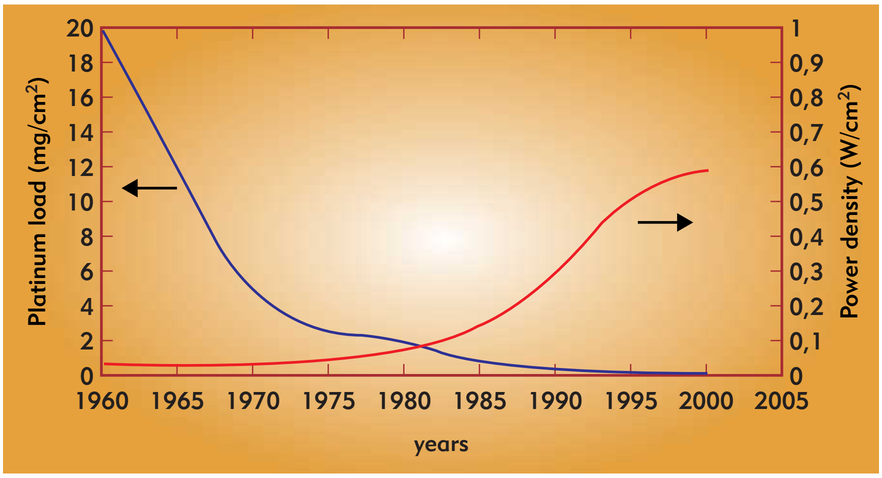
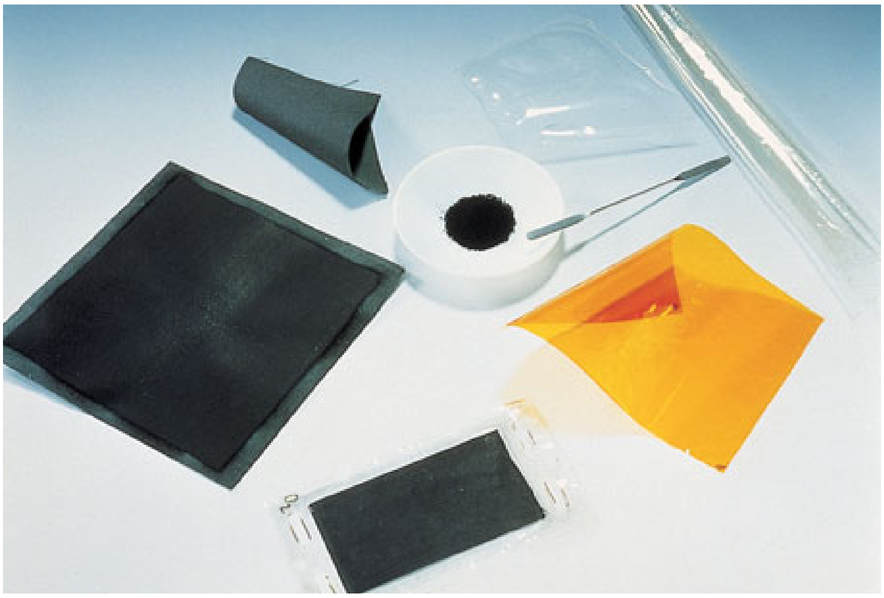


Figure. Changes in electrochemical performances and platinum load of the membrane/electrode assembly over the last few years.



Core components of a proton exchange membrane fuel cell: polyimide membranes (yellow), Nafion® membranes (translucid), powder catalyst, electrode (top). The large square is a membrane/electrode assembly.

Totem de Pierre/CEA

Increasing the electrically active surface

One of the primary objectives of the CEA and its industrial partners in this area is to optimise the cell core. Platinum volumes may have been decreased but the electrochemical performances (fixed voltage current or power) of the catalyst need to be significantly improved. In view of this, research work aims to increase the electroactive surface area, facilitate access of the reactive gases (air and hydrogen) to the catalyst particles, while optimising the structure and composition of the electrodes.

A growing concern in research is the catalysts' resistance to poisoning by carbon monoxide at the anode, and to the oil particles in the air surrounding the cathode. These pollutants come from using a fuel produced by **reforming** alcohol or **hydrocarbons** and from the non purified air supply to the cell. The use of platinum alloys (Ru, Mo or Sn at the **anode** and generally transition metals at the **cathode**), the injection of oxidising additives in the anode gases or the increase in operating temperature are all objects of current research.

Finally, the last area of research concerns the direct use of liquid fuels such as **methanol**. These cells have the advantage of being able to store liquid fuel but with the drawback that the reaction at the anode is very slow resulting in a sharp drop in cell voltage, and therefore cell power. New catalysts still based on platinum binary or ternary alloys have been developed in an effort to overcome these problems.

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Optimising the generating set around the fuel cell

Designed especially for electrically-powered vehicles, the **fuel cell** will be the central link in an electrogen system whose hydrogen production makes it all the more complex. In order to optimise the output from this unit, scientists at the CEA have directly taken into account the technical and economic restrictions that affect its development.

In recent years, the arrival of proton-exchange membrane fuel cell (PEMFC) technology has awakened enormous interest in this electrochemical energy generator, particularly in the field of electrical traction. Heralded as the high-performing replacement for **batteries**, a number of projects exist for its integration in prototypes of electrically-powered vehicles. Apart from their rather exotic nature, these projects clearly indicate the path of future development by showing the real restrictions and challenges facing the fuel cell if it is to take up reign in the industrial world. Its application in electrically-powered cars for use by the general public is undoubtedly the most difficult challenge. The functions to be fulfilled are numerous, the difficulties of integration and costs are high, the rival technology (heat engines) is powerful and its associated products are constantly improving.

A concrete example, that of the *Nebus* car produced by Daimler-Benz, powered by compressed hydrogen, illustrates the performance already obtained on prototypes of bus traction systems with maximum wheel power of 205 kW (see table).

Since 1992, the CEA has worked on this application with French car manufacturers through national (VPE/PAC) or European (Hydro-Gen) programmes. Asked to design or improve fuel cells for the electrical traction of private cars, it decided from the outset to take into consideration all technical and economic requirements affecting the cell's specifications (in terms of functions and basic components).

Inside the power system of electrically-driven vehicles, the fuel cell is located in the part called "electrical energy source" or "generating set" and acts as this part's central

traction type	emissions (CO, NOx, etc.)	efficiency	weight/ power	volume/ power	price/kW
fuel cell system	0	44 to 37%	> 10 kg/kW	> 18 l/kW	> 38 000 euro/kW
heat engine	< 2 g/km	25 to 35%	< 4 kg/kW	< 4 l/kW	< 150 euro/kW

Table. Comparison of a fuel cell system and a heat engine system for the propulsion of a bus with a maximum wheel power of 205 kW.

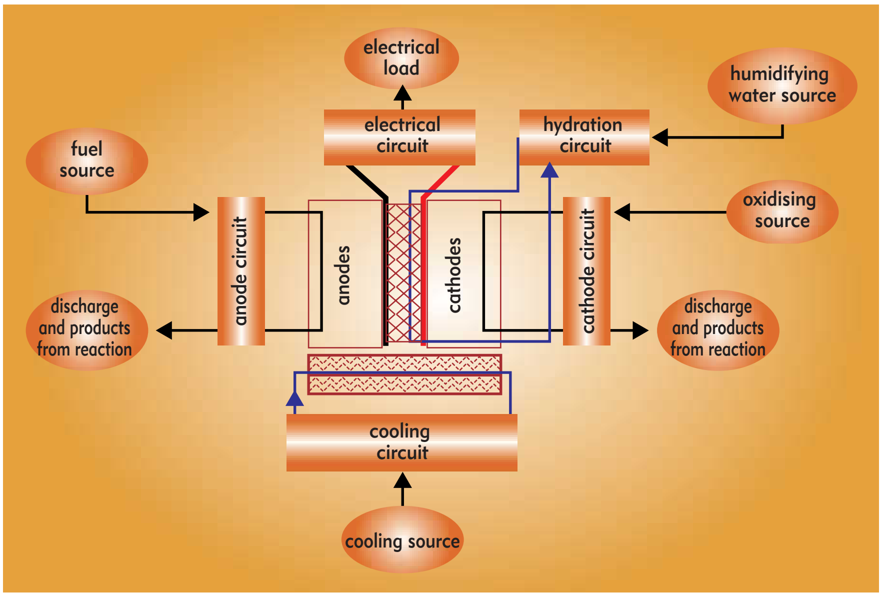


Figure 1. Diagram of a fuel cell generating set.

link (figure 1). This unit is located between the fuel tank and the motor system, composed of the motopropulsion unit (electrical engines) and the transmission system.

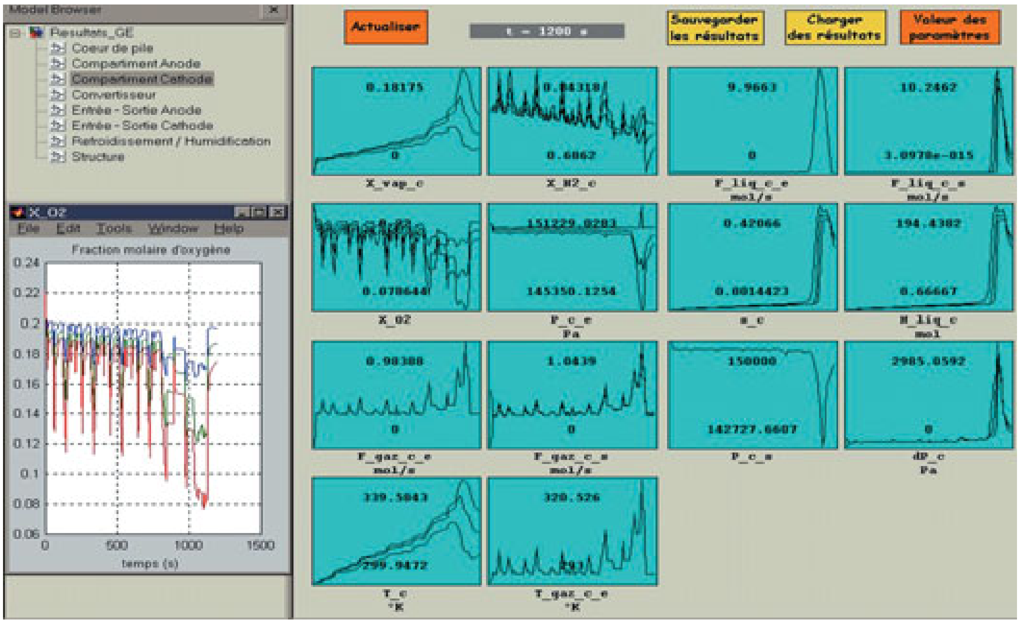
Given the extensive interactions between each of the sub-systems in terms of energy response, size, weight and cost, the search for the ideal power system cannot be done by simply juxtaposing optimal components. It can only be found through compromise, and the ideal compromise cannot be obtained by designing prototypes alone.

To find a solution to this problem and continue its technological research into the fuel cell, the Technological Research Division of the CEA has started to produce an in-depth study to fully understand the basic concepts of fuel cells, in particular PEMFC fuel cells, and test them through experiments.

A complex unit

An "energy source" or generating set using a PAC fuel cell is a complex unit whose basic function is the conversion of combustion energy into electrical energy, inside an electrochemical reactor. The cell is built of a stack of elementary converters or "cell units" (see previous articles) connected in series to achieve usable voltages (several tens to several hundreds of volts). In a PEMFC cell, the **fuel** burnt is hydrogen and the **oxidant** is oxygen, usually taken from ambient **air**, and the product of the chemical reaction is water. All these elements require special equipment with optimum integration. This is also the case for energy delivered by combustion, transformed into electrical energy and heat.

The voltage at the converter terminals depends on the current drawn by the power



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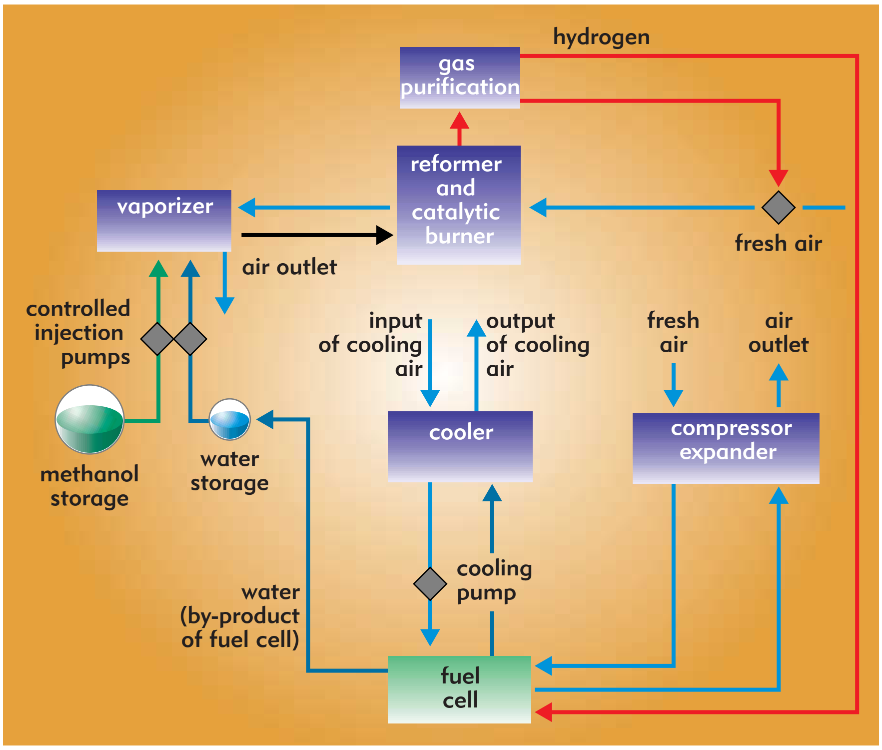
Calculations of changes to the internal parameters of a fuel cell built into the energy source of an electrically-powered vehicle driven in city conditions.

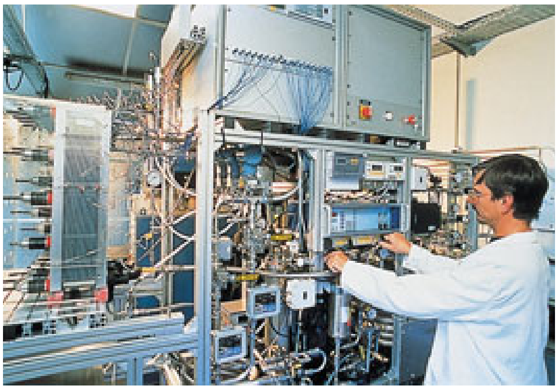
Figure 2. The Daimler-Benz methanol-based fuel cell system.



supply of the motopropulsion unit. To operate, this converter must be connected to at least five components: a hydrogen source (may be a **hydrocarbon**), an oxygen source (usually ambient air), an evacuation system for reaction discharge and products, a cooling source to enable the heat from the reaction and the Joule effect in the electrolytes and electrodes to be evacuated and, finally, an electrical load (motopropulsion unit with or without battery type energy storage or super-capacitors) or the electricity distribution grid. In the specific case of PEMFC, the cell must also be linked to a water source to keep the membrane wet. These connections are *via* specific circuits, i.e. a minimum of four fluid circuits and an electrical circuit.

The complexity of the circuits depends on the quality of the fuel and oxidising sources and on the autonomy required. If the chosen fuel is a hydrocarbon, a **reformer** is necessary. If the oxygen is taken from ambient air, it must be filtered to remove dust and grease, and compressed to obtain the required cell voltage without using too much energy in the process. Above all, the unit must present a positive hydric state. The search for a satisfactory global energy source requires the recovery of all forms of energy leaving the reactor, including the mechanical energy available in the gas discharged. The organic diagram of the electrochemical energy source of the prototype vehicle *Necar 3* built by DaimlerChrysler illustrates the complexity of the unit in terms of components and connections between the different circuits (figure 2).

The management of such a unit using a control system is dictated by problems of thermal, hydraulic, hydric and reactional stability and the compromise between the demand for upstream electrical power that has to be met (in range and dynamics) and the overall output of the energy conversion, which must of course be determined in consideration of the loss caused by the demultiplication effect according to thermodynamic principles.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Experimental characterisation of energy and operational response of a De Nora cell on the PacMod 10 kW test bench at the CEA/Grenoble.

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The art of not blocking the bubble

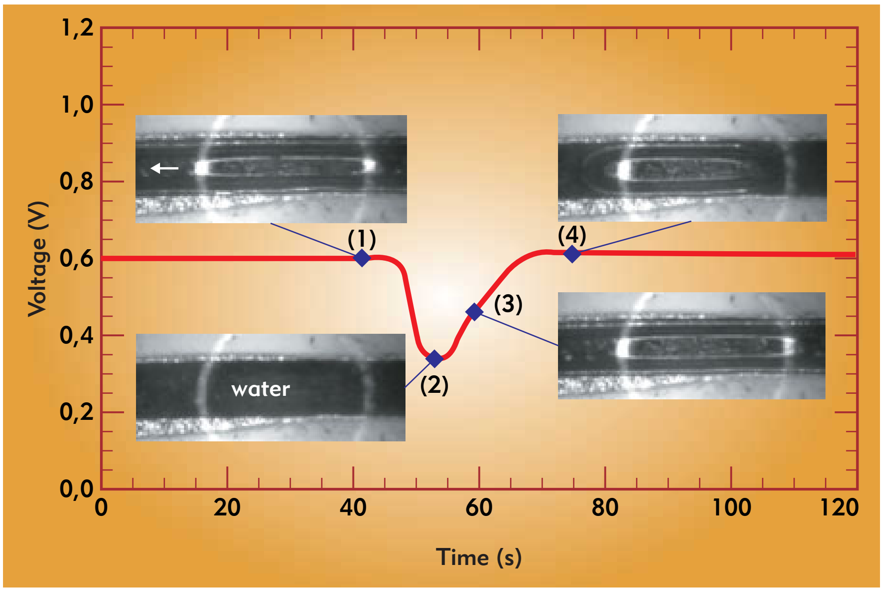

Figure. The changes in voltage occurring when a water lock passes through a rectangular PEMFC channel (height 1 mm). In (1), doubly stratified flow (stable state), in (2), flooded channel, in (3), a gas bubble travels through the channel, in (4) return to a normal state.

The working of a **polymer** membrane **fuel cell** depends, among other things, on the distribution of reagents (hydrogen and oxygen), the hydration of the **electrolyte** membrane and the simultaneous evacuation of residual gases and of the liquid water formed at the **cathode**. These electrochemical **converters** operate at reduced pressure and temperature, which stimulates the development of two-phase water-gas flows inside the reagents' distribution structures, at the **electrodes**. These distributors may consist of machined channels inside the bipolar plates (see *Towards a new conception of the bipolar plate*) or a metal foam. Their role is to make sure that gases are evenly distributed over the electrodes, in order to guarantee optimal use of their active surface, and, as a result, help to reduce the high cost of PEMFCs.

CEA

Overall view of the Gesteau test bench, an experimental device used to study flows in PEMFC fuel cells at the CEA/Grenoble.

Having acquired a high level of expertise in this area through nuclear research and engineering, it was only natural for the CEA to conduct research into the thermal hydraulics of PEMFCs. This work is based on one experimental device in particular, which was designed for the purpose of studying flows in fuel cell monocells *via* viewing windows. The experiments carried out so far have enabled researchers to identify the flow patterns to be found within millimetric distribution channels and to determine their impact on the electric response. So, the two-phase flow patterns usually to be found in horizontal pipes also occur here but present specific differences owing to the small size of the channels, which causes **capillary** effects. The generation and maintenance of a liquid film on the upper surface of the channels (doubly stratified flow) is, in this respect, an original facet. However, the main result concerns the impact of hydraulic phenomena on the fuel cells' electrical behaviour. At a given current, the fuel cell will operate more reliably, and at the highest possible voltage, if there is no liquid film on the surface of the electrodes, as this film slows down the transfer of gases to the reactive sites. On the other hand, water locks (discontinuous flow), or even the flooding of the channels, cause a spectacular, and more or less lasting, drop in performance levels (figure).

Besides improving our understanding of physical phenomena, the experiments conducted on channel distributors have enabled us to optimise these elements geometrically. At the same time, thanks to similar proceedings, we will be able to analyse flows in porous distributors, and their impact on the electric response, with a view to enhancing the system's efficiency.

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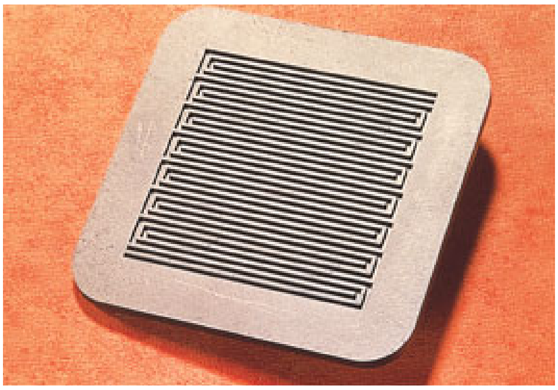
Towards a new conception of the bipolar plate

Organic compound bipolar plate, made by thermal pressing. The active gas distribution surface measures 50 cm^2.



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The development of a PEMFC **fuel cell** for applications such as the electric vehicle involves the creation of new, enhanced-performance materials, at a cost low enough to satisfy industry requirements. This is why the CEA is working on a number of new developments in bipolar plates, the purpose of which is to collect the electrical current and to distribute and separate gases at the **anode** and the **cathode**. Bipolar plate materials must therefore exhibit an adequate level of **electric conductivity** (above 10 mho/cm), greater impermeability to gas than the proton exchange membrane, and good chemical inertia with respect to the fluids present in the cell core (water, acid, oxygen, etc.).

The most commonly used bipolar plates are made out of graphite, and the gas distribution channels are produced by machining. These plates are commercially available but they are extremely expensive, primarily because of the machining process. They are therefore not suitable for industrial use.

This is why the CEA, on the basis of its knowledge in the using of both organic and metallic materials, is developing two new types of bipolar plate: organic compounds and sheet metal.

Organic compounds

The idea behind the organic compound bipolar plate is based on the use of fillers (carbon, graphite...) which are diffused through a **thermoplastic** or **thermosetting** material. These fillers provide the bipolar plate with the electric conductivity required to collect the current, and the polymer binder gives them the mechanical resistance necessary for the assembly of the different elements. The major advantage lies, on the one hand, in the low cost of the basic materials and, on the other hand, in the fact that the distribution channels can be manufactured directly by moulding the **polymer**. Subsequent machining is not required.

Thanks to a number of parameters, such as the nature and geometry of the fillers, the type of polymer binder used, the proportion of filler in terms of volume, and **formulation** and implementation conditions, the material's properties can be adjusted to meet the main specifications. Electrochemical tests have shown that, in a fuel cell configuration, over a period of several hundred hours, organic compound bipolar plates behave in a similar way to graphite collectors.

Two applications for a patent have been filed for this new type of bipolar plate. The objective of current developments is to optimise compositions and implementation conditions, so that these bipolar plates can be used by industrial partners involved in the development of Proton Exchange Membrane (PEM) fuel cells.

Sheet metals

Metals and alloys, especially stainless steels, possess a number of characteristics (mechanical resistance, tightness, electric conductivity, easy shaping and joining by mass production process) which make them the ideal choice for the design and development of compact, lightweight and cheap bipolar plates. Due to their density, which is greater than that of graphite, they must be used in thin layers, which are easy to form by pressing. In these conditions, heat dissipation and temperature control can be performed accurately while the module is running, by introducing an internal cooling liquid. A first series of prototype plates in 316L stainless steel, manufactured by laser welding or brazing pressed plates onto a pre-cut frame, has been developed. These plates are substantially thinner, and their weight, per active surface unit, is 27% lower. In addition, the cost of manufacturing a limited series (50 units) could, potentially, be divided by 3. As a result of this study, the constraints specific to this approach have been determined. The alloy's maximum breaking elongation has a strong impact on the design of the distribution channels' geometry, meaning that the cell's hydraulic and electrical parameters, during operation, will probably have to be optimised. The metal plates' *in situ* resistance to corrosion is also being studied. Indeed, excessive plate corrosion and the formation of metallic cations can alter cell operation and performance in a number of different ways, by reducing the membrane's **ionic conductivity**, or even impairing tightness or obstructing channels. The objective of this study is to identify alloys which will not excessively reduce operating performance, over cumulated operating periods of 3 000 to 5 000 hours for automobile applications, and even 30 000 to 50 000 hours for stationary electricity production.

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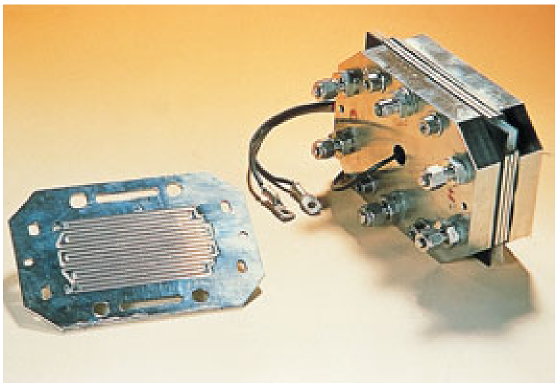

Sheet metal bipolar plate. The active gas distribution surface measures 66 cm^2.

Totem de Pierre/CEA