

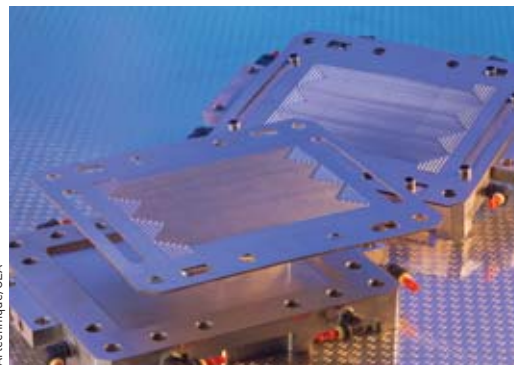
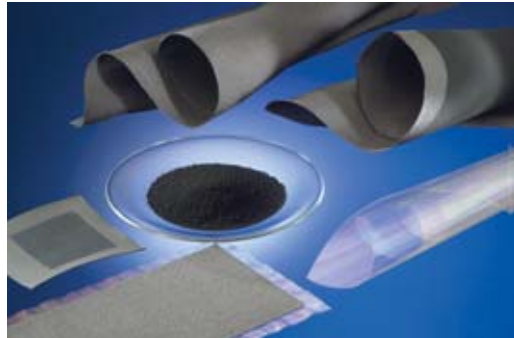
# Fuel cell Q&A

Fuel cells convert, directly and continuously, the chemical energy of a fuel into electric energy, heat, and water. While the principle involved may seem simple, its implementation is complex, and costly. Major research and development efforts are being carried out, with the aim of securing acceptable levels of performance, and cost, for these technologies.

Formation of water from oxygen and hydrogen yields electricity. This is the principle, discovered 165 years ago, on which the fuel cell is based (see Box C, *How does a fuel cell work?*). In the meantime, fuel cells have been diversified into a variety of technological pathways: “low-temperature” fuel cells, such as the proton exchange membrane fuel cell (PEMFC) - also known as the polymer electrolyte membrane fuel cell - and its direct methanol or ethanol (DMFC, DEFC) variants, the phosphoric acid (PAFC) or alkaline (AFC) fuel cell; and “high-temperature” fuel cells, such as the molten carbonate fuel cell (MCFC) or the solid oxide fuel cell (SOFC). These various types of fuel cell differ basically with respect to operating temperatures, the nature of the electrolyte used, and the kind of fuel involved (see Table 1).

## How does one get from cell to generator?

However, to get from mere electrochemical cell to true electricity generator, a number of steps are required. First, to achieve the desired voltage, basic cells are stacked in series to the required number. An interconnection material (bipolar plate) enables assembly of the cells together. The fuel-cell module thus constructed is then integrated into a complete system, managing fluid (reactant gases, water), heat and electricity flows. Among the key components to be noted, in such a system, are the fuel storage, compressor, humidifiers, and the inverter. Finally, this system needs must be integrated into its environment, and thus has to comply with all constraints set by the technical specifications - integration into an electric vehicle, for instance.



Essential components in PEM fuel cells: materials for the membrane-electrode assemblies, and for the bipolar plates. A module comprises a number of membrane-electrode assemblies, joined by means of bipolar plates. Each of these components is the object of much research and development work.

Artetechnique/CEA

## What are fuel cells used for?

Owing to its very principle, a fuel cell exhibits attractive conversion efficiencies, compared to those achieved by thermal generators. In environmental terms, its impact is relatively modest: high acoustic quietness, very low pollutant emissions. As regards green-

fuel cell type	anode (catalyst)	electrolyte	cathode (catalyst)	temperature	applications
proton exchange membrane (PEMFC)	$H_2 \rightarrow 2 H^+ + 2 e^-$ (Pt)	perfluorinated polymer ( $SO_3H^+$ ) $H^+ \rightarrow$	$\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (Pt)	60-90 °C	portable transportation stationary
direct methanol (DMFC)	$CH_3OH + H_2O \rightarrow CO_2 + 6 H^+ + 6 e^-$ (Pt)	perfluorinated polymer ( $SO_3H^+$ ) $H^+ \rightarrow$	$\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (Pt)	60-90 °C	portable transportation
phosphoric acid (PAFC)	$H_2 \rightarrow 2 H^+ + 2 e^-$ (Pt)	$PO_4H_3$ (85-100%) $H^+ \rightarrow$	$\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (Pt)	160-220 °C	stationary
alkaline (AFC)	$H_2 + 2 OH^- \rightarrow 2 H_2O + 2 e^-$ (Pt, Ni)	KOH (8-12 N) $\leftarrow OH^-$	$\frac{1}{2} O_2 + H_2O + 2 e^- \rightarrow 2 OH^-$ (Pt-Au, Ag)	50-250 °C	space transportation stationary
molten carbonate (MCFC)	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2 e^-$ (Ni +10% Cr)	$Li_2CO_3/K_2CO_3/Na_2CO_3$ $\leftarrow CO_3^{2-}$	$\frac{1}{2} O_2 + CO_2 + 2 e^- \rightarrow CO_3^{2-}$ ( $NiO_x + Li$ )	650 °C	stationary
solid oxide (SOFC)	$H_2 + O^{2-} \rightarrow H_2O + 2 e^-$ (Ni-ZrO <sub>2</sub> cermet)	$ZrO_2-Y_2O_3$ $\leftarrow O^{2-}$	$\frac{1}{2} O_2 + 2 e^- \rightarrow O^{2-}$ (perovskites $La_xSr_{1-x}MnO_3$ )	750-1,050 °C	stationary APU

Table 1. The various types of fuel cell.



Five 200-kW fuel cells provide all the power required for operation of the main Anchorage, Alaska post-office mail-sorting center. Quiet and nonpolluting, lending itself to implementations meeting a broad range of power output requirements, the fuel cell affords many benefits for stationary applications.



UTC Fuel Cells

**house gas** release, on the other hand, the benefit from fuel cells is less unequivocal, since this is essentially linked to the type of fuel used, and its source of production. Thus, it is the whole hydrogen cycle that must be considered (from well to wheel), if a fuel cell's impact is to be evaluated. However, **carbon dioxide (CO<sub>2</sub>)** emissions do remain lower than for a heat engine. Such characteristics mean fuel cells are natural candidates for a number of major application areas.

The first applications for fuel cells emerged in the 1960s, with the rise of the US space program. In particular, fuel cells were fitted to the Gemini and Apollo capsules. Today, the Space Shuttle still draws its power supply from fuel cells.

Since then, following the rising awareness of global warming-related issues, in the early 1990s, fuel cells have been seen as a credible alternative to **fossil energies**. More widely, deregulation of the electrical industry has spurred newcomers to stake out positions in the area of decentralized production equipment, of which the fuel cell is the most consummate example. Thus, one has seen a growth in programs aimed at demonstrating the benefits of fuel cells for **stationary power-supply applications**, whether for individual or collective housing, or for government or industrial premises, or remote locations, or yet to ensure secure electricity supplies. For such applications, furthermore,

fuel cells afford the benefit of being suitable for use in **cogeneration**: the heat generated may be either used directly for heating purposes, or transformed into electricity by means of a turbine (see Box 1).

*Transportation applications*, of course, have not lagged behind. These mainly concern electric traction for public transport (buses, urban transit systems), and for personal vehicles. Mention should also be made of developments in the area of auxiliary power units (APUs) designed to provide a vehicle with a complementary source of electric power, to run secondary onboard systems (air conditioning...).

Finally, more recently, fuel cells have come in for consideration to *power mobile communications devices* (mobile phones, portable computers...). For such applications, a major research effort is called for, to miniaturize the technology and make it compatible with targeted utilization.



Avane

Fuel cells offer major advantages as regards transportation applications, for public transport in particular. This Scania bus is fitted with a hydrogen-fed fuel cell.

## Why don't I have one back home?

Since the 1960s, significant technological advances have been achieved (the **power density** of fuel cells has risen by a factor 10, the amount of **catalyst** used has been cut by 10), and many prototype fuel cells have been built the world over. Several hundred are undergoing trials, unit power ranging from 200 kW to a few **megawatts (MW)** for stationary applications. Over 300 prototype vehicles have appeared since the 1990s. Prototypes of miniature fuel cells have also recently been shown. And yet, in spite of these many demonstrators, the fuel cell is still not truly available for end users. The main obstacle to industrial development of fuel cells is cost, even if some technological barriers do still need to be overcome.

One of the main areas of difficulty lies in the current *cost* of fuel cells. Indeed, nowadays a fuel cell costs some €6,000-8,000/kW, whereas market prices are systematically pegged under €1,500/kW (€750-1,500/kW for stationary applications, €150/kW for public transport, €30-50/kW for personal vehicles). A major research and development effort thus still needs to be carried out, to ensure the technology be made compatible with target market demands.

Further, it is essential to achieve *enhanced performance* for fuel cells, compared to present levels, as regards in particular durability, robustness, and reliability. In a number of cases, this entails identifying, and validating, definite and actual technological breakthroughs,



D. Michon-Artechnique/CEA

Fuel cells afford major prospects, in terms of utilization for portable applications.

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 **CO<sub>2</sub>** 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.<sup>(1)</sup> 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,<sup>(2)</sup> microturbines, Rankine cycles,<sup>(3)</sup> 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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Veolia Environnement

as for instance in the area of miniature fuel cells for mobile communications devices.

Since a fuel cell uses hydrogen for its fuel, *ensuring safe use* as regards fuel-cell systems is an imperative requirement. This involves demonstrating technological solutions optimized with respect to safety, but equally the definition of standards and regulations concerning use of hydrogen as an energy carrier.

Finally, since development of fuel cells is largely spur-

red on by concerns for *preservation of the environment*, it is crucial that their environmental impact be monitored. This involves careful consideration when selecting a fuel production pathway, but equally the taking on board of the entire life cycle of a fuel cell, particularly as regards recyclability.

By 2005, fuel cells of the PEMFC type should nevertheless become commercially available, most likely aimed at portable applications and the electric power



security market. Subsequently, niche markets will be targeted, such as stationary applications in the 5-kW range, or APUs, and bus or public transport applications. Looking to 2010-15, applications for the personal automobile sector could then take off (see Box 2).

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## Fuel cells: an automobile manufacturer's take

2

At last! The water engine...! Well... not quite. The fuel cell generates water, rather than consuming it. And it also generates, most importantly, electricity. This is what makes it relevant to automobile manufacturers, PSA Peugeot Citroën in particular.



Peugeot/Communications Directorate

The H<sub>2</sub>O demonstrator is a battery-powered electric vehicle, fitted with an electric generator in the guise of a fuel cell [5.5 kW]. This vehicle presents a novel utilization for the fuel cell. In this case, hydrogen is generated on board, by way of an aqueous solution of sodium borohydride and a catalyst.

### What is in it for a carmaker?

Fuel availability, and reduction of vehicle emissions are at the core of the PSA Peugeot Citroën Group's concerns. In order to respond to these issues, the Group is currently working on a large number of technologies, with the aim of improving the environmental behavior of its vehicles, while guaranteeing a satisfactory level of performance to the customer, at an acceptable cost. Available for just under ten years now, the electric vehicle, of which PSA Peugeot Citroën is the first and foremost manufacturer worldwide, is one of the technologies being developed. Other paths are being investigated, some of which are already commercialized, or about to be put on the market. For the longer term, expectations are focusing on fuel-cell vehicles.

### What are the benefits?

The benefits of fuel cells are many. Aside from lower CO<sub>2</sub> emissions, helping to curb the greenhouse effect (see Box B, *The greenhouse effect and CO<sub>2</sub>*), fuel cells contribute to improved quality of life in urban environments, through the quietness of fuel-cell vehicles, and the elimination of local pollutant emissions (NO<sub>x</sub>, particulates...). Fuel-cell vehicles are zero-emission vehicles (ZEVs), just as battery-powered electric vehicles are. Fuel cells will contribute to diversification of the primary energy sources used in personal transportation, currently 95% dependent on oil.

### Automotive issues

What is at stake is how to deal with a societal issue, of slight incidence on purchasing decisions (the reduction of CO<sub>2</sub> emissions), while not impairing performance or the joy of the driving experience, or raising purchase or operating costs.

Travel range is a crucial issue. Current technologies for vehicle onboard hydrogen storage do not allow driving beyond a 300-km range, without some impairment to vehicle accommodation quality. This remains inadequate. Advances have yet to be achieved in this respect. Range is also linked to conversion efficiency, when passing from the energy contained in the hydrogen to electric energy, through to mechanical energy. This efficiency should be as high as possible. Fuel cells theoretically allow very high efficiencies to be achieved. In practice, care must be taken not to degrade that high efficiency, while complying with constraints involved in integration into a vehicle, e.g. with regard to mass and volume. Efficiencies are particularly impressive in built-up-area operation, when fuel cell power output is low.

Finally, cooling and cold start are further areas of difficulty. A fuel cell yields pure water, which means start-up at temperatures below 0 °C is a problem. Cooling is mainly an issue of radiator size, related to cooling-fluid temperature and amount of power to be dissipated. PEM fuel cells are "handicapped" by their low operating temperature, leading to consideration of very large radiators, ill suited to positioning inside a vehicle. One pathway of research lies in raising operating temperature; however, a technological issue then arises, concerning the higher-temperature behavior of the fuel-cell core. The problem is a complex one, with all the parameters coupled in varying degrees one with the other. The problem can only be resolved through adoption of a systems engineering approach, taking in all of the technological and economic aspects. Research must be driven by the fuel-cell system and hydrogen storage system approach.

The final element that must be taken on board, and not of least importance, is cost. If this technology is to have an impact on our environment, it has to be sold! It should thus be amenable to production at costs competitive with those of internal-combustion engines.

Fuel-cell technology offers a strong potential for further evolution. It must, however, meet many technological and economic challenges, before it can be brought out on the market. Aside from the cost relating to production of the fuel cell itself, and of the hydrogen storage system, many technical issues still have to be resolved, e.g. cold start (freezing conditions), cooling, compactness and onboard durability. Further, deployment of a hydrogen distribution system will require massive investments. For all of which reasons PSA Peugeot Citroën is anticipating a gradual introduction into automobile production, with possible series production from 2020.

The Group has consequently taken up a pragmatic approach for research, in the medium and long term, aiming to explore and go on to master the various technologies that will allow the barriers to be overcome, that are still preventing introduction, at acceptable economic terms, of fuel cells into automobiles.

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# A The many states of energy

“Nothing lost, nothing created,” as Lavoisier, the father of modern chemistry, wrote in his day. This motto, true as it is of chemical species, applies equally to energy. Indeed, energy is a multifarious entity, which may transform into highly diverse aspects. However, the **primary energies** that may be directly accessed in nature are limited in number: such are **fossil energies** (coal, oil, natural gas), **nuclear energy**, and **renewable energies** (hydro energy, **biomass** energy, solar energy, wind energy, geothermal energy, tidal energy). These primary energies are the constituents of what is known as the **primary energy mix** (see Figure 1).

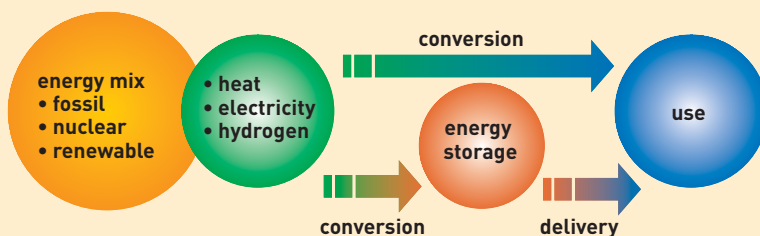


Figure 1. The energy scheme.

For most applications, energy must be **converted** to make it compatible with the use under consideration. Of course, nature, highly ingenious as it is, devised the very first **energy converters**, namely living beings. Plants, through **photosynthesis**, effect the conversion of radiant light energy into chemical energy. The human body itself allows, in particular, the conversion of chemical energy into mechanical energy, by way of the muscular system. Subsequently, humans went on to invent large numbers of converters (see Figure 2). The first such converter, chronologically, is quite simply fire, converting chemical energy (combustion) into light, and heat. Of more recent origin, a television set carries out conversion of electricity into light energy (pictures) and mechanical energy (sounds). In fact, many energy systems involve a combination of a number of converters, as e.g. a nuclear power station, effecting as it does the conversion of nuclear energy into thermal energy (reactor), then into mechanical energy (turbine), finally through to electric energy (alternator). Unfortunately, the **second principle of thermodynamics**

tells us that any energy transformation carries a cost: a more or less extensive portion of the energy involved is dissipated in the form of unusable heat (through friction in a mechanical system, for instance). In the case of a present-generation nuclear power station, the electric energy generated only amounts to one third of the nuclear energy initially contained in the fuel.

Of course, matters would be altogether too simple, however, if energy could be consumed as and when it is generated, on the very site where it is produced. In very many cases, energy-consuming sites may be far removed from the production site, production

and concomitant demand, moreover, not always being matched (as with photovoltaic electricity in nighttime, for instance). Sound energy management thus requires deployment both of an **energy distribution network**, and of **energy storage** capabilities.

**Energy transport** is effected by means of an **energy carrier**. Currently, the two main such carriers are **electricity**, and **heat**. Tomorrow, however, a new carrier may become dominant: **hydrogen**, this being converted into electricity and heat by means of **fuel cells**.

Finally, if energy is to be available at all times, it is essential that there should be the ability to store it: to “get it in a can,” so to speak. Such **storage** may take a variety of forms. Energy may be stored in **mechanical** form (*potential energy*, in the case of the water reservoir of a hydroelectric dam, or *kinetic energy*, in the case of a flywheel), or in **thermal** (hot-water tank), **chemical** (gasoline tank, primary and **storage batteries**), or even magnetic (**superconducting** coil) form.

Energy management is thus a complex, involved craft, combining production, transformation, transport, and storage. In the current context of energy debate, it is becoming increasingly apparent that, tomorrow, energy networks will grow in size and number, in accordance with a multimodal approach (concurrent management of a number of networks combining diversified energy sources). **New energy technologies** are thus bound to play an essential part in these developments.

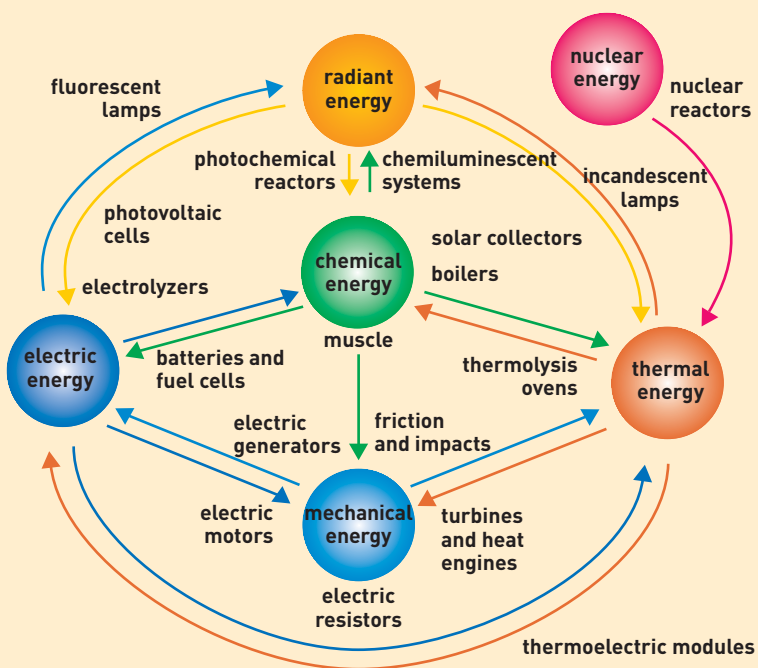
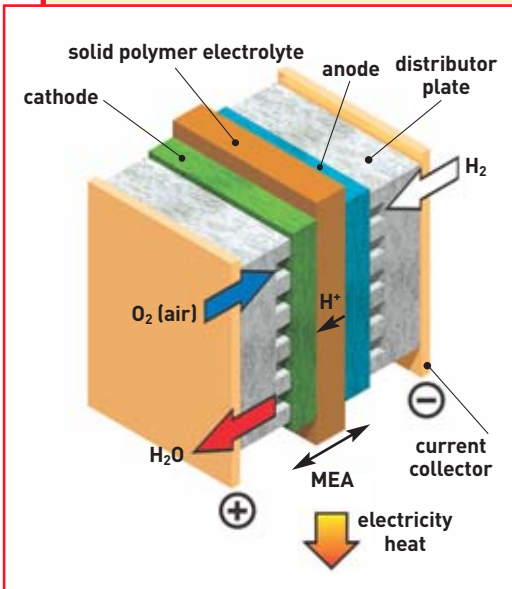


Figure 2. Conversions of the six main forms of energy, with a few examples of energy converters.

**C**

# How does a fuel cell work?



Operating principle of the fuel cell: the example of the proton-exchange membrane fuel cell. MEA stands for membrane-electrode assembly.

The fuel cell is based on a principle discovered quite some time ago, since it was in 1839 that Sir William Grove constructed the first electrochemical cell working with **hydrogen** as its **fuel**, thus demonstrating the ability to generate electric current through direct conversion of the fuel's chemical energy. Since the fuel cell has the special characteristic of using two gases - hydrogen  $H_2$  and oxygen  $O_2$  - as its electrochemical couple, the **oxidation-reduction** reactions occurring inside the fuel cell are particularly simple. The reaction takes place inside a structure (the **basic electrochemical cell**), consisting essentially in two **electrodes** (the **anode** and **cathode**), separated by an **electrolyte**, i.e. a material that lets **ions** through. The electrodes employ **catalysts**, to activate, on the one side, the hydrogen **oxidation** reaction, and, on the other, the oxygen **reduction** reaction.

In the case of an acid-electrolyte cell (or **proton** exchange membrane fuel cell), the hydrogen at the anode is dissociated into protons (or hydrogen ions  $H^+$ ) and **electrons**, in accordance with the oxidation reaction:  $H_2 \rightarrow 2 H^+ + 2 e^-$ . At the cathode, the oxygen, the electrons and the protons recombine to yield water:  $2 H^+ + 1/2 O_2 + 2 e^- \rightarrow H_2O$ . The principle of the fuel cell is thus the converse of that of water **electrolysis**. The thermodynamic potential for such an electrochemical cell, consequently, stands at around 1.23 volt (V). However, in practice, the cell exhibits a voltage of about 0.6 V for **current densities** of 0.6-0.8 A/cm<sup>2</sup>. The efficiency of such a fuel cell is thus equal to about 50%, the energy dissipated naturally being so dissipated in the form of heat.

# E Storage batteries, cells and batteries: constantly improving performance

**S**torage batteries – also known as accumulators, or secondary **batteries** – and batteries – so-called primary batteries – are electrochemical systems used to store energy. They deliver, in the form of electric energy, expressed in watt-hours (**Wh**), the chemical energy generated by electrochemical reactions. These reactions are set in train inside a basic cell, between two **electrodes** plunged in an **electrolyte**, when a load, an electric motor, for instance, is connected to its terminals. Storage batteries are based on reversible electrochemical systems. They are rechargeable, by contrast to (primary) batteries, which are not. The term “battery” may further be used more specifically to denote an assembly of basic cells (whether rechargeable or not).

A storage battery, whichever technology is implemented, is essentially defined by three quantities. Its **gravimetric** (or **volumetric**) **energy density**, expressed in watt-hours per kilogram (Wh/kg) (or in watt-hours per liter [Wh/l]), corresponds to the amount of energy stored per unit mass (or per unit volume) of battery. Its **gravimetric power density**, expressed in watts per kilogram (W/kg), measures the amount of power (electric energy delivered per unit time) a unit mass of battery can deliver. Its **cyclability**, expressed as a number of cycles,<sup>(1)</sup> characterizes storage battery life, i.e. the number of times the battery can deliver an energy level higher than 80% of its nominal energy; this quantity is the one most frequently considered for portable applications.

Up to the late 1980s, the two main technologies prevalent on the market were lead-acid storage batteries (for vehicle start-up, backup power for telephone exchanges...), and nickel-cadmium storage batteries (portable tools, toys,

emergency lighting...). Lead-acid technology, more widely referred to as lead-acid batteries, or lead batteries, is also denoted as lead-acid systems. Indeed, the chemical reactions employed involve lead oxide, forming the positive electrode (improperly termed the cathode), and lead from the negative electrode (anode), both plunged in a sulfuric acid solution forming the electrolyte. These reactions tend to convert the lead and lead oxide into lead sulfate, further yielding water. To recharge the battery, these reactions must be reversed, through circulation of a forced current. The disadvantages found with lead-acid technology (weight, fragility, use of a corrosive liquid) resulted in the development of alkaline storage batteries, of higher capacity (amount of energy delivered during discharge), yielding however a lower electromotive force (potential difference between the system's terminals, under open circuit conditions). Electrodes for these systems are either based on nickel and cadmium (nickel-cadmium storage batteries), or nickel oxide and zinc (nickel-zinc storage batteries), or silver oxide coupled to zinc, cadmium, or iron (silver-oxide storage batteries). All these technologies use a potassium hydroxide solution as electrolyte. Lead-acid technologies, as indeed alkaline batteries, are characterized by high reliability, however gravimetric energy densities remain low (30 Wh/kg for lead-acid, 50 Wh/kg for nickel-cadmium).

In the early 1990s, with the growth in the portable device market, two new technological pathways emerged: nickel-metal hydride storage batteries, and lithium storage batteries ([see Box on Operating principle of a lithium storage battery](#)). The first-mentioned pathway, involving a nickel-based positive electrode and a negative electrode – made of a hydrogen-absorbing alloy – plunged in a concentrated potassium hydroxide solution, allowed gravimetric energy

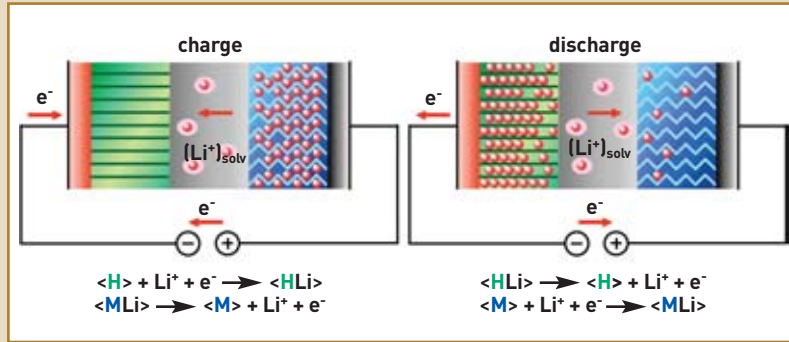
densities of 70–80 Wh/kg to be achieved. The second pathway had already been targeted by research around the late 1970s, with a view to finding electrochemical couples exhibiting better performance than the lead-acid or nickel-cadmium storage batteries used up to that point. Initial models were thus designed around a metallic-lithium-based negative electrode (lithium-metal pathway). However, that technology was faced with issues arising from poor reconstitution of the lithium negative electrode, over successive charging operations. As a result, around the early 1990s, research was initiated on a new, carbon-based type of negative electrode, this serving as a lithium-insertion compound. The lithium-ion pathway was born. Japanese manufacturers soon made their mark as leaders in the field. Already in business as portable device manufacturers, they saw the energy source as numbering among the strategic components for such devices. Thus it was that Sony, not initially involved in battery manufacture, decided, in the 1980s, to devote considerable resources to advance the technology, and make it suitable for industrialization. In February 1992, Sony announced, to general stupefaction, the immediate launching of industrial production of lithium-ion storage batteries. These early storage batteries exhibited limited performance (90 Wh/kg). Since then, these batteries have seen notable improvement (from 160 Wh/kg to over 180 Wh/kg in 2004), owing, on the one hand, to the technological advances made (reduction in the unproductive fraction of battery weight and volume), and, on the other, to optimization of materials performance. Gravimetric energy densities of over 200 Wh/kg are expected around 2005.

<sup>(1)</sup> One cycle includes one charge and one discharge.

## Operating principle of a lithium storage battery

During use, hence during discharge of the **storage battery**, lithium released by the **negative electrode** (<H>: host intercalation material) in **ion form** ( $\text{Li}^+$ ) migrates through the ion-conducting **electrolyte** to intercalate into the **positive electrode** active material (<MLi>: lithium-insertion compound of the metal oxide type). Every  $\text{Li}^+$  ion passing through the storage battery's internal circuit is exactly compensated for by an **electron** passing through its external circuit, thus generating a current. The **gravimetric energy density** yielded by these reactions is

proportional both to the difference in potential between the two electrodes, and the quantity of lithium intercalating into the insertion material. It is further inversely proportional to system total mass. Now lithium is at the same time the lightest (molar atomic mass: 6.94 g), and the most highly **reducing** of metals: electrochemical systems using it may thus achieve voltages of 4 V, as against 1.5 V for other systems. This allows lithium batteries to deliver the highest gravimetric and volumetric energy densities (typically over 160 Wh/kg, and 400 Wh/l),



50% greater, on average, than those of conventional batteries. The operating principle of a lithium storage battery remains the same, whether a lithium-metal or carbon-based negative electrode is employed. In the latter case, the technological pathway is identified as lithium-ion, since lithium is never present in metal form in the battery, rather passing back and forth between the two lithium-insertion compounds contained in the positive and negative electrodes, at every charge or discharge of the battery.



## B The greenhouse effect and CO<sub>2</sub>

The Sun's energy reaching the ground warms the Earth, and transforms into **infrared radiation**. Just like the panes of a greenhouse – hence the name given to this mechanism – some of the gases present in the atmosphere trap part of this radiation, tending to warm the planet. Thus, in terms of power, the Earth receives, on average, slightly less than 240 **watts/m<sup>2</sup>**. Without the **greenhouse effect**, mean temperature on Earth would stand at  $-18\text{ }^{\circ}\text{C}$ , and very little water would be present in liquid form. This effect thus has a beneficial influence, since it allows our planet to experience a mean temperature of  $15\text{ }^{\circ}\text{C}$ .

However, from the beginning of the industrial era, i.e. for more than a hundred years, humans have been releasing into the atmosphere gases (**carbon dioxide**, **methane**, **nitrogen oxides**, etc.) that artificially augment the greenhouse effect. Since 1750, this increase, with respect to “well-mixed” gases, has amounted to  $2.43\text{ W/m}^2$ . Contributing as it does an “additional radiative forcing” of  $1.46\text{ W/m}^2$ , carbon dioxide (CO<sub>2</sub>) accounts for more than half of this “additional greenhouse effect,” well ahead of methane ( $0.48\text{ W/m}^2$ ), **halocarbons** [chlorofluorocarbons [CFCs], hydrochlorofluorocarbons [HCFCs], and hydrofluorocarbons [HFCs]), accounting for  $0.34\text{ W/m}^2$ , and nitrogen dioxide ( $0.15\text{ W/m}^2$ ). Further, the **ozone** in the troposphere exhibits a *positive* radiative forcing of  $0.35\text{ W/m}^2$  (however, it is estimated that depletion of the stratospheric ozone layer observed between 1979 and 2000 has resulted in a *negative* radiative forcing, of  $0.15\text{ W/m}^2$ ).

This addition to the natural greenhouse effect ( $155\text{ W/m}^2$ ) is small, correspon-

ding to an increase of about 1%. Nevertheless, it is practically certain that this has contributed to the rise in mean temperature, for our planet, of about  $0.5\text{ }^{\circ}\text{C}$ , observed over the 20th century (see Figure 1). If nothing is done to curb these emissions, carbon dioxide concentration in the atmosphere (see Figure 2) could double by 2100. From current world consumption <sup>(1)</sup> of **fossil** fuels (7,700 Mtoe), the mass of CO<sub>2</sub> currently produced may easily be computed: 20 billion tonnes per year!

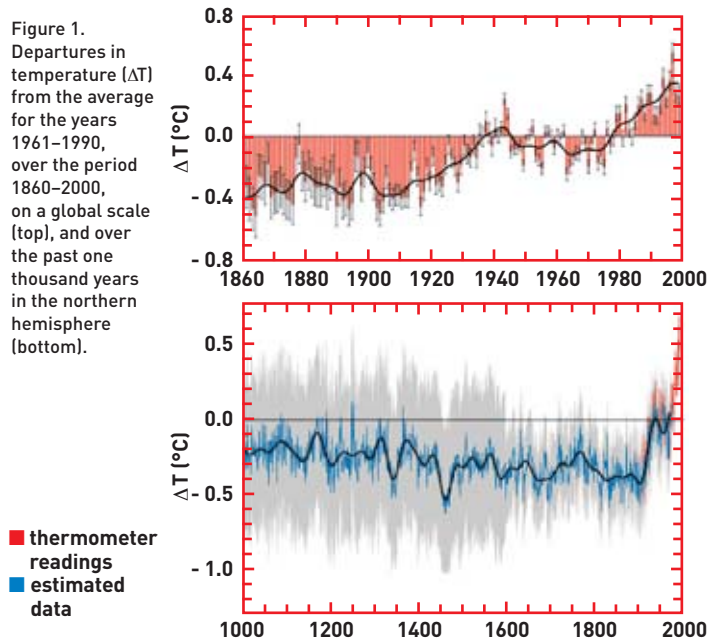
This could result in a substantial increase in the greenhouse effect, causing, through nonlinear amplifying effects,

(1) European Community, Directorate General for Energy (DG XVII), “Conventional Wisdom” scenario (*European Energy to 2020: A scenario approach*, 1996).

profound alterations in climate. Most models predict that doubling the present carbon dioxide concentration would result, by the end of the 21st century, in a rise in temperature of some  $2\text{--}3\text{ }^{\circ}\text{C}$ . Some models even yield a bracket of  $1.5\text{--}4.5\text{ }^{\circ}\text{C}$ , meaning dramatic consequences could be foreseen for the environment, such as a substantially rising sea level.

Such figures may seem small, entailing only minor consequences for the climate; that, however, is not the case. To understand this point, one should bear in mind that during the “little ice age,” from 1450 to 1880, mean temperature only fell, in France, by  $1\text{ }^{\circ}\text{C}$ , on average. Some 6,000–8,000 years ago, as Western Europe experienced a war-

Figure 1. Departures in temperature ( $\Delta T$ ) from the average for the years 1961–1990, over the period 1860–2000, on a global scale (top), and over the past one thousand years in the northern hemisphere (bottom).



## B The greenhouse effect and CO<sub>2</sub>

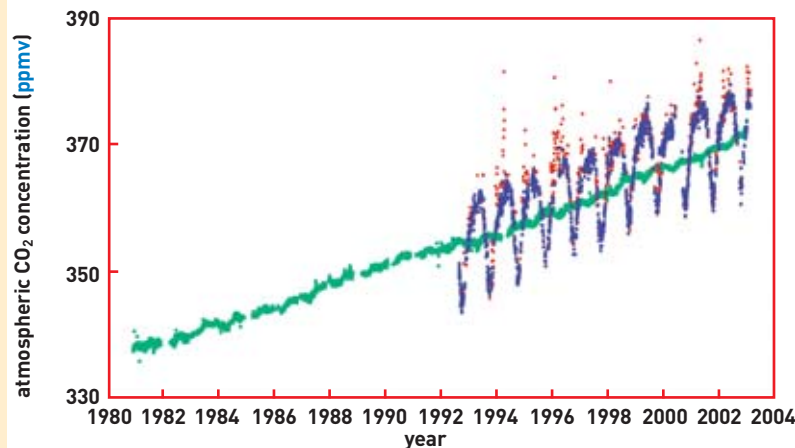


Figure 2.

Evolution of atmospheric CO<sub>2</sub> concentration since 1980, as measured on a daily basis by the automatic stations of the Climate and Environmental Science Laboratory (LSCE: Laboratoire des sciences du climat et de l'environnement), since 1981 on Amsterdam Island (Indian Ocean), and since 1992 at Mace Head, on the western coast of Ireland.

Readings on Amsterdam Island (shown in green), well away from any direct perturbation of human origin, essentially evidence the constant rise in concentration. The Mace Head site basically measures oceanic atmosphere (under normal conditions, westerly winds: blue). When wind conditions are reversed, the site receives a continental atmosphere, showing a strong excess in CO<sub>2</sub> (red plots), compared to oceanic atmosphere. Over the mean rise in CO<sub>2</sub> concentration is superimposed a marked seasonal modulation, due to plant vegetative cycle (chlorophyll photosynthesis), plants being CO<sub>2</sub> emitters in winter, and CO<sub>2</sub> absorbers in summer.

mer spell, with a mean temperature 2–3 °C higher than it is today, the Sahara was not a desert, but a region of abundant rainfalls. It is not so much the rise in temperature that gives cause for concern, as its rapid variation (in the course of one century). The large variations previously observed in nature all occurred over much longer timescales, for those at least of a global character. Thus, the last glaciation lasted 100,000 years, and the corresponding deglaciation took 10,000 years. The rapid variation we are currently experiencing may induce major, unexpected perturbations in the climate and the ecosystem, which will not always have time to adapt.

### From Rio to Kyoto: the major conferences on the global environment

The evolution of the global environment has led to major conferences being organized, starting in the closing decade of the 20th century.

At the Earth Summit, held in **Rio de Janeiro** (June 1992), the United Nations Framework Convention on Climate Change was signed, this setting the goal of a stabilization of **greenhouse gas** emissions (this convention came into force on 21 March 1994).

At the Kyoto Conference (December 1997), the protocol was signed providing for a global reduction in emissions of such

gases, by an average 5.2% in the period 2008–2012, compared to 1990 levels, for **OECD** countries and Eastern European countries (including Russia). Reduction targets for the **European Union** and France are set at 8% and 0% respectively. The ways and means to meet these targets were debated, unsuccessfully, in November 2000 at **The Hague**. Subsequent conferences, held in **Marrakech** (2001), **Johannesburg** (Earth Summit held in August–September 2002), **New Delhi** (October 2002), **Moscow** (September–October 2003), and **Milan** (December 2003) had still not enabled, by 2004, this **Kyoto Protocol** to be brought into force, until Russia finally decided to ratify the document, at last allowing this enforcement in February 2005.

Under the impetus provided by the United Nations Environment Program (**UNEP**), the issues raised by substances that deplete the ozone layer in the atmosphere were addressed in **Vienna** (1985), and most importantly in **Montreal** (1987), where the protocol was signed, imposing a reduction in production and use



The Mace Head monitoring station, Ireland.

of chlorofluorocarbons (CFCs). This protocol was specified by amendments adopted in **London** (1990), imposing a ban on CFCs from 1 January 2000, and extending controls to other compounds (including HCFCs), **Copenhagen** (1992), **Montreal** (1997), and **Beijing** (1999).

## 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.

fuel cell type	anode (catalyst)	electrolyte	cathode (catalyst)	temperature	applications
proton exchange membrane (PEMFC)	$H_2 \rightarrow 2 H^+ + 2 e^-$ (Pt)	perfluorinated polymer ( $SO_3H^+$ )  $H^+ \rightarrow$	$\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (Pt)	60-90 °C	portable transportation stationary
direct methanol (DMFC)	$CH_3OH + H_2O \rightarrow CO_2 + 6 H^+ + 6 e^-$ (Pt)	perfluorinated polymer ( $SO_3H^+$ )  $H^+ \rightarrow$	$\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (Pt)	60-90 °C	portable transportation
phosphoric acid (PAFC)	$H_2 \rightarrow 2 H^+ + 2 e^-$ (Pt)	$PO_4H_3$ (85-100%)  $H^+ \rightarrow$	$\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (Pt)	160-220 °C	stationary
alkaline (AFC)	$H_2 + 2 OH^- \rightarrow 2 H_2O + 2 e^-$ (Pt, Ni)	KOH (8-12 N)  $\leftarrow OH^-$	$\frac{1}{2} O_2 + H_2O + 2 e^- \rightarrow 2 OH^-$ (Pt-Au, Ag)	50-250 °C	space transportation
molten carbonate (MCFC)	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2 e^-$ (Ni +10% Cr)	$Li_2CO_3/K_2CO_3/Na_2CO_3$  $\leftarrow CO_3^{2-}$	$\frac{1}{2} O_2 + CO_2 + 2 e^- \rightarrow CO_3^{2-}$ ( $NiO_x + Li$ )	650 °C	stationary
solid oxide (SOFC)	$H_2 + O^{2-} \rightarrow H_2O + 2 e^-$ (Ni-ZrO <sub>2</sub> <b>cermet</b> )	ZrO <sub>2</sub> -Y <sub>2</sub> O <sub>3</sub>  $\leftarrow O^{2-}$	$\frac{1}{2} O_2 + 2 e^- \rightarrow O^{2-}$ (perovskites $La_xSr_{1-x}MnO_3$ )	750-1,050 °C	stationary <b>APU</b>

Table 1.  
The various types of fuel cell.