



Hydrogen is seen as the energy carrier of the future. In economic terms, however, current production processes are ill-suited to this. While steam methane reforming is the process yielding, on a large scale, gas having the best production cost – comparable to the price of gasoline before tax – water electrolysis is presently up to five times more expensive. Hydrogen could nonetheless be dispensed locally in fueling stations for a final cost before tax only 2.5 times higher than the price of gasoline at the pump. The economics of hydrogen energy must thus be understood over the entire energy path, from production to utilization.

Hydrogen from **chemistry** to **energy**

The nature of hydrogen demand is about to change...

If a demand directed more at the energy carrier than the chemical feedstock is to be met, the economics of hydrogen must involve the evaluation of cost trends and the potentials for cost reductions, so that only those technological paths and options are taken up that are best suited to the local specificities of demand.



Le Square des photographes/Air Liquide

Hydrogen PSA production unit operated by Air liquide's Group, at Waziers (Nord département, northern France).

Currently, **hydrogen** is used in industry above all for its chemical properties, mainly in ammonia plants (accounting for half of world consumption) and oil refineries, in particular for gasoline and diesel fuel desulfurization, and for production of **methanol**. Limited amounts, however, do go to users in other sectors, such as welding, the glass industry, semiconductor fabrication, and the food industry. Hydrogen is very little used for its specific energy, aside from highly specific applications, such as spacecraft propulsion.

World hydrogen production currently stands at around 550 billion cubic meters, corresponding to some 130 **Mtoe**, i.e. 1.5% of global primary energy production. Hydrogen is either produced as a byproduct from the chemical industry and oil refining, or is specifically generated through a variety of processes, usually designed to yield **synthesis gas** from **fossil** carbon compounds (**hydrocarbons**, coal...). The most commonly used specific process, and the most economical, on a large scale, is steam **methane reforming**. Water **electrolysis**, owing to its high cost and poor overall energy efficiency, is presently restricted to a niche market, to generate high-purity hydrogen.

Only a small fraction of the world production of hydrogen (less than 5%, according to Air liquide) is outsourced as "over-the-fence" (OTF) supply, i.e. is carried out by industrial gas suppliers able to avail themselves of the required infrastructure (gas pipeline, for instance). This proportion should rise in coming years, particularly since the stricter environmental regulations burdening **hydrocarbon fuels** mean ever more merchant hydrogen is called for.

However, hydrogen has not so far achieved the status of an **energy carrier**, in particular owing to the fact that the costs for this technology path remain daunting, with the integration of the entire chain, from pro-

duction from various **primary energy** sources to distribution to end-users (e.g. users of personal **fuel-cell** powered vehicles).

There is nevertheless a fairly broad consensus, nowadays, in Europe and beyond, agreeing that significant commercial growth for hydrogen and fuel cells is a possibility, by 2010–20, for certain prioritized niche markets, such as captive-fleet vehicle propulsion, high-reliability stationary power generation or long-duration power supply for portable electronic devices. This consensus found its formal expression in June 2003, under the auspices of the **High-Level Group on Hydrogen and Fuel Cells** set up by the **European Commission**. The latter subsequently set up a technology “platform”, steered by an Advisory Council representing the public- and private-sector protagonists in the field, and charged with carrying through the High-Level Group’s vision for the future.

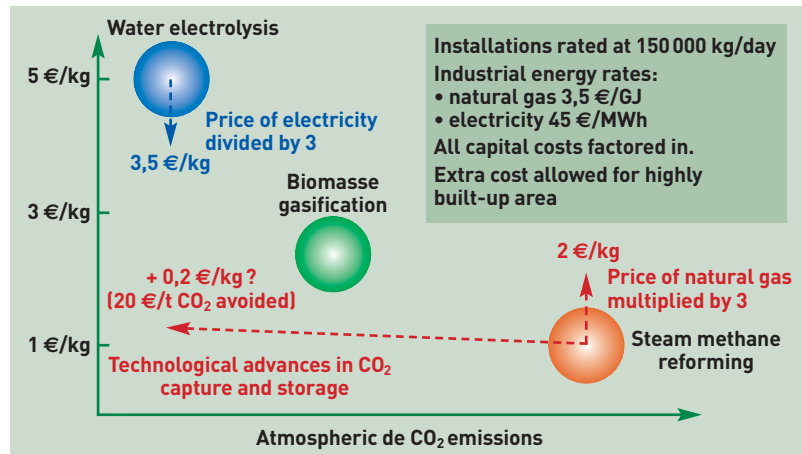
There is likewise broad agreement that initiating commercial manufacture of personal vehicles powered by hydrogen fuel cells cannot be anticipated before 2020–30, bearing in mind that the European Union has opted to bring forward a vision whereby hydrogen production is to proceed gradually, from non-fossil (nuclear or renewable) energies, or even from fossil energies, provided the carbon yielded by combustion is captured and stored before it is emitted into the atmosphere.

The European Roadmap

In this context of expected growth in hydrogen energy markets, evaluation of the costs for each technology path (hydrogen production, transport and storage, and distribution to users), of future trends affecting these costs, and of their potentials for reduction is of paramount importance, providing that the technology paths and options taken up be truly suited to the specific features of local and regional demand, with respect for instance to primary energy sources, and transport and distribution infrastructure. Which is, moreover, a tricky exercise, when this involves comparing industrial technologies with others at the R&D stage, considering a common timeline has to be defined for the short, medium and long terms.

As part of its R&D effort on hydrogen and fuel cells, CEA has committed itself to the European HyWays techno-/socio-economic project, coordinated by German consultants **LBST**, setting out to develop the European Hydrogen Energy Roadmap. One of the resources implemented in this project is the E3 database techno-economic tool, developed by LBST, in collaboration with CEA and **IFP**, to assess energy requirements, and the emissions and costs of hydrogen technology paths. It will thus be possible to access, through its use, data from the latest international studies. In the meantime, orders of magnitude for energy path costs may nevertheless be arrived at, drawing on recent available data, provided these are culled from serious, consistent and detailed investigations.

The data presented here are taken from a study, dating from July 2002, by US consultants SFA Pacific, Inc. (working in collaboration with US **DOE**), dealing with the costs of hydrogen pathways for fuel-cell powered vehicles. In that study, hydrogen is produced, through a variety of processes, in large facilities having a design capacity of 150,000 kg/d, then transported to the point



of consumption (411 filling stations, spread around the central production plant at an average distance of 150 km, along supply lines radiating in four directions), either in gaseous form (gas pipeline at 75 bars) or in liquid form (**cryogenic** truck). Each filling station is sized to dispense 470kg/d (design capacity), and may also house a decentralized hydrogen production unit. Figure 1 shows the undiscounted costs of centralized hydrogen production, for three processes, ranked according to their relative atmospheric **CO₂** emissions: steam methane reforming (the reference process), water electrolysis (using electricity of non-fossil provenance), and biomass gasification (a process at the R&D stage). For reasons of consistency, to preclude taking into account intermediate costs (liquefaction), comparison is restricted in this paper to production of compressed gaseous hydrogen.

Steam methane reforming is the most economical centralized hydrogen production process (in terms of both capital and operating costs), with production costs of the order of €1/kg, with natural gas, however, accounting for over half of that cost. Water electrolysis in this case is five times more expensive, with electricity however again accounting for half of the production cost. Biomass gasification stands at an intermediate position, with feedstock accounting for slightly more than a quarter of production cost.

The impact of energy prices is thus decisive (Figure 1): dividing the price of electricity by 3 leads, in this case, to production costs for water-electrolysis generated hydrogen dropping by one third, whereas multiplying the price of natural gas by 3 doubles the production cost for hydrogen from steam methane reforming. Such trends are not unrealistic over the long term: in a context of scarcer low-cost fossil resources, with the rise of renewable energies (consistently declining cost of wind-turbine electricity) and the gradual renewal of the nuclear power-station fleet (with uncertainties as to the funding), the price of electricity supplied to industry will be a key parameter for the competitiveness of the water-electrolysis process in years to come.

In the shorter term, the coming into effect, from January 2005, of the European Directive of October 2003 setting up a European Community-wide scheme for the trading of **greenhouse gas** emission quotas should result in taxation of **CO₂** emissions from industrial installations, which may penalize, over time, hydrogen production through steam methane reforming, unless **CO₂** capture and storage technologies are implemented, at economically favorable conditions (Figure 1). However,

Figure 1. Relative costs for centralized production of gaseous hydrogen. Sources: SFA Pacific 2002 and IFP (CO₂ capture and storage).



the true impact of this Directive can only be evaluated once the initial national quota-allocation plans have all been approved by the European Commission, for the three-year period (2005–7) leading up to the five-year commitment period provided for by the Kyoto Protocol, from 2008 on (2008–12).

At the same time, as part of its ongoing programs devoted to nuclear systems of the future, CEA has been investigating the feasibility of improved hydrogen-production economics, by use of the high-temperature heat output from an innovative nuclear power station. The aim is to achieve a sizeable reduction in electricity consumption (in the water electrolysis case), to substitute non-fossil heat for fossil, taxed heat (in the steam methane reforming case), or to use thermochemical cycles to effect water splitting directly, with the hope of better overall energy efficiencies than those achieved for the water electrolysis process (*see How is hydrogen to be produced?*).

Figure 2 shows undiscounted final costs for hydrogen delivered to the filling station forecourt, in euros per liter gasoline equivalent (lge), using the same data from SFA Pacific, for hydrogen produced through steam methane reforming or water electrolysis, and transported via pipeline or truck.

The cost of gaseous hydrogen produced through steam methane reforming is of the order of € 0.27/lge – comparable, in other words, to the price of gasoline before

tax – while final cost, taking into account hydrogen delivery and filling-station dispensing (including onsite storage), is three to five times higher, this being burdened by transport costs (gas pipeline) or in-plant liquefaction costs (cryogenic truck).

For steam methane reforming, final cost before tax of dispensed hydrogen is thus close to that of gasoline at the pump (around €1/lge), while for water electrolysis it is only 2–2.5 times greater than the latter. For reference purposes, Figure 2 also shows the target set by DOE for 2010 (€ 0.40/lge for hydrogen from natural gas at the pump, untaxed, with no CO₂ capture or storage).

Owing to high capital costs (especially in built-up areas), hydrogen transport by gas pipeline would appear to be best restricted to short distances. On the other hand, road transport of liquid (or gaseous) hydrogen is probably better suited for growing markets, where the quantities involved are smaller.

With decentralized production at the fueling station, the local economics of hydrogen are penalized, as a whole, by higher unit capital costs (no economies of scale), lower yearly utilization rates (70% in this case, as against 90% for the central production plant) and higher energy (natural gas, electricity) commercial rates (as against industrial rates for the central plant).

In the case of steam methane reforming, the final cost for dispensed hydrogen from a central production plant is comparable to the cost of hydrogen produced and dispensed on site, the absence of delivery costs compensating overall for the higher cost of local production. On the other hand, such compensation remains altogether inadequate in the case of water electrolysis. Such pointers show simply that the economics of “energy hydrogen” must take on board the hydrogen infrastructure, from source to use, as a dynamic industrial system, the many technical–economical parameters of which must be adjusted according to the specific features of local demand. Attention should be directed, in particular, to potentials for cost reductions by bringing in new technologies or novel operating methods. The feasibility of using extant natural-gas grids to transport a small fraction of hydrogen comes under that heading.

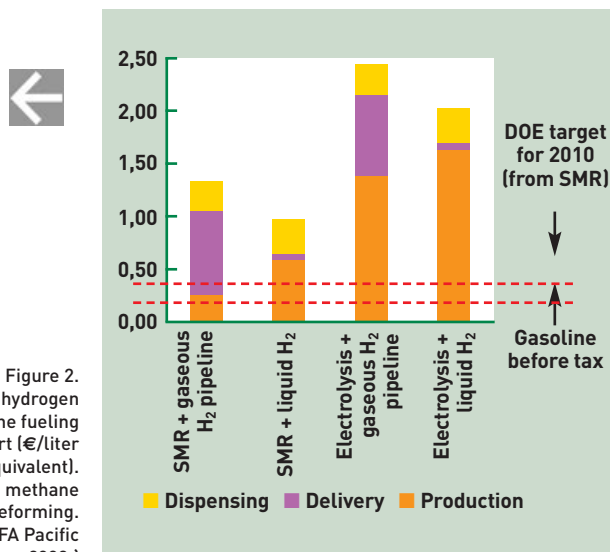


Figure 2. Cost of hydrogen dispensed at the fueling station forecourt (€/liter gasoline equivalent). SMR = steam methane reforming. [Source: SFA Pacific 2002.]

➤ **Jean-Marc Agator**

Technological Research Division
CEA Fontenay-aux-Roses Center

... and offer must gradually adjust to meet it

Looking to the somewhat longer-term prospect of mass hydrogen utilization, production will be one of the key points in the success of the entire energy path. Production should very gradually switch away from fossil feedstocks, going for processes drawing on sustainable energy sources: renewable energies and nuclear energy.

World production of **hydrogen** nowadays is largely generated through well-known industrial processes, providing a capability for large-scale production, most notably **natural gas reforming**. The foreseeable evolution in hydrogen demand (*see Figure 1*) will show initially a strong growth in requirements, in the coming decades, both in order to meet the growing energy requirements of developing countries (China, India, South America) and to comply with future standards for **hydrocarbon fuels** (with growing requirements in the refining and petrochemicals sec-

tor...). Subsequently, a very gradual falling off may be expected, paradoxically, as regards hydrogen requirements for refining, this being simply due to the tailing off of petrol production, say from 2040 on. Such an evolution is quite independent from the breakthrough of hydrogen as an **energy carrier**, which will show up concurrently, with the appearance, also very gradually, of a specific demand, initially to supply early markets (public transportation, utility fleets, heavy transportation, and demonstrations), and subsequently to cater for the gradual introduction of personal vehicles, say from 2020 on. Owing to the long time required for automotive fleet replacement (12 years), it will indeed be necessary to wait some 15–20 years to see significant hydrogen demand assert itself. Finally, use of hydrogen for stationary facilities or in **cogeneration** will probably come last, stationary applications for **fuel cells**, on the other hand, experiencing growth much earlier, this involving however **fossil hydrocarbon fuels** (natural gas, **LPG**, diesel fuel ...).

To take an example, European hydrogen requirements to cater fully for transportation (assuming only fuel cells were used as **converters**) are assessed at an amount representing 1–2 times current world production of hydrogen, this standing at around 550 billion m³.

Production technologies

By contrast to other technologies, such as fuel cell technology itself, the main issue with respect to hydrogen production is not that of the existence of low-cost technologies so much as of their replacement, in the medium and long term, by new technologies that will meet sustainable development criteria. Indeed, while it is perfectly feasible as of now to produce hydrogen in large quantities, at relatively low cost, by means of a number of technologies, in particular the reforming of natural gas in huge plants, these technologies labor under a twin disadvantage. The first being that they involve use of a primary energy source of the **hydrocarbon** (natural gas, petroleum) or coal type, and such resources have a limited lifespan. And the second is that they release heavy emissions of **greenhouse gases** (GHGs) and other pollutants.

Processes such as low-temperature electrolysis could easily be adapted to use more sustainable energy sources, however they offer fairly poor energy efficiency (owing to the efficiency of the electricity generation process itself), and generate hydrogen at a very high cost. They are not suited to mass production so much as to niche markets.

In the long term, other processes must thus be developed, drawing on sustainable energy sources (renewable energies, durable nuclear energy) while guaranteeing acceptable cost levels for the then-prevailing economic conditions. Such processes, which currently are neither technologically mature nor competitive, may be classified in a number of ways, by temperature for instance.

Among high-temperature processes may be ranged thermochemical cycles, using heat sources of varying temperature (300–1,800 °C) and diverse provenance (geothermal, solar concentrator, nuclear), high-temperature electrolysis (700–1,000 °C), catalytic water-splitting and physical separation processes (500–800 °C), or other processes, of the thermal-plasma splitting of



Stuart Energy

Portable hydrogen production unit made by Stuart Energy. As an intermediate between stationary applications and vehicle-borne onboard applications, this concept makes it possible to cater for impermanent requirements, or those of customers on the move, for supply of electricity and/or hydrogen fuel.

water or aqueous solutions type (temperatures of several thousand degrees, e.g. through use of a plasma torch). Biomass gasification (700–1,400 °C) may also be classified under this heading.

Included in the category of low-temperature processes are photoelectrochemical processes, photobiological processes, **biomimetic** processes or equally fermentation processes.

Current hydrocarbon-based processes will be required for several decades yet. One major challenge will be that of making such technologies clean, to circumscribe their impact on the environment, until sustainable processes take over. A further challenge, in the short and medium term, will be that of the miniaturization of reforming processes, for onboard vehicle utilization, allowing, in a transitional stage, use of the present energy chain while bringing in fuel-cell technologies.

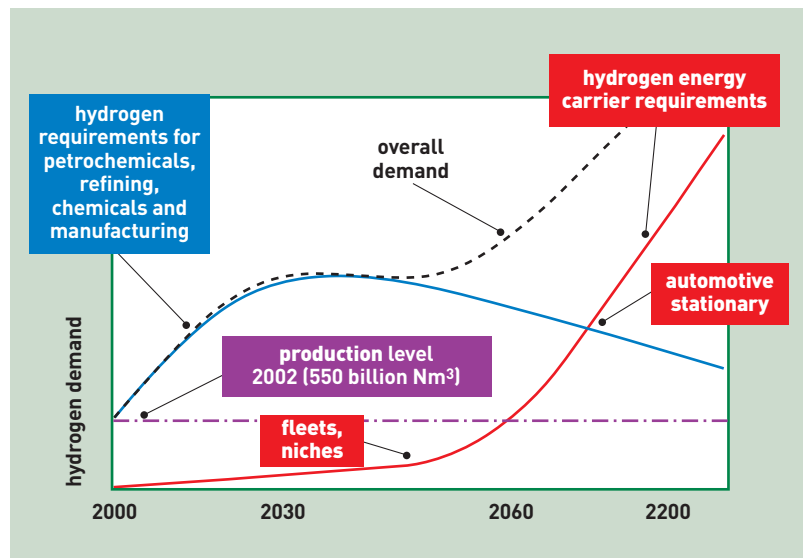


Figure 1. Foreseeable evolution of hydrogen demand



Table. Production costs and final costs for hydrogen from a variety of processes, compared to gasoline costs (according to a CEA-IFP-Total in-house study).
 (1) Including storage, delivery and dispensing.
 (2) The filling-station element accounts for over 75% of infrastructure cost, pipeline transport accounting for around 10%.

process	production type	feedstock cost (€/GJ)	hydrogen production cost (€/GJ)	hydrogen final cost (including infrastructure) ⁽¹⁾ (€/GJ)
reference: gasoline (2003)	extraction refining	2,5 €/GJ	gasoline: 6 €/GJ	gasoline: 7 €/GJ
natural gas reforming ^l	centralized (3 million m ³ /day)	3 €/GJ	5-8 €/GJ	22-30 €/GJ ⁽²⁾
natural gas reforming	decentralized	4-5 €/GJ	7-12 €/GJ	28-33 €/GJ
coal gasification	centralized	1,2 €/GJ	13-16 €/GJ	32-37 €/GJ
Biomass gasification	intermediate	2,4 €/GJ	17-22 €/GJ	33-40 €/GJ
electrolysis	decentralized	14 €/GJ (5 c€/kWh)	20-25 €/GJ	35-40 €/GJ

Production, costs and infrastructure

A comparison of the orders of magnitude of costs achieved with present-day processes (see Table) shows that natural gas makes possible hydrogen production at a cost, ex-factory per unit of energy, that is broadly similar to that of gasoline. It is indeed the contribution of distribution (mainly at the filling station, with compression and storage) that is penalizing in terms of final cost for hydrogen. Electrolysis is an extremely expensive process, even for low prices per kilowatt-hour. The conclusions that may be drawn from this Table are thus twofold. First of all, mass-production processes will have to be developed, to achieve production costs ex-factory, as evaluated by CEA, around double those for the least expensive of the current processes, i.e. costs of around €10–12/GJ. The assessment indeed is that rising hydrocarbon prices and CO₂ taxation should bring about a doubling in hydrogen prices, compared with the present. Distribution costs must also imperatively be brought down, these being 15–20 times higher than such costs for present-day liquid hydrocarbon fuels. Even though

it be not possible to match the latter's performance, in physical terms, such costs needs must be divided by 3, if economic viability is to be hoped for within a few decades.

A possible four-period evolution

The probable evolution of hydrogen production processes (see Figure 2) then makes it possible to distinguish four successive periods, or eras, each "cleaner" than the preceding one.

The current ("fossil") era could be drawn out for a further 15–30 years, conventional, low-cost processes (natural gas reforming, partial oxidation of petroleum fuels, coal gasification) making it possible to meet a growing hydrogen demand. Processes such as electrolysis may cater for niche or demonstration markets, in the absence of a distribution infrastructure. Finally, bringing in vehicle-mounted, onboard reformers would enable initial experiments with fuel-cell technologies to be made in the field of transportation.

In the subsequent (20–30-year) era, the part played by hydrocarbons in hydrogen production will remain dominant, however large-scale CO₂ capture and sequestration techniques should lead to making them less heavy GHG emitters. Depending on prevailing pricing conditions and the taxation and regulatory context, a proportion of decentralized production from renewable energies and/or (nuclear) electrolysis may co-exist with hydrocarbon-based production.

A third, much longer (50–200 years?) era would follow, during which clean processes for generation from primary sources having long-lasting reserves (coal, uranium providing breeder technology is used, fusion) or renewable sources will take over, with novel, efficient processes such as thermochemical cycles, photoelectrochemical and photobiological processes, and gasification processes with CO₂ sequestration.

Ultimately, in a final era, sustainable sources (renewables, fusion) will be able gradually to take over from previous ones.

► Paul Lucchese

Technological Research Division
CEA Fontenay-aux-Roses Center

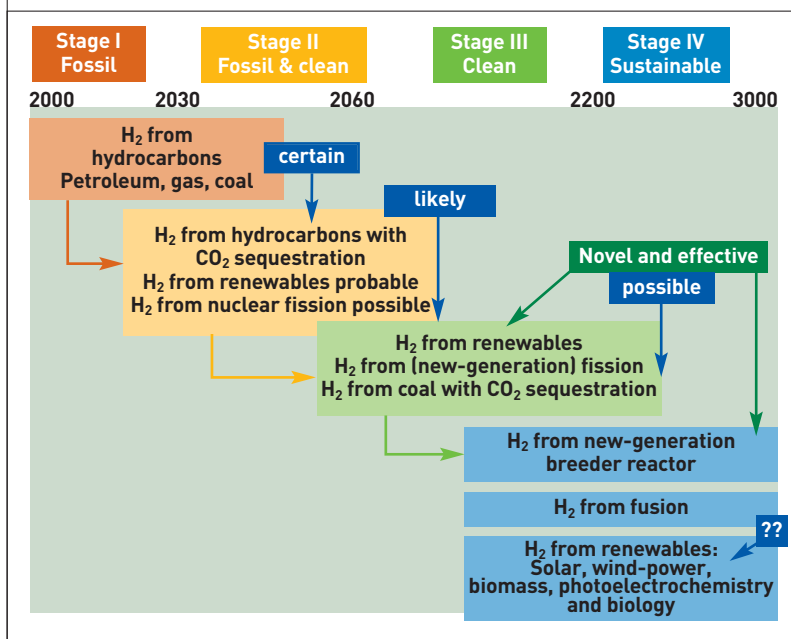


Figure 2. Foreseeable evolution of hydrogen production processes.

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).

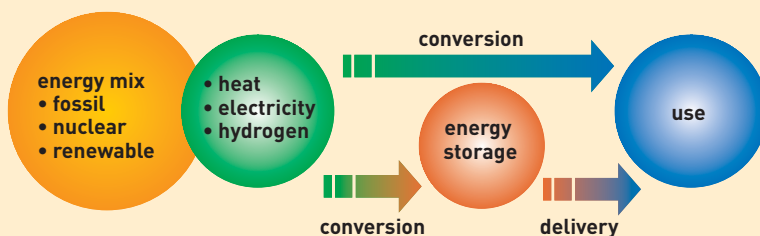


Figure 1. The energy scheme.

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.

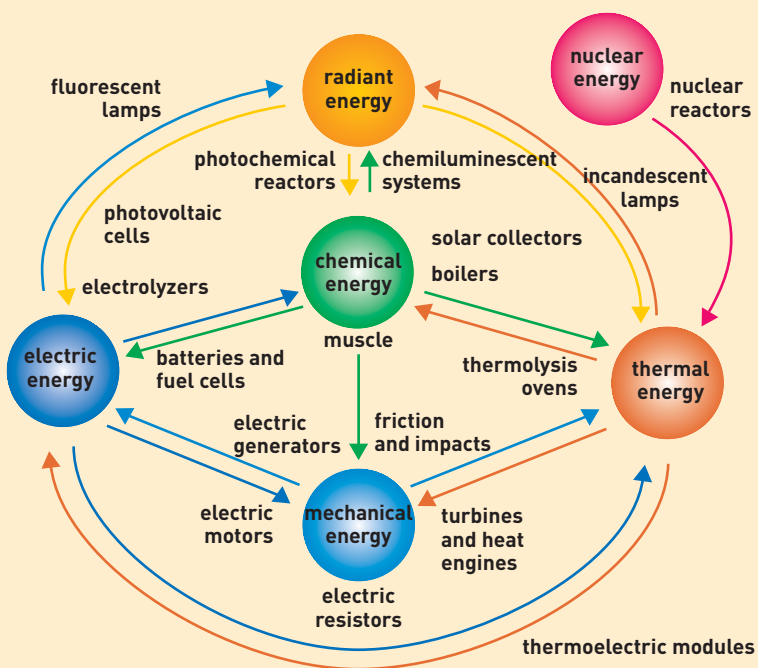
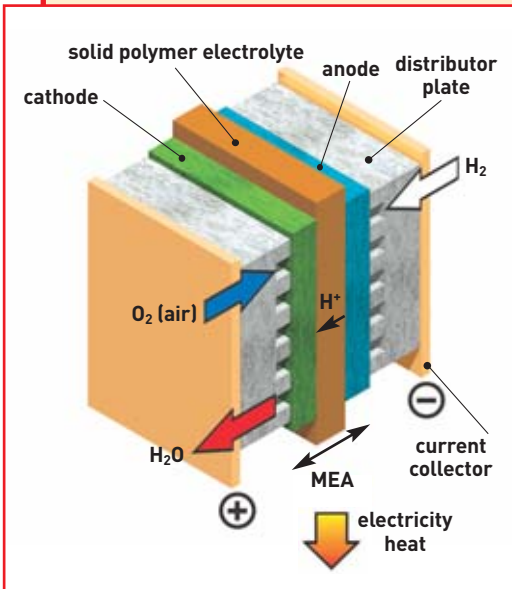


Figure 2. Conversions of the six main forms of energy, with a few examples of energy converters.

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 H₂ and oxygen O₂ - 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: $\text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^-$. At the cathode, the oxygen, the electrons and the protons recombine to yield water: $2 \text{H}^+ + 1/2 \text{O}_2 + 2 \text{e}^- \rightarrow \text{H}_2\text{O}$. 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/cm². 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

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.

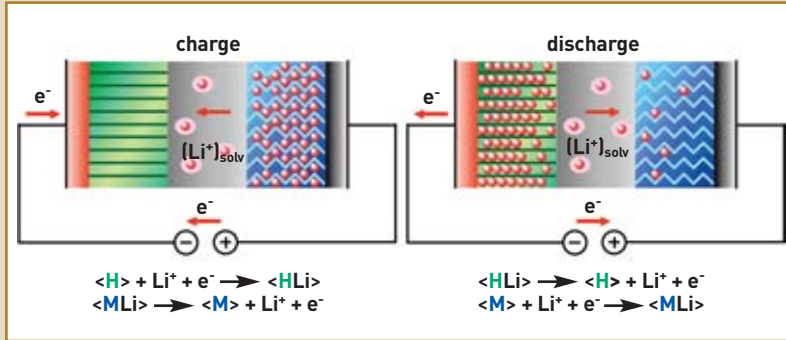
I (1) One cycle includes one charge and one discharge.

Operating principle of a lithium storage battery

1

During use, hence during discharge of the **storage battery**, lithium released by the **negative electrode** (<H>: host intercalation material) in **ion form** (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 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.