

HIGH TEMPERATURE SOFC CELLS

State of the art and prospects

Just one of a large family of fuel cells, the SOFC (Solid Oxide Fuel Cell) seems to inspire a certain degree of unanimity as to its technical potential, and in terms of applications. The CEA has chosen to develop this technology, along with the PEMFC (Proton Exchange Membrane Fuel Cell). Yet it is one of the least technically and economically advanced technologies. So, what are the advantages which account for such a contradiction between this technique's potential and the actual progress it has made ?



SOFC cell prototype developed at the Jülich research centre in Germany.



Forschungszentrum Jülich

On the power generation or **cogeneration** applications market, R&D teams have, up until now, capitalised less (by a factor of 2 to 3) on SOFC **fuel cell** technology than on

rival technologies. PAFC (Phosphoric Acid Fuel Cell) technology, which has already reached the marketing phase, and MCFC (Molten Carbonate Fuel Cell) technology cumu-

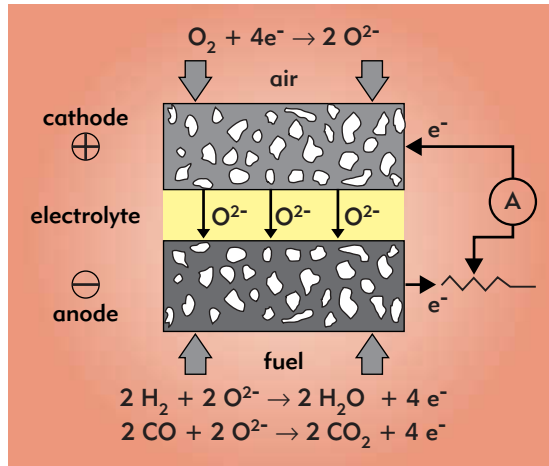
late investments in demonstrators together with subsidies equal to more than one billion Euro. Moreover, some car manufacturers have invested hugely in PEMFC technology, turning it into a credible alternative for the "stationary" market (see table). Yet the SOFC technology seems to be a serious outsider.

An SOFC cell operates according to the following mechanism (see figure): the oxygen is dissociated at the **cathode** into O²⁻, then the cation travels through the high-temperature (around 800°C) ionic conducting **electrolyte** (around 800°C) and mixes with the hydrogen at the **anode** to form water and release electrons.

technology	current state of advancement	market share in 2025 (%)
PAFC	marketing phase (3000 Euro/kW)	10
MCFC	development/prototypes	25
SOFC	R&D (planar technology) development/prototype (tubular technology)	40
PEMFC	R&D	25

Table: How the market for stationary application fuel cells will look in 2025 (according to a survey by "Décision", August 1999).

Figure: Simplified diagram of an SOFC fuel cell.



The main characteristic of SOFCs is therefore their high operating temperature (from 700°C to 1000°C), which is needed to attain an adequate level of **ionic conductivity** in the ceramic electrolyte. There is a dual advantage to this high temperature. Firstly, it allows the direct use of **hydrocarbons**, in the first instance natural gas, which can easily be **reformed** without using **catalysts** based on **noble metals**. Secondly, it provides a source of intense heat, that can be used without difficulty in a **cogeneration** system, either with or without a gas turbine: in this way, the overall efficiency increases reaching up to 80%. But there is a drawback: the heating up process is long, and therefore not appropriate for short, repetitive cycles.

For all these reasons, SOFC technology is particularly suitable for decentralised electricity production and for cogeneration (areas which involve powers ranging from 1 electrical kW to a few dozen electrical MW). It is, moreover, modular, meaning that scale economy factors are relatively unimportant, which is not the case of, say, MCFC technology. Thanks to its high efficiency and its potential ability to operate directly with liquid hydrocarbons, it will also find an outlet in naval, or even land-based (trains, trucks, etc.) propulsion.

Due to its high operating temperature, the development of this type of cell necessarily involves solving problems related to the

thermo-mechanical resistance of rather complex materials, as well as dealing with assembly and tightness issues (see following articles). As with other technologies, it is very important to achieve a service life of several thousand hours without impacting performance levels. Therefore, the focus is on studying how SOFC materials age in oxidising or reducing environments, in order to be sure that the chosen materials are chemically and physically stable.

Finally, and this is true for all fuel cells, a significant reduction in costs is absolutely essential if the SOFCs is to make its mark. Cost has a considerable impact on the design of the cell and on the choice of material forming processes, which must comply with economic objectives.

Three types of structure

Three types of SOFC cell structure exist: tubular, planar and monolithic. The Westinghouse group (which has now been taken over by Siemens and is known as Siemens-Westinghouse) has been developing tubular geometry technology for over twenty years in the United States. Since 1998, this group has invested 200 million Euro in this technology with the aim of putting it on the market in 2003 for use in 250 kW generators, at prices of around 1000 to 1500 Euro per electrical kW. It is therefore an undisputed *leader* in the

field of SOFC, getting ready to launch a competitively priced technology for industrial-type power generation. Here is one example of a possible application: the assembly of 250 kW units to be used, alongside a gas turbine, in the construction of a 3 electrical MW factory, the overall efficiency of which would reach 70-75%. Several prototypes have been tested over a long period of time. The most recent, a 105 electrical kW demonstrator installed in Nuon (the Netherlands), provided an overall energy efficiency of 76% and ran for 4 000 hours without a hitch.

The Japanese, backed by the NEDO (New Energy Development Organization) are also developing this technology, and are concentrating on reducing costs by choosing the appropriate materials (the quality of Japanese research into ceramics is renowned) and attaining a power range of 1 -100 electrical MW.

Planar geometry technology is more advanced. Naturally more compact than tubular technology, it will reach better performance levels, especially in terms of specific power. But it is also more difficult to develop (sealing problems for example). Several companies have been set up over the last few years, mainly offshoots of large groups or research centres: in Australia, Ceramic Fuel Cells Limited, established in 1992, is planning to bring out generators of 25 to 100 kW or more by 2002; in the United States, companies like Ztek or Sofco are also trying to propose attractive, short-dated solutions such as systems based on 250 electrical kW cells and a gas turbine. R&D programmes backed by the Department of Energy (DOE) – 24 million dollars over three years – aim to cut costs by half to achieve a target of 500 Euro per electrical kW! Some Japanese companies (Mitsubishi, MHI) are also working on this technology, with the backing of several organisations and universities.

In Europe, Sulzer Hexis have announced the 2001 commercialisation of gas boilers for private houses, able to deliver around 1 electrical kW and 3 thermal kW. The overall system should be connected to the grid, which provide peak supply and absorb excess current during off-peak hours. It will be managed at first by electricity companies, who will draw up a rental agreement with individuals in a given area. The excess cost in relation to a standard boiler should, in the long run, be around 700 to 1000 Euro for the actual cell. The cell's service life would therefore be at least 5 years (40 000 hours). Sulzer Hexis have been working on this concept for nine years, within the framework of a 30 million euro project, 75% of which is financed by the group, and 25% by Swiss government subsidies. Around ten experimental installations throughout the world have been under-

100 kW cogeneration unit, incorporating an SOFC unit, installed by Siemens-Westinghouse in Werstervoort, near Arnhem (the Netherlands).



Siemens-Westinghouse

going long-term testing for the past three years. It should be noted that in the Netherlands, an offshoot of ECN (Energysonderzoek Centrum Nederland), In Dec, is selling SOFC ceramic elements while, in Great Britain, Rolls Royce are investigating a concept known as Integrated Planar SOFC, made up of multi-cellular electrode-membrane modules, using vapour phase deposition or printing techniques. The main objective, during the development phase, is to achieve costs lower than 300 Euro per electrical kW.

Finally, **monolithic** technology would provide more compact solutions and high current densities. Very little information is available on the progress of this concept, developed by the American group Honeywell (Allied Signal), except that the structure, which is corrugated, is made up of thin layers of compound.

The R&D scientists involved in the field of SOFC in Europe are fewer and less committed than in the United States. The main European teams are the following: the ECN centre (Netherlands), the DLR (Deutsches Zentrum für Luft- und Raumfahrt, Germany), Keele University (United Kingdom) and the Jülich centre (Germany). Industrialists are showing a certain interest in the use of SOFC. They mainly include gas companies (GDF, British Gas), electricity companies (EDF), industrial groups such as Alstom, BMW and Renault for an auxiliary electrical energy generator, boiler manufacturers (Vaillant in Germany) or generating set manufacturers (Houvenaghel-Hennequin in France).

What can France do ?

Besides the interest shown by industrialists, some of whom have already been mentioned (EDF, GDF, Alstom, Rhodia...), the



Le Square des photographes/CEA

Solid titanium electrolyte, before and after sintering, developed by the CEA's material processing centre.



situation in France is characterised by quality R&D work on very precise aspects of specific physical phenomena (catalysis, ceramic material). However, no cells have been developed. The work of the following laboratories and institutes are just some examples: the Lepmi (Laboratory of electrical chemistry and physical chemistry of materials and interfaces) in Grenoble, the Lace (Laboratory for the application of chemicals in the environment) in Lyon, the ICMB (Institute of condensed materials in Bordeaux) and the LCMI (Laboratory of inorganic chemistry in Toulouse).

The reluctance of the French to join the race can be explained, in part, by the lack of market demand, due to the highly centralised nature of French electricity production. The situation is, however, changing as the electricity market is very gradually being opened up and there is a general trend towards decentralising production. The cost of transporting and distributing electricity, and of maintaining the network in sparsely populated, climatically vulnerable areas (see December 1999 storms in France) also militates in favour of decentralisation.



Sulzer Hexis

Sulzer Hexis installation, undergoing operational testing. Includes a gas boiler and a tubular SOFC cell and delivers 1 electric kW and 3 thermal kW.



Technological breakthroughs in view

The CEA became involved in this field in 1999. It, of course, disposes of all the skills required to develop SOFCs, in addition to those of its university partners: development and characterisation of new materials, **thermo-hydraulic** and electrochemical modelling, the ability to perform cell tests, cell test benches. It also masters all the main ceramic forming techniques: strip casting, sintering, plasma projection. The CEA aims to bring development work up to the European level, and to make the technological headway required to reduce costs. The CEA is also looking for an electrolyte which would operate at relatively "low" temperatures (600 to 700°C), making it possible to use stainless steel double-pole plates and less inhibiting structures. The integration of "progressive internal reforming", in view of optimising the operating capacities of a cell directly supplied by **methane** at the anode (without prior reforming) is also part of the CEA's programme. The development of an SOFC cell prototype around 2003 will be a first in France.

A promising system

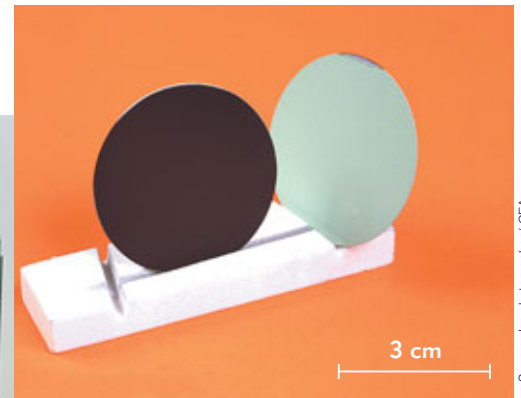
France is certainly behindhand as far as SOFC technology is concerned. But it does have a great range of expertise, both within its universities and its research organisations, which should enable it to come up with innovative solutions in relation to the present state of the art as well as make technological breakthroughs. It will therefore have no problems in joining a dynamic European community and participating in the emergence of a system full of promise.

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Drawing back the bolts on SOFC development



SOFC cell measurement bench. The cabinet is used to control the input of gas into the oven, and its temperature. The cell is inserted into the bell-shaped oven. Its voltage is measured according to the temperature, the intensity of the discharge and the gaseous environment.



A complete cell, developed at the CEA and ready to be incorporated between gas distributor and current collection plates.



The constraints peculiar to SOFC-type **fuel cells** are, *a priori*, an impediment to the development of economically viable operational cells. Researchers, notably those from the CEA, are looking into possible solutions, some of which involve lowering the operating temperature. Another line of research could also prove to be decisive, namely the direct use of varying fuels, and especially of **hydrocarbons** which are currently used following **reforming**.

The operating temperature of an SOFC (Solid Oxide Fuel Cell) is, at present, somewhere between 900 and 1 000°C. As we can see from the simplified diagram of a fuel cell's core (see figure in previous article), an elementary cell consists of two porous ceramic **electrodes**, separated by a dense, oxygen ion conducting **electrolyte**: yttrium stabilised zirconia (YSZ). The **ionic conductivity** of the YSZ reaches 0.1 mho/cm at 1 000 °C. In

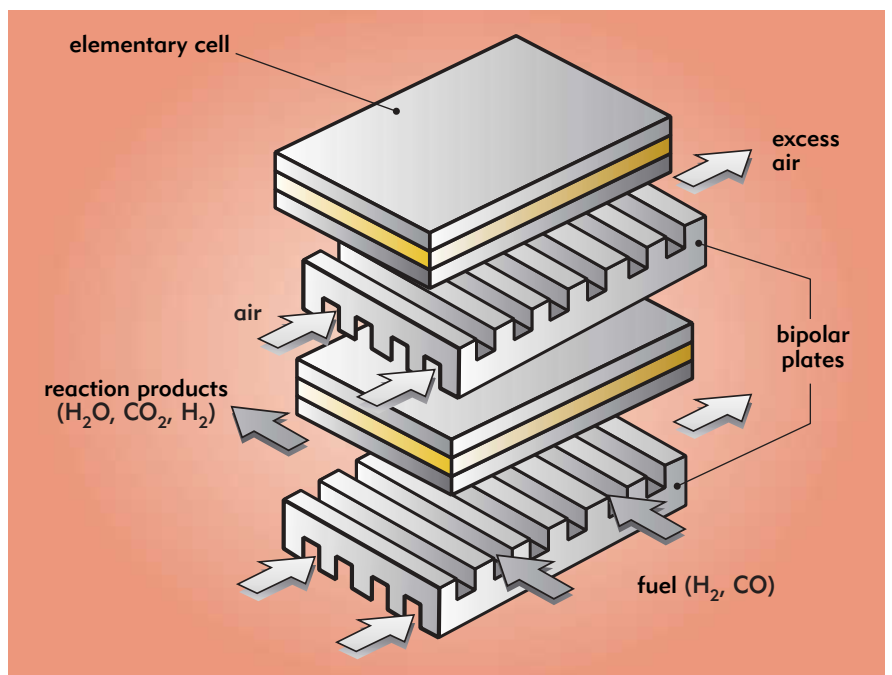


Figure 1. Diagram of a planar SOFC. The bipolar plates (1) distribute the gases separately and (2) collect the electric current.



G. Houlbreque/TotalFinaElf

Regenerative reforming installations at the Donges oil refinery. Reforming is to take place in a miniature factory, close to the solid oxide fuel cells.



today's technology, the **anode** is a *cermet* (ceramic-metal compound) of nickel and YSZ. Doped lanthanum manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) is a stable and effective cathode material. When oxygen from the air comes into contact with the **cathode**, it is broken down into O^{2-} ions which spread through the electrolyte towards the anode. The combination of these oxygen ions with the hydrogen results in the formation of water at the anode and the release of electrons (e^-) into the external circuitry. These systems currently provide surface **power densities** of 0.2 to 1 W/cm^2 .

Getting over the technological barriers

As the ionic conductivity of the standard YSZ electrolyte decreases at temperatures below 900°C , SOFCs must operate at high temperatures. This is very restrictive as far as the cell's structure, which is almost entirely composed of ceramics, is concerned. Engineers are therefore looking to reduce the operating temperature to bet-

ween 600 and 800°C , so that less costly metallic bipolar plates can be used to connect two cells up (see figure 1). Cutting back the temperature would also reduce thermal constraints and slow down the ageing of materials, which is a heat-activated process. The CEA has set about developing new ceramic electrolytes with, at reduced temperatures, an oxygen ion conducting capacity and a chemical stability comparable to those of YSZ. Another means of maintaining the system's performance levels at reduced temperatures is to coat either one of the electrodes with a very thin layer of electrolyte. A first measurement bench, adjustable to different temperatures, gaseous environments and configurations, has just been set up at the CEA to test SOFC cells of varying geometries. A second is in the design phase.

Besides being economically viable, SOFC technology must, if it is to be developed, provide an adequate **mass** or **volume power density** and be adaptable to different types of application (constant or variable current

operation). The main technological obstacles lie in the architecture of these systems. Two types of geometry are currently being developed. Siemens Westinghouse has opted for the tubular configuration, which provides an elegant solution to the tightness problem and is more resistant to thermal cycling (going from a heating and operational phase, to the total shutdown of the system). In comparison, the planar geometry (figure 1), which the CEA is backing, is propitious to an increase in power density and a minimising of assembly constraints. The problems to be solved with respect to this second type of structure have been identified. Given that 300 to 600 elementary cells must be connected in series to provide a usable voltage of 200 to 400 V, the questions of how the charge can be recovered from the electrodes and how mechanical constraints can be resolved are crucial. The electrical connection between the elementary cells can therefore significantly impede the cell's efficiency, through losses imputable to the Joule effect. Mana-

ging the air and fuel in the cell core also raises the issue of sealing between the different gaseous compartments and of how to optimise the distribution of gases over the entire surface of the electrodes. At present, glass seals are used to make the stacks tight but these seals are fragile and likely to react to the bipolar plates inserted between the elementary cells (figure 1). Metal seals, which are more resistant to harsh thermal cycling, would be more technologically efficient than these glass seals.

Towards the direct use of varying fuels

A number of fuels could be used to supply SOFC type cells. They can be split up into three categories: those which are currently used in the majority of research work (**natural gas** or petrol), those which have been used in feasibility studies (liquid gases, gas oil and the gas used to incinerate household waste) and, finally, those which represent new areas of research, such as **bio-gas**, **biomass** fuels such as **methanol**, **ethanol**, synthetic gas (a mixture of carbon monoxide and hydrogen obtained *via* **thermolysis** of the biomass or of various types of organic waste), dimethyl ether (DME), etc. At present, these fuels are used indirectly, at the end of a reforming phase during which the hydrogen that the cell will actually consume is produced. This transformation phase takes place in a reformer outside the cell (figure 2). However, the direct use of these fuels within the cell itself, *via* an internal reforming process, would not only improve efficiency but would also simplify and reduce the system's volume. Internal reforming has therefore become a key issue and a major technological factor in the future development of this type of fuel cell.

Why introduce an internal reforming phase ?

Using a hydrocarbon such as natural gas in a fuel cell naturally leads on to the possibility of producing electricity directly by the electrochemical oxidation of **methane**, according to the following: $\text{CH}_4 + 4 \text{O}^{2-} \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + 8 \text{e}^-$. This reaction is very appealing as it produces 8 electrons. However, with current anode materials, it is very slow and induces a very significant drop in the cell's efficiency. All of the SOFC prototypes that run on natural gas today require an additional phase, known as the reforming phase, to convert the gas into hydrogen.

As far as high temperature SOFCs are concerned, reforming can be performed directly within the fuel cell's anode: this is known as internal reforming.

There are three reactions which produce hydrogen from methane: partial oxidation (5), steam reforming (1) and **cracking** (7) (see table). Cracking (7) should of course be avoided as it produces a carbon deposit in the anode and gradually poisons it. At temperatures of 800 to 1 000°C, the partial oxidation of methane (5) is difficult to control, especially since complete oxidation must be avoided (6) as it does not produce any hydrogen. Steam reforming (1) is therefore the most commonly used reaction in industry, either in external reformers or in internal reforming within high temperature cells such as those based on dissolved salts (MCFC - Molten Carbonate Fuel Cell) or SOFC prototypes. Moreover, this reaction provides the SOFC with a specific advantage: up until now, it is the only cell capable of consuming the carbon monoxide (CO) produced during reforming.

fuel-producing reactions	electrochemical oxidation reactions	carbon-producing reactions
(1) steam reforming reaction $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$ $\Delta H^\circ(800 \text{ }^\circ\text{C}) = +242 \text{ kJ/mol}$	(3) $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ (4) $\text{CO} + \text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{e}^-$	(7) gas cracking reaction $\text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2$ $\Delta H^\circ(800 \text{ }^\circ\text{C}) = +92 \text{ kJ/mol}$
(2) gas to water reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ $\Delta H^\circ(800 \text{ }^\circ\text{C}) = -38,6 \text{ kJ/mol}$	(5) partial oxidation of the gas $\text{CH}_4 + \text{O}^{2-} \rightarrow \text{CO} + 2 \text{H}_2 + 2 \text{e}^-$	(8) Boudouard reaction $2 \text{CO} \rightarrow \text{CO}_2 + \text{C}$ $\Delta H^\circ(800 \text{ }^\circ\text{C}) = -189 \text{ kJ/mol}$
	(6) total oxidation of the gas $\text{CH}_4 + 4 \text{O}^{2-} \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + 8 \text{e}^-$	

Table. Summary of the different reactions occurring at the anode of an SOFC type cell, running on methane. ΔH° represents the reaction's standard **enthalpy**, i.e. the total amount of energy consumed (positive value) or produced (negative value) per transformed mole, at atmospheric pressure.

The characteristics of internal reforming

A number of secondary reactions occur simultaneously to the main steam reforming reaction that we are interested in. Some of them improve the cell's performance, such as the **exothermic** gas to water reaction (2), which produces hydrogen, or the carbon monoxide oxidation reaction (4), which contributes to the cell's electrochemical efficiency. Others, on the other hand, are detrimental to the cell's performance, especially those which produce carbon and progressively poison the anode (reactions (7) and (8)). This is why today's external reformers, like the anodic compartments of internal reforming cells, operate in conditions that prevent the latter two reactions (from a thermodynamic and kinetic point of view), i.e., the gas is introduced with a high partial steam pressure (usually $p_{H_2O} \approx 2 p_{CH_4}$).

As the steam reforming reaction is highly **endothermic**, it is only activated at temperatures above 800°C and therefore restricts SOFC operating temperature ranges. Moreover, it is essential to make sure that the active sites participating in the reaction are evenly distributed over the entire surface of the anode. Indeed, a local concentration of this reaction would lead to a local drop in temperature and could cause the appearance, on the one hand, of a carbon deposit and, on the other hand, of cracks in the ceramic anode. Finally, even at temperatures above 800°C, its relatively slow kinetics make it necessary to use catalysts. Internal reforming

therefore requires that the reaction's catalyst be dispersed throughout the anode material.

Specific anode materials

In decreasing order of efficiency the steam reforming catalysts used are: Ru > W > Rh > Ir > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag.

Nickel (Ni) is the most widely used today because of its excellent cost/efficiency ratio. Moreover, it is contained in today's most commonly used SOFC anode material: a zirconia-nickel compound belonging to the cermet family. However, nickel also tends to catalyse the formation of carbon: to avoid this, the gas must be saturated with steam. This operating method is detrimental to the system's overall efficiency. Research is therefore being conducted into directly using the steam produced by the electrochemical oxidation of hydrogen for the internal steam reforming of the gas, thereby reducing the addition of steam (figure 3). The use of progressive internal reforming involves changing the anode material. Lanthanum chromites offer a thermal expansion coefficient close to that of the cell's other ceramics, a good level of **electronic conductivity** and, in addition, they reduce the formation of solid carbon. They are, when associated with a specific steam reforming catalyst, a very promising material that French researchers are developing within the framework of projects financed by the PACo network in particular (see box p. 44).

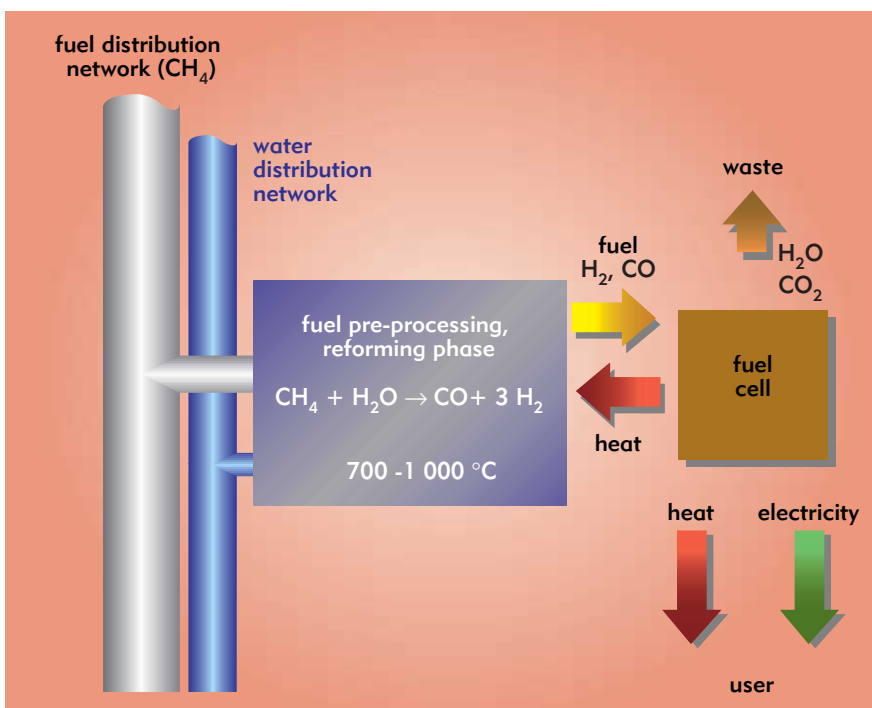


Figure 2: Simplified diagram of how a fuel cell with external reforming operates.

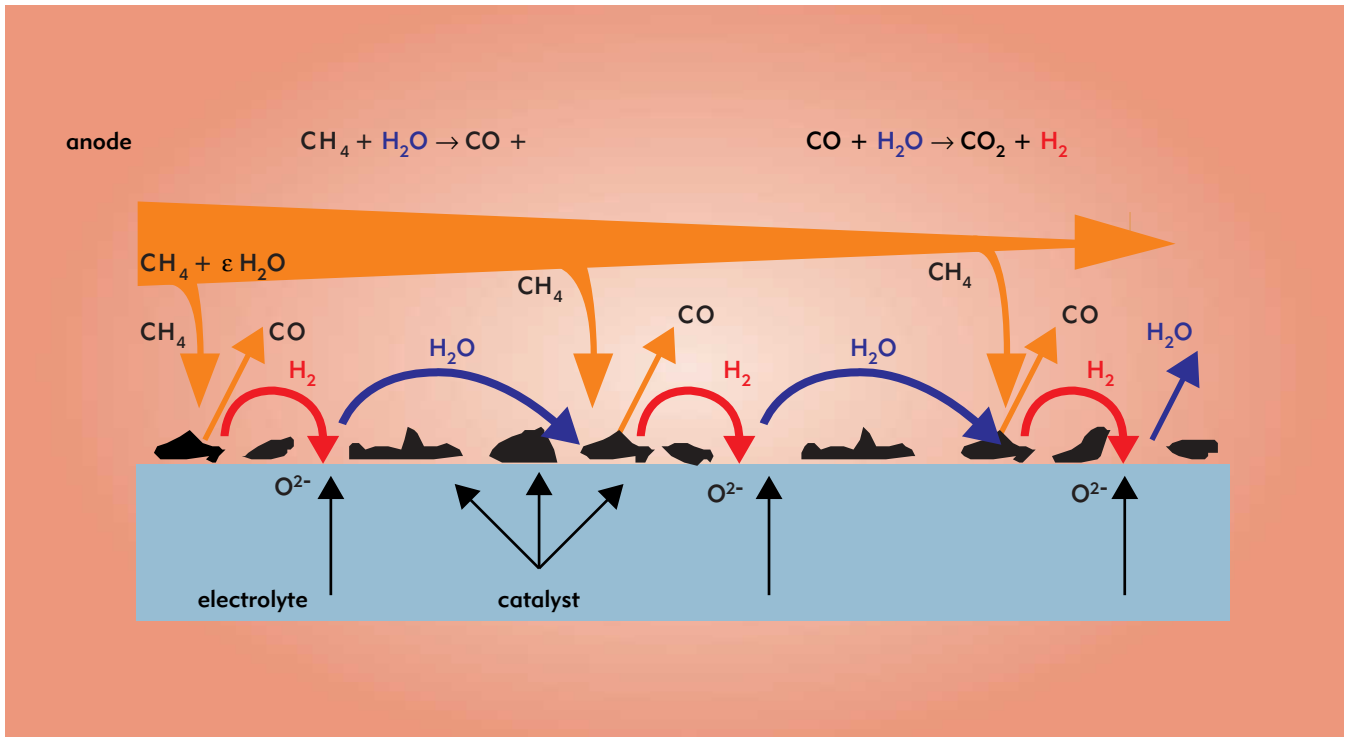


Figure 3: Diagram of the progressive internal reforming of methane (taken from a PhD thesis by P. Vernoux, INPG, 1998).



Until tomorrow's fuels arrive

It is still not known for sure what tomorrow's fuel(s) will be (hydrogen, natural gas, bio-methanol, bio-ethanol, synthetic gas, etc.). But, whatever they are, the SOFC fuel cell can, and will have to, adapt to them. Such is today's technological challenge. A development project for an SOFC prototype of several hundred watts has just come into being. Its main objective is to test the validity of internal reforming in planar geometry modules. The external reformer's flexibility (it is possible to use varying hydrocarbons for the same cell

core) will be matched against the compactness of internal reforming using specific materials from the chosen fuel. The final choice will depend upon the application's requirements and implementation costs.

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Low temperature SOFCs or high temperature PEMFCs ?

With regard to both of the fuel cell technologies studied at the CEA, namely SOFC on the one hand and PEMFC on the other, it is tempting to break away from current temperature ranges in order to improve performance. SOFCs could last longer and cost less at lower temperatures, whereas PEMFCs could be more efficient and competitive if "hotter" conductors were used.

Solid oxide conductors

Reducing SOFC operating temperatures (currently between 950 and 1 050 °C) could increase their service life by reducing damaging reactions at the interfaces. It could also make them much less expensive, thanks to the use of metal interconnectors instead of costly ceramic ones. Operating temperatures of 600 to 800°C would not undermine the SOFC's main advantages, such as the rapidity of electrochemical reactions, the use of carbon monoxide as a **fuel**, the possibility of incorporating direct **reforming** and the absence of costly **catalysts**.

As an SOFC's temperature is determined by the **ohmic drop** in the **electrolyte**, the latter must be equally resistant at lower temperatures to avoid harming performance levels. There are two possibilities: on the one hand, reduce the thickness of the customary electrolyte and, on the other hand, use a different electrolyte, with better conducting properties at lower temperatures. Various techniques (PVD, CVD, plasma) have been used to reduce the thickness of the electrolyte to 10 micrometers (µm), as opposed to 100 to 200 µm in standard systems. The **fuel cell** is therefore generally supported by the anode and correct operation is possible at temperatures around 850°C. If the thickness of the electrolyte is further reduced, a number of technological difficulties arise: the electrolyte must be impermeable to gas, and its reactivity to the electrodes is not inconsiderable. Moreover, the electrolyte must exhibit as high an **ionic conductivity**, and as low an **electric conductivity**, as possible, in order to avoid short circuits.

Other electrolyte materials have been suggested. Oxides such as doped lanthanum gallates ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{MgO}_{0.2}\text{O}_{2.85}$) have been proposed as a replacement for zircon. Their ionic conductivity is satisfactory from 700°C upwards. But, in spite of their very good **conduction** properties, these oxides have technological drawbacks which are difficult to overcome (high cost of gallium and che-



Totem de Pierre/CEA

mical instability of lanthanum gallate). Doped albanite ($\text{CeO}_2 - \text{Gd}_2\text{O}_3$) displays even higher ionic conductivity levels at these temperatures, but its instability in a reducing environment and its excessively high **electronic conductivity** seem to rule out its use in a fuel cell.

In view of the growing interest in SOFCs, other materials are currently being developed (doped bismuth oxides, perovskites, apatites, etc.), but this work, although highly promising, is still at the research stage.

Reducing the temperature also raises the question of how the **electrodes** function at lower temperatures. In any case, an anode composed of a nickel-electrolyte cermet (a mixture of nickel and the ceramic electrolyte) will operate satisfactorily at temperatures below 700°C. On the other hand, this reduction provokes an additional catalysis constraint (drop in voltage) in regard to the slow oxygen reduction reaction which is highly dependent on the temperature at the cathode. It seems that if a triple contact electrode were used (electrode with combined **ionic** and **electronic conduction** properties) satisfactory operation would be possible at reduced temperatures.

Test benches for studying fuel cell core materials at the CEA/Grenoble.



Protonic conductors

In view of the difficulties encountered with oxide ion conductors, researchers have also, for several years, been looking into protonic conductors. As the hydrogen ion is smaller, it is reasonable to believe that it may be more mobile, and spread more quickly than the oxygen ion. Studies have revealed the protonic conduction properties of a certain number of oxides (based, notably, on BaCeO_3 , SrZrO_3 and $\text{Ba}_3(\text{CaNb}_2)\text{O}_9$). Conductivity levels of around 10^{-1} ohm/cm have been measured at 600°C in perovskites based on BaPrO_3 . Often, however, these ceramics are also electronic conductors at high temperatures (>600°C) and in an oxidising atmosphere. These ceramics should be taken into account primarily for applications at temperatures between 400 and 600°C. Other types of electrolyte have been suggested for equivalent operating temperatures, e.g. salt-oxide compounds, or for lower

temperatures, alumina β'' (a specific form of aluminium oxide) as a substitute for hydrogen between 150 and 300°C.

In addition to oxides, protonic conducting **polymers** could also be used at temperatures up to 350°C. At present, maximum PEMFC temperatures are around 100°C, due to the necessary hydration of these polymers and the stability of acid (sulphonate) functions.

Research aims to increase polymer stability by adjusting the chemical formulation of the matrix and of the acid functions, or

by using composite membranes in which the different functions are spread over various materials. These potential protonic conduction systems cover a wide area, from low temperature (700°C) SOFCs to high temperature (150°C) PEMFCs, and could be suitable for a large number of applications. However, many points must still be cleared up: the efficiency of these cells and the way in which the electrodes really operate (particularly their catalytic activities at low temperatures), possible fuels and, above all, the

stability of the electrolytes and the electrode-electrolyte interfaces over long operating periods. ●

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All-round safety studies for the fuel cell



Testing, at the CEA/Cesta, of a safety device used to cut off a vehicle's electricity supply when an accident occurs.



which falls within the scope of the PACo network and in which the CEA is participating alongside the Ineris, the Inrets, Alpeha and several industrial groups (Air Liquide, Creed, Snecma).

Safety studies of this type are generally conducted along the same lines. First of all, the system's service life is recreated, from its construction to its destruction at the end of its life. Secondly, each phase is analysed then simulated using digital models or by testing specimens on a reduced scale (mechanical, thermal, electric, etc.). Failure modes are identified through these studies and their consequences are quantified. "Failure trees" (a series of incidents) are used to determine how probable it is that the feared event will occur. Finally, these models are used to study suitable protection methods ("barriers"). These different steps are carried out with the help of a variety of tools which are already used in the nuclear industry: system simulation (specific models), risk analysis (e.g. Amdec-Hazop, Mosar, Serenade, Comrel), simulation of the effects of an accident on the system (e.g. Castem 2000, Plexus). Moreover, representative scale tests can be used to validate previous results and recommended solutions.

These studies improve the safety of systems without losing sight of their competitiveness, and will therefore help the general public to accept these emergent techniques. ●

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CEA/Cesta

Although the **fuel cell's** potential is beyond all question, it does involve taking risks in two areas: competitiveness and, of course, safety. Safety aspects are all the more important since the fuel under consideration is hydrogen and the applications for this type of cell concern nearly all of us, as consumers, whether we are talking about the electricity supply for vehicles, houses, computers or mobile phones. Indeed, although hydrogen is a clean fuel, which produces much less chemical pollution than a standard internal combustion engine for example, it is also a potentially dangerous gas which can catch fire or explode in the presence of air and in certain conditions. Two possible ways of using hydrogen are being studied: storage, or on-site production from another fuel (e.g. **methanol**). Various storage systems are being investigated: the very high pressure (700 bars) storage of significant quantities of

hydrogen (containers), very low temperature (21 degrees Kelvin) liquid phase storage, nanotubes or hydride. The CEA should be completing a technical and economic evaluation of the latter method by 2003. Each potential application and each storage solution involves its own specific risks which must be assessed and, of course, controlled (see chapter III).

Although a lot of research into fuel cells is still in the preliminary stages, safety studies must be carried out from the initial design phases onwards, which is something that the nuclear industry has been doing for a long time. These studies must be based, on the one hand, on a set of regulations established by European authorities and, on the other hand, on the analysis of results from experiments on fuel cell systems and other systems involving the same type of risk. These are the main objectives of the Serepac project,