

SOFC high-temperature fuel cells

SOFCs are deemed promising as a technology, in terms of the overall efficiency they offer, and their ability to operate with a variety of fuels. Research work under way is addressing definition and development of novel types of ceramic electrolytes, and specific anode and cathode materials, to achieve lower operating temperatures, and enable internal fuel reforming. Such investigations go hand in hand with development and optimization of material fabrication and forming processes, with the aim of bringing down manufacturing costs.

Research challenges and directions

While SOFC technology offers major advantages, it does require much research and development work. CEA, through its expertise, in particular in the areas of materials, processes, electrochemistry, and modeling, is in a strong position to ensure this technology achieves acceptable performance and cost levels.

Fuel cells of the SOFC family work according to the following principle. Air is carried to the **cathode**, where oxygen is dissociated, yielding O^{2-} **anions**. These migrate through the crystal structure of the **electrolyte**, going on to oxidize the **hydrogen** atoms carried to the **anode** by the **fuel**. This reaction yields **electrons**,

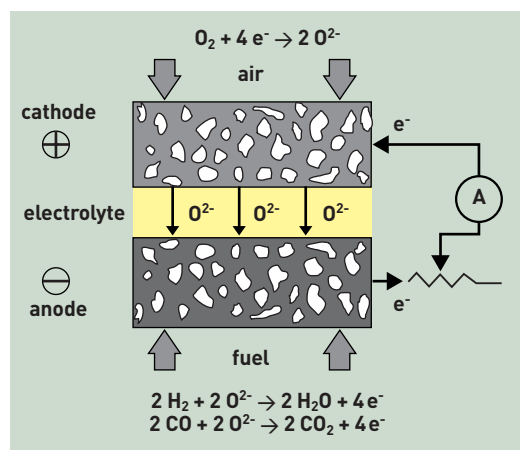


Figure 1.
Basic principle schematic, showing in simplified form the electrochemical mechanisms involved in a SOFC.

and water (see Figure 1). The specific feature of SOFCs lies in their high operating temperature, in the range 700-950 °C, this being required if adequate **ion conductivity** is to be exhibited by the **ceramic** electrolyte.

Advantages of SOFC fuel cells

Since a fuel cell acts as a direct converter of chemical energy into electric energy, according to theory, **electrical efficiencies** close to 70% should be achieved. Currently, gas turbines achieve an electrical efficiency of 36%, as against the 51% (Mitsubishi Materials



SOFC fuel cell being positioned on a test bench allowing determination of single-cell and stack voltage and current characteristics.

Corporation and Kansai) to 54% (Kyocera) claimed by corporations leading the field in SOFC research. The high operating temperature makes it possible to obtain high-temperature steam, suitable for added-value utilization, whether for the purposes of **cogeneration**, or coupled to a gas turbine. In the latter case, Rolls-Royce and Siemens Westinghouse indicate



overall electrical efficiencies close to 70%. One final advantage lies in the possibility, upwards of 800 °C, of effecting the **reforming**, directly inside the anode, in the presence of water, of a **hydrocarbon**. This operation may be carried out with no need to resort to **noble-metal**-based **catalysts**. The **electric power** range accessible to SOFCs is quite extensive, ranging as it does from the **kilowatt (kW)** (Sulzer Hexis) to several hundred kilowatts (Siemens Westinghouse, Rolls-Royce).

Attractive applications

The main area of application for this type of fuel cell is **stationary** energy supply (both electric, and thermal). The major reason for such a direction being taken relates to the technology adopted, using as it does metal-ceramic assemblies, thus dictating slow rises and falls in temperature, to preserve the integrity of materials and assemblies. Be that as it may, SOFCs, owing to their low sensitivity to contaminant poisoning, may be used with a number of hydrocarbons for fuel, affording them

attractive potentials in the area of **auxiliary power units (APUs)**. Delphi Corporation, with support from **US DOE**, under the aegis of

the Solid-State Energy Conversion Alliance, is working on development of a 5-kW electric automotive APU, drawing on the conventional **hydrocarbon fuel** tank for its operation.

However, demonstration programs remain few. Sulzer Hexis

have announced a preproduction run of 400 units for their HXS 1000 Premiere system.

This is a unit rated at a maximum 1-kW electric power, associated to a gas burner rated at 12-22 kW thermal, depending on the configuration selected. This unit is intended to be made available to private households, through local energy utilities (on the Swiss and German markets, essentially). Siemens Westinghouse announced in February 2002 the construction of a power plant, designed to deliver 225 kW electric power, further supplying 160 kW heat. This system is intended for the city of Hannover, Germany, and is scheduled to come on stream in the near future.

Major challenges

There are still major challenges to be met for SOFCs, in terms of cost reduction, target cost being in the €1,000-1,500/kW bracket (Rolls-Royce currently indicate €1,930/kW), extended longevity, target value being set at 5 years minimum, while undergoing several shutdown-startup cycles, improved reliability, and successful transition from the laboratory scale to high-power prototype. The best results obtained in laboratory conditions on single cells, with hydrogen, exceed the 1 W/cm² mark. However, best performance obtained for multicell stacks only runs to 0.3-0.5 W/cm².

Working on technological breakthroughs

The goals pursued at CEA are to bring solutions to meet these major challenges. For that purpose, research efforts at CEA concern development of innovative architectures (4 patents being applied for) together

with development (**formulation**, forming) of materials enabling operation with a variety of fuels (**biomass**, **natural gas**), and at lower temperatures, in the 700-800 °C range.

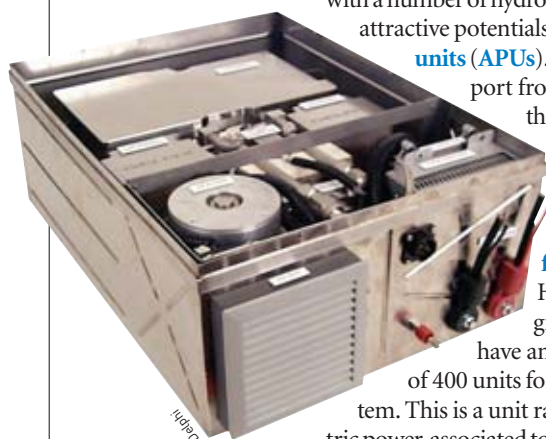
The GECOPAC Program

The GECOPAC (Génération d'énergie combinée par pile à combustible: Combined Energy Generation by Fuel Cell) Program, bringing together the French Centre Region, CEA, the Orléans-Tours *académie* (educational district), and industrial partners Dalkia and SNECMA Moteurs, aims at development of the first French prototype complete **cogeneration** system to comprise an SOFC fuel cell. The cell is to be designed, developed, and constructed by CEA. Rated at 5-kW power, the system will be fed from the **natural gas** grid, being coupled to the electricity system of the premises where it is installed, a high school selected by the *académie* rectorate. The GECOPAC Program will comprise a cell core, a **fuel** processing unit, developed by société N-GHY, a power-conversion, monitoring and control unit, developed by Ainelec, together with the modules required for system internal and external heat management. Program partners will build, initially, a 1-kW scale model, featuring the same subsystems as the future prototype. An initial overall assessment will be carried out on completion of 6 months' trials, to decide on construction launch and bringing into operation of the 5-kW prototype.

As a focus for research and development, the GECOPAC Program will channel technical and funding support, in particular as regards the cell core at CEA. It will further afford the possibility of a first operational feedback for a complete cogeneration system, this being of interest to Dalkia, as system user, and SNECMA Moteurs, as potential system assembler. Moreover, inclusion, from the start of the program, of a partnership with the Orléans-Tours rectorate will make it possible to develop the training and teaching structures required to train the professionals and technicians taking part in the integration of such systems into the energy scene of the future.

The cogeneration market, evaluated as standing, in France, at some 10,000 MW in coming years, will probably open up from 2005, as a result of the implementation of European Directives promoting cogeneration ([see Box on Fuel cell cogeneration](#)). Fuel cells are deemed to be competitive on the market for residential cogeneration (1-100 kW), by comparison with other cogeneration techniques (gas micro-turbines, for instance). The 5-kW prototype will provide excellent experience, as regards the future "building block" for such modular systems to come.

The GECOPAC Program is crucial, as regards bringing SOFC work in France up to grade. It should enable mastery to be achieved, of the key technologies for SOFC systems. It will foster the emergence of an expertise and excellence center to be set up at Le Ripault, due to form an integral part for a European technological platform of prime importance.



Prototype APU developed by Delphi.



HXS 1000 Premiere system by Sulzer Hexis.

Investigations carried out in France, in particular by CEA in association with **CNRS** and academic laboratories, are concerned with lowering SOFC operating temperature, through development of novel ceramic materials for the electrolytes. Forming techniques and processes (**plasma projection**, tape casting, **screen printing**) are also being addressed, with a view to optimizing fabrication costs, through a reduction in the number of steps required to obtain the end product. To improve investigation of basic cell aging, resulting as it does in steady performance loss, a test bench was set up at CEA/Grenoble. This allows monitoring and analysis of SOFC basic cell behavior - whether in single-cell or small-stack configuration - depending on the nature and origin of the fuel introduced at the anode. These investigations are being carried out under the aegis of French or European multi-partner programs.

This development process is combined with research work addressing upstream issues, ranging from detailed **modeling**, on the scale of electrochemical processes at the anode, carried out in collaboration with LEPMI (Laboratoire d'électrochimie et de physico-chimie des matériaux et des interfaces: Material and Interface Electrochemistry and Physico-Chemistry Laboratory, Joseph-Fourier University, Grenoble), to thermal-mechanical and fluidic modeling on the stack scale.

Finally, design work carried out by two CEA engineering and design departments has made it possible to identify novel structural pathways, taking as initial criteria the operational constraints of a future generator. These initiatives are presently taking a concrete shape in the form of the GECOPAC Program, endorsed by the **PACo Network** and launched in January 2004, with



F. Vigouroux/CEA

Programming the temperature cycle of the oven in which SOFC fuel-cell performance is measured.

the goal of designing and constructing by 2007 the first French SOFC cogeneration unit (*see Box*). The system's prime object will be to monitor and investigate the behavior of a complete generator, in actual utilization conditions. On the other hand, its power range of a few kilowatts is already making it a candidate for residential applications, whether for individual households or small communities. It is hoped it will further be a stepping stone to a generator suitable for industrial production.

> **Franck Blein**

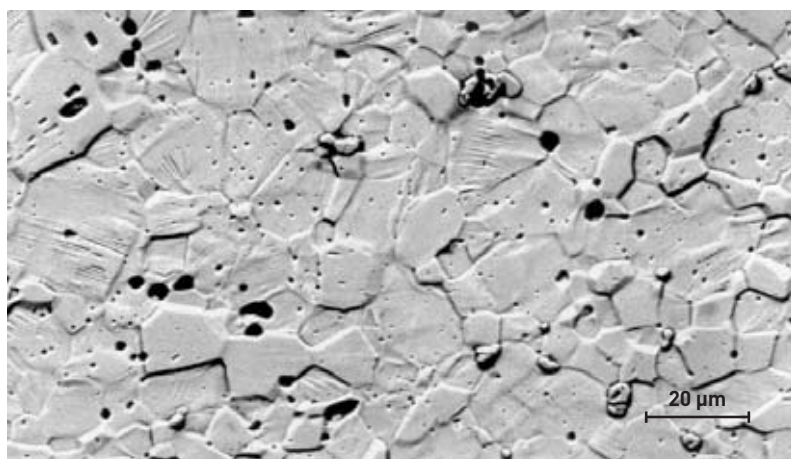
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Development of new ceramic electrolytes

Development of new ceramic materials, functioning at intermediate temperatures, and mastery of related fabrication processes number among the major directions of research with respect to SOFC technology. CEA is currently directing its efforts to the apatite family.

The Materials Department at CEA/Le Ripault is involved in a program, endorsed by the **PACo Network** and jointly funded by **Ademe**, for which the goal is the design of an SOFC fuel cell operating at lower temperatures (700-800 °C). This technological breakthrough entails research work on new **ceramic electrolytes**, exhibiting **ion conductivity** of the order of 0.05 S/cm for that temperature range.

Good oxide-ion **conduction** properties at low temperature have been found, to date, in a number of families of ceramic material (**doped** cerium [Ce] oxide and bismuth [Bi] oxide, perovskites, oxides of the Aurivillius BIMEVOX type). However, these materials also exhi-



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bit high **electron conductivities** in a **reducing** atmosphere, and/or strong contact reactivity to **electrode** materials.

Apatites: open-structure ceramics

CEA therefore looked into oxides exhibiting hexagonal symmetry, featuring open structures, with channels that might favor oxide ion mobility: **rare-earth** silicate oxyapatites, of general formula

Analysis, under scanning electron microscopy, of the microstructure of a germanium apatite, with composition $\text{La}_{9.6}\text{Ge}_6\text{O}_{26.4}$. Germanium apatites exhibit outstanding properties over the temperature range 700-800 °C.

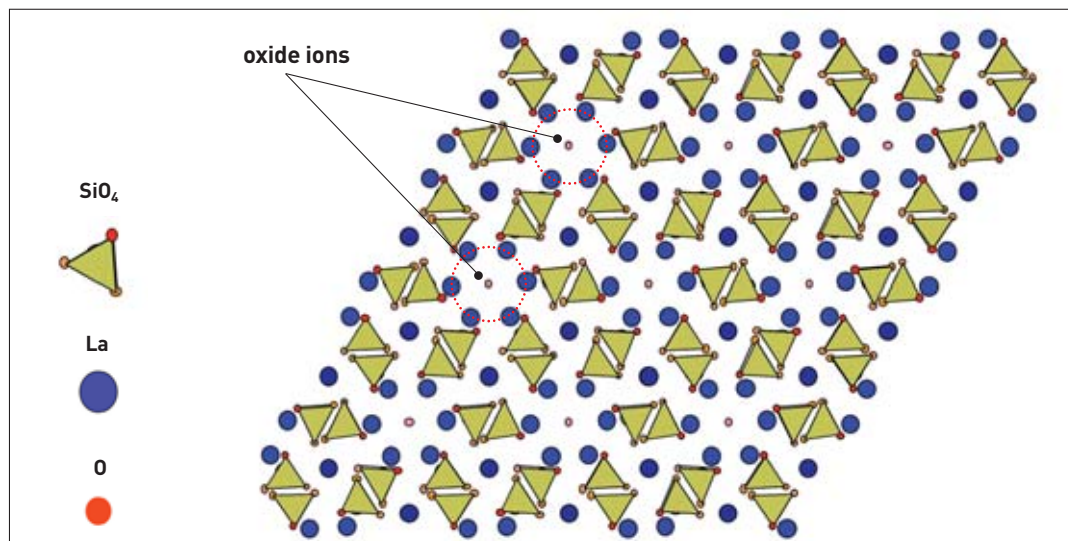


Figure 1.
Schematic representation
of the mesh of a silicate
apatite, projected along
plane (001).

$\text{Re}_{10}^{3+}(\text{SiO}_4)_6\text{O}_{25}^{2-}$, where Re = lanthanum (La), neodymium (Nd), gadolinium (Gd), erbium (Er)... These materials consist in a near-compact stacking of SiO_4 tetrahedra and Re octahedra, exhibiting tunnels containing the oxide ions not bound to silicon (Si) (see Figure 1).

Initial work involving investigation of various rare earths (La, Gd, Er, yttrium [Y]) occupying the Re site showed that conductivity of silicate oxyapatites rises when the ionic radius of the rare-earth (Re) **cation** increases. The best conduction properties are thus found with La^{3+} . This cation, the bulkiest in the rare earth family, enlarges the size of the previously-identified tunnels, thus facilitating oxide ion migration.

A variety of substitutions at the La^{3+} site, with **bivalent** cations such as Ca^{2+} (calcium ion) or Sr^{2+} (strontium ion), or **trivalent** ions such as Y^{3+} , were then examined, with a view to improving conduction properties. The main aims of such substitutions were, on the one hand, to introduce, for bivalent cations, **anion** vacancies into the ion-oxide migration tunnels, and, on the other, to alter, depending on the size of the **doping** cations, the size of these tunnels. Complete substitution of silicon with germanium (Ge) was also

investigated. The expansion of the hexagonal **mesh** resulting from the larger ionic radius of germanium ($0.54 \text{ \AA}$ [Ge^{4+}] versus $0.40 \text{ \AA}$ [Si^{4+}]) may facilitate diffusion of the oxide ions.

Germanium apatites: outstanding conductivity

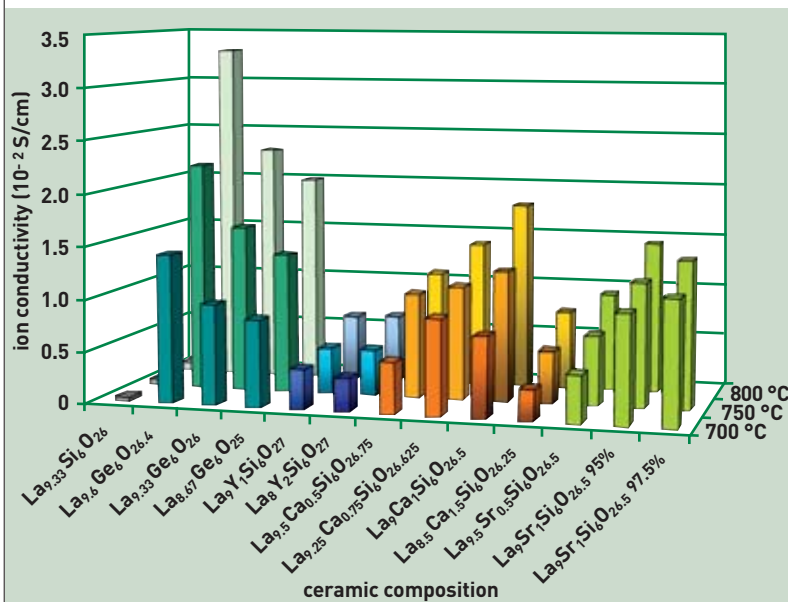
Apatites appear to be electrolytes highly suited to use in SOFCs operating at $700\text{--}800^\circ\text{C}$. Mastery of the fabrication process yields dense ceramics, guaranteeing good impermeability to gases.

Doping improves the conductivity of silicate apatites, in the order $\text{Sr} > \text{Ca} > \text{Y}$ (see Figure 2). Thus it is the largest bivalent cation that allows the best performance to be achieved, through introduction of anion vacancies into the oxygen sublattice, and greatest expansion of the hexagonal mesh. Germanium apatites exhibit the best conductivity, over the temperature range investigated. The conductivity of these materials is less strongly affected by variations in temperature than is the case with the classic electrolyte, yttria-stabilized zirconia. Indeed, the activation energy for the conduction mechanisms in germanium apatites is lower than that measured for commercially-available yttria-stabilized zirconia powders.

In the near future, a number of criteria will be tested, including the influence of these ceramics' microstructure (grain size, porosity) on conduction properties, their thermochemical stability in a reducing environment, and their reactivity with respect to water generated at the **anode**. Investigations will further address understanding of conduction mechanisms in these materials, for better guidance in the choice of electrolytes for future-generation SOFCs, and research on forming by way of low-cost techniques, with a view to early construction of a prototype single cell.

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Figure 2.
Ion conductivities for
materials investigated
over the temperature
range $700\text{--}800^\circ\text{C}$.
Percentages refer to
densities [density %/
theoretical density]. It
will be seen that the
higher the density, for the
same composition, the
larger the increase in
conductivity.



Use of some low cost fabrication processes

Bringing down construction costs is a point of importance for the development of fuel cells of the SOFC type. Optimization of fabrication and forming processes for electrode and electrolyte materials, together with development of specific materials, are being addressed by current investigations.

Various strategies may be adopted to achieve cost reductions for SOFC fuel cells, such as use of less expensive materials (by going, for instance, for lower purity, or preparation of powders through low-cost processes), development of novel materials enabling operation at lower temperature, optimization of forming processes... Fabrication by means of a conventional technique, such as **cold isostatic pressing**, spray deposition or **screen printing**, these being processes employed on an industrial scale, with subsequent **sintering**, is a step in that direction, and is covered by ongoing development work at CEA.

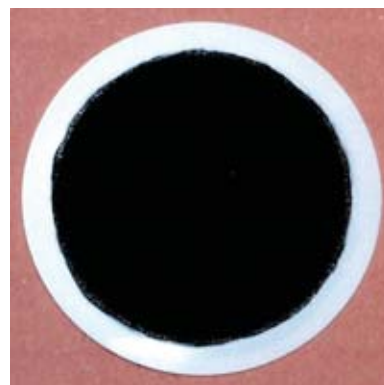
Use of conventional fabrication processes

Spray deposition consists in spraying a powder-, solvent- and organic additives-based suspension. Screen printing is a mechanical printing process. A viscous ink is prepared from **ceramic** material powder, solvent and organic additives. This paste is spread onto a screen, being transferred through the screen mesh by means of a squeegee. These deposits are then heat-treated in air or in a controlled atmosphere. Spray deposition and screen printing thus allow production of thick layers.

Using the materials most commonly employed in SOFC construction (nickel–yttria-stabilized zirconia **cermet** for the **anode**; yttria-stabilized zirconia for the **electrolyte**; strontium-doped lanthanum manganite for the **cathode**), single cells comprising the two electrodes, deposited onto a supporting electrolyte, were fabricated by means of these conventional ceramic-forming technologies. As part of a program concerned with direct conversion of **methane** into **hydrogen** within the fuel cell, novel anode materials were deposited by spray deposition or screen-printing onto supporting electrolytes. A doped lanthanum-manganite cathode was deposited in turn, the cells then being tested to monitor their electrochemical performance.

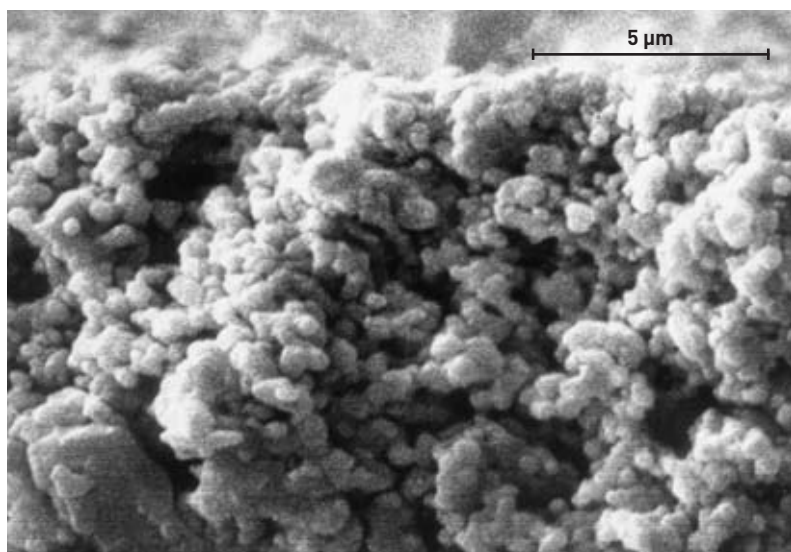
The supporting electrode: a favorable geometry

The electrolyte-supported geometry dictates fairly large electrolyte thickness. On the other hand, an electrolyte of moderate thickness may be deposited onto a supporting electrode. Lower electrolyte thickness allows a reduction in electric resistance, and thus in induced **ohmic loss** (by comparison with a thick electrolyte). Performance equal to that of electrolyte-supported single cells can be achieved at a lower operating temperature. Such lower temperature should in turn allow use of less expensive materials, for interconnects in particular. Thus, electrode-supported geometry such as anode-supported single cells are being developed at CEA, using the same fabrication processes as for electrolyte-supported cells. The anode is prepared by com-



CEA

Left, composite anode in nickel oxide–yttria-stabilized zirconia, spray-deposited onto an yttria-stabilized zirconia supporting electrolyte. The nickel oxide will undergo *in-situ* reduction. Right, strontium-doped lanthanum-manganite cathode, spray-deposited onto an yttria-stabilized zirconia supporting electrolyte.



CEA

Microstructure of a strontium-doped lanthanum-manganite cathode.

pression, the electrolyte and cathode then being deposited by either spray deposition or screen printing. Use of conventional, low-cost fabrication processes, and construction of electrode-supported fuel cells are among the factors that may contribute to bring down SOFC prices.

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Cogeneration is the combined production of heat and power, from a single **fuel** source. Currently, this involves three principal technologies: steam turbines, heat engines, and combustion turbines. Cogeneration is characterized by outstanding energy efficiency, since the heat generated is recovered, by contrast to what happens in thermal power stations. This is a decentralized power-generation system, close to end users, thus allowing electrical grid development and deployment costs to be avoided, and transport-line losses to be eliminated. A distinction should be made between industrial applications (requiring continuous steam and electricity supply), and tertiary-sector (government and business premises, hospitals...) and collective (heat distribution networks, high-rise apartment blocks, housing estates...) applications.

A European Directive to promote cogeneration

In 1997, the **European Commission** set out the doubling of the share of cogeneration in electricity generation in Europe, as an objective between 1994 and 2010 (from 9% to 18%). The main argument being that cogeneration enables a saving of 500 kg **CO₂** formation per **megawatt-hour (MWh)** generated, compared to centralized heat and power generation.

An increase of cogeneration production has been experienced in France, from 1995, with a total installed power, by the end of 1998, of 5,323 **MW**, for a total of 948 installations.⁽¹⁾ However, the share of cogeneration in electricity generation remains modest (around 2.5%), especially when compared with other countries, such as Denmark or the Netherlands. Moreover, cogeneration has shown a strong growth in the power range above 1 **MWe**, for industrial and heat-distribution network applications, but very little growth, on the other hand, for tertiary-sector and collective applications, or in the power range below 1 MWe. This is due, in particular, to connection costs, and the relative high cost of these technologies. Nevertheless, there is a very large potential market in the power range below 1 MWe. The European Directive for the promotion of cogeneration was published in 2004. It sets the entry threshold, for qualifying the cogeneration, at an overall efficiency of 75-80%, and the threshold for the "high-efficiency cogeneration" category at **primary energy** savings of over 10%, compared to separate production of heat and electricity. The Directive further promotes new cogeneration technologies afforded by such as Stirling engines,⁽²⁾ microturbines, Rankine cycles,⁽³⁾ and fuel cells.

Fuel cells: unquestionable advantages

Fuel cells can claim a position as a cogeneration process offering overall efficiency and operating costs such that major gains may be anticipated, compared to conventional technologies.

(1) Source: direction générale de l'énergie et des matières premières (DGEMP: Directorate-General for Energy and Raw Materials), at the French Ministry for the economy, finance and industry.

(2) Stirling engine: an external-combustion engine, where the working fluid operates in a closed circuit (fluid heating and cooling being effected by external hot and cold sources).

(3) Rankine cycle: steam generation cycle "by way of boiler, turbine, condenser, and pump," using an organic fluid as heat-transfer fluid.

High-temperature fuel-cell technologies exhibit high electrical efficiencies, and temperature levels which allow ready use of the heat generated for added-value applications, in all its forms (steam, superheated water, heat-distribution networks, sanitary hot water, refrigeration). They further make it possible to look for energy diversification, through use of liquid fuels, such as **ethanol** and biofuels, or gaseous fuels, such as **biogas**, even though, in the short term, **natural gas**, entailing as it does the resort to internal **reforming** (production of **hydrogen** from a carbonaceous fuel), would appear to be unavoidable. However, in the case of cogeneration, the lower efficiency due to use of a reformer can be offset, in part at least, by added revenue from the system's heat.



Bruno Clergue-Dalkia Photo Library

Cogeneration installation at Freyming-Merlebach (Moselle *département*), supplying the local heat-distribution network.

Low-temperature fuel-cell technologies may be used as means of cogeneration, with low-temperature added-value applications (sanitary hot water and low-temperature heating for collective and tertiary-sector uses, for instance). Further, developments for mobile applications, concerning membranes working above 100 °C, make it possible to consider widespread adoption for heating purposes in buildings and premises. There is a need to demonstrate on the ground the advantages of fuel-cell technologies. Dalkia France and their research center (CReeD: Centre de Recherches pour l'environnement, l'énergie et le Déchet - Environment, Energy and Waste Research Center) have thus initiated a large demonstration program, focusing on low- and high-temperature technologies. Their aim is to achieve performance validation, and the definition of operating and maintenance conditions and requirements, on actual sites (see Box on *The GECOPAC Program*).

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