



Micro-fuel cells

Since the end of 2000, CEA has been engaged in development of a micro-fuel cell technology, targeting mobile communications devices, this including two variants, with respect to fuel conditioning: the direct methanol path, and a more innovative path, based on hydrogen generation from solid materials, chemical hydrides. For the fabrication of such miniature energy sources, CEA, drawing on its microelectronics expertise, has developed a novel concept, implementing, for fuel cells production, silicon-chip fabrication techniques.

A new generation of electrochemical microgenerators

Miniature fuel cells could power mobile phones and portable computers within the next few years. These afford many advantages: extended autonomy (ten hours, rather than the two or three provided by lithium batteries), simplicity and fast recharging.

The stages of micro-fuel cell technology: from bare silicon wafer, through cells fabricated by means of thin-layer techniques... to cut-out, integrated cells, ultimately associated to a small tank of hydrogen-precursor fuel.



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The rise of portable electronic devices, most conspicuously cell phones, digital organizers and portable computers, brings to the fore the crucial issues of power supply. The foreseeable evolution in functionalities and utilizations, as regards portable electronic devices, together with the introduction of novel electronic components, entail considerable changes in requirements, in terms of power consumption and autonomy.

Numerous investigations are addressing both component optimization and development of miniature energy sources, as alternatives to current **lithium-ion or lithium polymer storage batteries**, concerning which further advances are constantly being made (see *New paths in lithium storage batteries and battery electrolytes*). It should also be noted that Asian countries (Japan, Korea, China) take the lion's share in the area of portable energy sources, with over 90% of market share.

In this context, the miniature fuel cell may be seen as an attractive solution, representing as it does a true technological breakthrough, which could be of benefit to Europe, particularly with regard to the micro-electronics industry.

Two pathways under investigation

A fuel cell is an electric generator which, in the presence of a variety of **fuels** (**hydrogen**, alcohol) and oxygen, effects the direct transformation of chemical energy into electric energy. Currently, two pathways are the main subjects for investigation the world over, for low-energy applications: PEMFC and DMFC fuel cells (see *Fuel cell Q&A, Table*).

These two types of fuel cell basically differ with respect to the fuel used at the **anode**, this being hydrogen for PEMFCs, and liquid **methanol** for DMFCs. The

approach, as regards miniature fuel cells, hinges on two technological choices: the nature of the fuel to be used at the anode, and fuel cell architecture.

Choice of fuel for the anode

This choice is a fundamental one. Indeed, the amount of energy stored in a given volume of liquid methanol is markedly higher than for an equal volume of gaseous hydrogen. However, conversion of that chemical energy into electric energy (fuel cell efficiency) is much more readily effected in the gaseous hydrogen case. The low efficiency exhibited by fuel cells of the methanol type is essentially due to **catalysis** issues inside the fuel cell, which may only be resolved after a research effort of many years. Note should also be taken of the requirement for development of a system having the capability to recycle the water forming at the **cathode**, to dilute the methanol at the anode, thus obviating the need to include water in the fuel cartridge, which would negate the advantages of this technology. The issues with hydrogen fuel cells, on the other hand, are those of hydrogen storage and generation, in miniature devices.

In the area of miniature energy sources, most research teams, the world over, have opted to prioritize development of the DMFC pathway, mainly due to consideration of the energy theoretically available in a cartridge of pure methanol. Constant advances notwithstanding, performance levels remain poor, around 20 mW/cm^2 at ambient temperature.

Fuel cell architecture

Aside from choice of fuel, the architecture of the fuel cell is a key parameter, with respect to the success and emergence of this technology. CEA has gone for a structure of the *thin layer* type, obtained by means of techniques issuing from microelectronics. Rather than mere scaling down of a conventional fuel cell, this involves a true technological breakthrough, based on the implementation of a variety of processes used in microelectronics (**PVD**, **CVD**, **screen printing**, ink-jet printing, **lithography**).

This technology, protected by some twenty patents, relies on use of a **silicon** substrate, onto which fuel cells, veritable electric microgenerators, are fabricated. This is consistent with existing industrial equipment, and with the cost targets set by the current competitor technology, lithium-ion storage batteries, which remain the reference for mobile energy sources. After undergoing numerous electrochemical tests, the various “fuel-cell chips,” fabricated in large numbers on the silicon wafer, are separated, sorted, and connected together, to form a true electric generator, working with hydrogen from a cartridge, and oxygen from the atmosphere. This technology is now well mastered by CEA teams. Performance readings for the hydrogen-fed cell attain close to 300 mW/cm^2 , most commonly stabilizing at around 150 mW/cm^2 over several hundred hours (see **Figure 1**). The team has set itself the goal of achieving, within 4 years, about 1 W/cm^2 ; this means it would only take 1 cm^2 of silicon to power a portable phone. Concurrently with work on the cell core, recent advances with respect to the hydrogen storage and generation device, using **chemical hydrides**, have been achieved in CEA laboratories. A disposable cartridge, exhibiting gravimetric and volumetric energy densities close to 800 Wh/kg and 800 Wh/L , is being constructed.



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After undergoing a battery of tests, micro-fuel cells are cut out, sorted, and integrated into a housing, to make electric microgenerators.

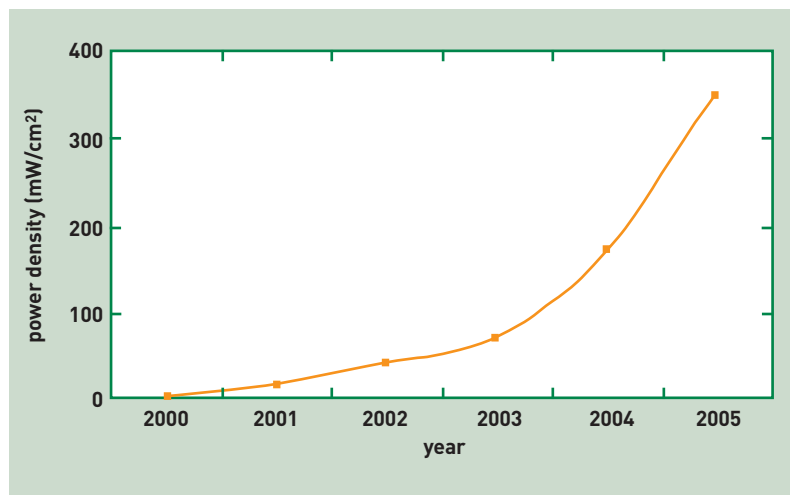


Figure 1. Evolution of micro-fuel cell on silicon performance, using hydrogen for fuel, from program start.

The “disposable cartridge” and “cell core on silicon” technologies are presently being integrated into technology demonstrators. An industrial consortium is being set up, this involving a chipmaker for the cell core on silicon, a disposable-object manufacturer for the cartridge, and finally a cell phone manufacturer. This will enable the technological transfer stage to be initiated from the end of 2004, to ensure the capability to embark on industrial production by late 2008–early 2009.

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E Storage batteries, cells and batteries: constantly improving performance

Storage 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, ⁽¹⁾ 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.

I (1) One cycle includes one charge and one discharge.

| 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 ₃ H ⁺) H ⁺ → | $\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (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 ₃ H ⁺) H ⁺ → | $\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (Pt) | 60-90 °C | portable transportation |
| phosphoric acid (PAFC) | $H_2 \rightarrow 2 H^+ + 2 e^-$ (Pt) | PO ₄ H ₃ (85-100%) H ⁺ → | $\frac{1}{2} O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$ (Pt) | 160-220 °C | stationary |
| alkaline (AFC) | $H_2 + 2 OH^- \rightarrow 2 H_2O + 2 e^-$ (Pt, Ni) | KOH (8-12 N) ← 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 ₂ CO ₃ /K ₂ CO ₃ /Na ₂ CO ₃ ← 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 ₂ cermet) | ZrO ₂ -Y ₂ O ₃ ← O ²⁻ | $\frac{1}{2} O_2 + 2 e^- \rightarrow O^{2-}$ (perovskites La _x Sr _{1-x} MnO ₃) | 750-1,050 °C | stationary APU |

Table 1.
The various types of fuel cell.