

Thermochemical water splitting cycles

Two processes to effect splitting of the water molecule by means of an external heat source are competing for adoption, for the long-term production of hydrogen: high-temperature electrolysis, and splitting the water molecule through a succession of chemical reactions: a thermochemical cycle. Both processes form part of a strategy of voluntary reduction of greenhouse-gas emissions, and of alternatives to ever-scarcer fossil resources, and thus do not involve hydrocarbons.

Since hydrogen is only an energy carrier, not a primary energy source, some such source must be available if hydrogen is to be generated. Aside from hydrocarbons, only nuclear energy currently has the capability to supply such energy, for the mass production of hydrogen. Hydrogen demand should experience strong growth in coming years. At present, and for the short term, hydrogen is mainly used in the chemical and oil industries, in particular to produce lighter fractions from heavy hydrocarbons. If, in the decades to come, hydrogen were to be used in transportation, the energy landscape would undergo an upheaval. To take an example: if in France hydrogen were to substitute wholly for gasoline in transportation, and if that hydrogen were to be generated by means of nuclear power stations, the current fleet of such power stations would have to be increased practically fourfold! Which shows how important the stakes are, and the need to subject these two paths to detailed investigation, in order to be in a position to make the right choices, when the time arrives. It should be noted that this research is a long-term effort, and that, for several decades yet, hydrogen will be produced, in the main, by methane reforming.

The first papers on thermochemical cycles (TCs) were published in 1964. Research work went through a fallow period, before experiencing a heady growth after the 1973 oil crisis. Activity remained strong up till 1984, tailing off thereafter, except in Japan, and ending up in a near suspended state, right up to the present. Presently, nuclear programs, which had been frozen in most industrialized nations since the Three Mile Island accident, are attracting renewed interest, owing to growing energy demand, and the requirement to renew extant power station fleets. France is particularly looking into high-temperature gas-cooled reactors, under the aegis of the international Gen IV agreements. Since such generators can yield both electricity and heat, the issue of the best utilization of these energies for the production of hydrogen naturally arises.

At first, direct use of heat for TC hydrogen generation seemed to have the potential of resulting in very high efficiencies. By using heat to produce thermal energy, nothing, at first blush, could prevent efficiency equal



P. Stroppe/CEA

Testbed at CEA/Saclay for the investigation of thermochemical-cycle water splitting for hydrogen generation by the iodine-sulfur process. This process is based on the decomposition of two acids at high temperature, sulfuric acid, which yields oxygen and SO₂, and hydrogen iodide (HI), yielding hydrogen and iodine. Iodine and SO₂ react at low temperature in the presence of water, thus regenerating the two acids (Bunsen reaction).

to unity from being achieved. Professor James Funk, from the University of Kentucky, was the first to refute this fallacy, in 1966, and he showed that, since any cycle produces work, TCs are limited by the Carnot efficiency. The question then arose, as to what efficiency could be hoped for from a TC.

A chemical reaction, just as any thermodynamic transformation, exhibits maximum efficiency when it is effected in reversible fashion. Work and heat requirements can thus be predicted by means of the second principle of thermodynamics, if the thermodynamic functions of the initial and final states are known, bearing in mind that the total energy required (work + heat) is known from the first principle of thermodynamics. Work itself being produced by heat, in a heat engine, it will be advantageous to use a maximum



amount of heat in a TC, restricting work to the minimum required to allow a good efficiency to be hoped for. This line of reasoning leads to the conclusion, in particular, that, in order to split the water molecule by means of a single reaction, providing only heat, the operation must be carried out at 4,500 °C. Many writers have shown that the work required could reduce to zero, provided splitting is effected via several chemical reactions. It is thus necessary to bring into the process intermediate agents that will be recycled. Establishing whether good efficiencies are thereby achieved is the whole object of R&D (see Figure 1).

Aside from efficiency, a TC must meet a number of other criteria, such as nontoxicity of the compounds used, natural abundance of the elements involved, and ease of implementation of the reactions. Further, in

difficulty was overcome at the end of the 1970s, with the discovery by General Atomics (GA) that it was possible to separate the two acids, in the presence of excess iodine and water.

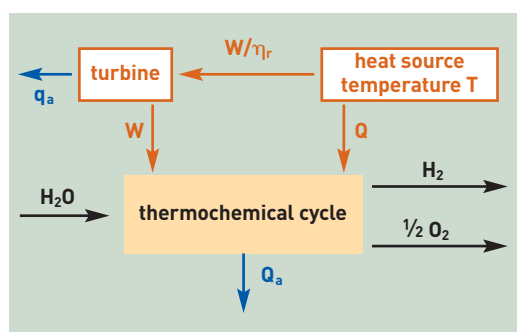
Among the hard points in this process may be counted, on the one hand, the difficulty of achieving efficient separation of HI from water and excess iodine at the outcome of the Bunsen reaction (investigations are ongoing to find the best distillation scheme, and regarding use of membranes), and, on the other, the high-temperature decomposition of the acids. Currently, the SO₃-helium exchanger is the largest capital-outlay item for the process, according to ongoing economic evaluations.

One small laboratory loop was operated in Japan for 48 hours, generating 45 liters of hydrogen. A second loop, of 50-l/h capacity, is being tested. This process is currently undergoing thorough investigation in France. Collaboration agreements have been passed between CEA and US DOE, under the aegis of the Gen IV Program, to carry out a detailed assessment of the cycle's potentials. At the same time, the European Hythec Program, which has just been launched, will allow investigation of some special points, such as membrane distillation, the liquid-vapor equilibria for H₂O-HI-I₂ mixtures, and sulfuric acid decomposition.

Figure 1. The efficiency of a chemical cycle is defined as the ratio of the recombination heat for the oxygen and hydrogen generated (ΔH), over the total heat supplied by the hot source:

$$\eta = \frac{\Delta H}{Q + \frac{W}{\eta_r}}$$

Q and W stand for the heat and work required by the cycle, η_r for the turbine conversion efficiency, Q_a and q_a for the amounts of heat rejected into the atmosphere.

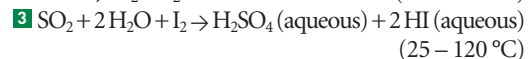
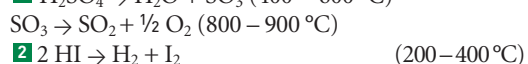
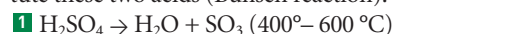


nearly all cycles, material recirculation flows of recycled elements are very large. Cycles involving transport of solid reactants between reactors are thus to be avoided, in favor of cycles which only involve fluids (liquids or gases), or gas-solid reactions on fixed or **fluidized beds**. Bearing in mind that a large number of TCs have been mooted since 1964, CEA opted to direct its programs along two main research thrusts. The first one is concerned with assessment of those cycles that have shown lasting power, and are still subjects of research in other countries. Such is the case of the iodine-sulfur cycle, as of the UT-3 cycle. The benefit, when investigating these cycles, is that many findings are available, and R&D may be shared. The second thrust concerns the quest for new cycles, an ongoing intellectual effort from which novel processes may arise.

Such work, obviously, only makes sense once referred back to electrolysis, which is why the program involves, as a final step, comparison of hydrogen generation via TC, and via alkaline electrolysis.

The iodine-sulfur cycle

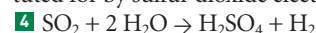
This process is based on the decomposition of two acids at high temperature, sulfuric acid, which yields oxygen and SO₂, and hydrogen iodide (hydriodic acid: HI), yielding hydrogen and iodine. Iodine and SO₂ react at low temperature in the presence of water to reconstitute these two acids (Bunsen reaction):



This process has been subjected to much investigation by a variety of research teams, since it has the advantage of only involving liquids and gases. One major

The Westinghouse hybrid cycle

This process may be seen as a variant of the iodine-sulfur process, where reactions (2) and (3) are substituted for by sulfur dioxide electrolysis:



$$(20 - 110^\circ \text{C}) \quad E_{\text{reversible}} = 0.17 \text{ V P} = 2 - 10 \text{ bar}$$

This has the advantage of requiring only one intermediate element, sulfur, which moreover is quite abundant. Possible issues linked to chemical composition drift in the mass flows are thus limited, by contrast with cycles involving several elements. Resulting recirculation mass flows, furthermore, are decidedly smaller (see Figure 2).

On the other hand, it does require electric energy for part of the cycle, which restricts efficiency. Electrolysis is carried out in a strong acid medium, leading to corrosion issues. Moreover, this would require several compartments, to restrict parasitic sulfur and H₂S production at the cathode.

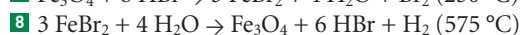


Bunsen reaction: separation of the two acids obtained in an experiment, carried out at CEA/Saclay, on thermochemical-cycle water splitting for hydrogen generation by the iodine-sulfur process.

A pilot was built in Russia in the early 1980s. Research work at CEA is devoted to assessment of the electrolyser, compared with conventional alkaline electrolysis (actual electrolysis voltage, materials, corrosion). These investigations will lead on to an overall "reassembly," taking on board the assessment of the electrolytic component specific to this cycle, as of the thermochemical sulfuric acid decomposition component, shared with the iodine-sulfur cycle.

The UT-3 cycle

The UT-3 cycle is based on two pairs of chemical reactions. The first two chemical reactions, (5) and (6), yield hydrobromic acid, accompanied by release of oxygen, while the two subsequent reactions, (7) and (8), consist in reduction of water by a bromide, accompanied by release of hydrogen. Reactions (6) and (8) are endothermic.



In the original Japanese concept, this cycle operates discontinuously. Reactions (5) and (6), on the one hand, and (7) and (8), on the other, are effected sequentially in two separate reactors, through the reaction of gases and solid reactants embedded in solid inert matrices. The main difficulty encountered by the Japanese was the cycling behavior of these matrices. In the reactor where reactions (5) and (6) are carried out, for instance, the inert matrix initially holds CaO, which is turned into CaBr₂ in the first cycle. The reverse transformation, reaction (6), occurs during the second cycle, and so on. Since the design proved difficult to extrapolate to an industrial scale, investigations were initiated at CEA to imagine a process design closer to industrial reality. Thus, as the reactions involved are heterogeneous, agitation of the systems would seem to be required, to accelerate the diffusion of the gaseous reactants and reaction products. This consideration, together with the fact that the matter flows required for mass production of hydrogen are very large, led to processes using the principle of fluidized beds, within which the systems undergo natural agitation.

Investigations are also devoted to the possibility of simplifying the cycle, by devising reactors having the capability to effect concurrently two twinned reactions, thus carrying out in-situ regeneration of the reactants. Continuous hydrogen production may thus be envisaged. Provided, that is, the means is found to effect gas separation at the reactor outlet, and to supply the reactor with the heat required for the reactions. Figure 3 shows a design of this type, applied to the first two reactions in the cycle, a design for which many technological barriers will need to be overcome.

Other cycles under consideration

Other cycles have been the object of simplified assessments, using previously mentioned criteria (efficiency, reactant abundance, toxicity...). Such are, for instance, the "sulfate" cycles, for which the reactions take the form:

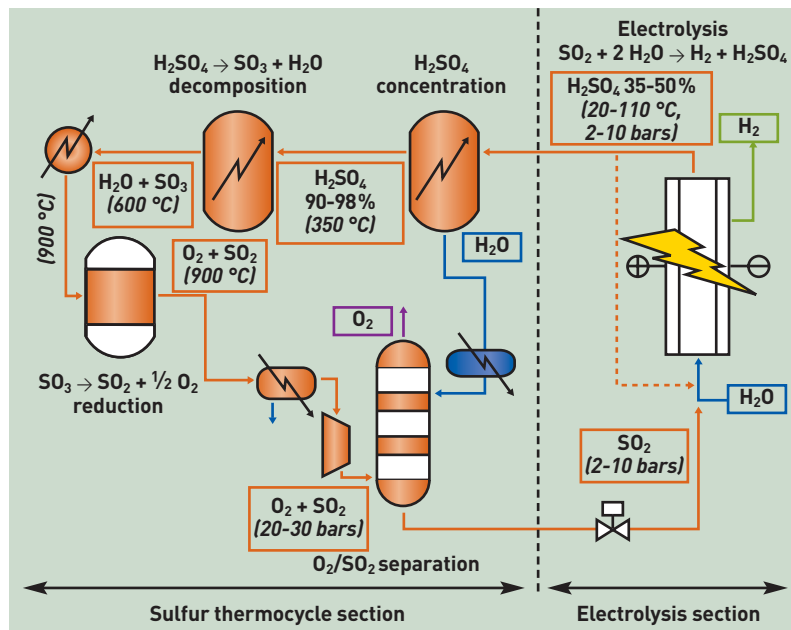
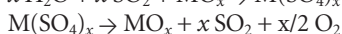


Figure 2. Simplified schematics of the Westinghouse hybrid cycle.

where M is a metal. The first reaction actually corresponds to the superposition of two sub-reactions, SO₂ fixation by MO_x, and reduction of water by the SO₂-MO_x system. Thermal decomposition of the sulfate allows SO₂ recycling, accompanied by release of oxygen.

A number of metals may be used (Mn, Fe, Ni, Zn, Cd...), reaction kinetics and cycle efficiency being the criteria for choice of metal. Initial studies carried out to date show that major difficulties are encountered, regarding secondary reactions, such as sulfide formation resulting in cycle stoppage.

Other cycles have also been considered, owing to their simplicity. Such are for instance systems involving only oxides, where valence transitions ensure the successive oxidations and reductions. This is the case, for instance, for an iron-oxide based cycle, where hema-

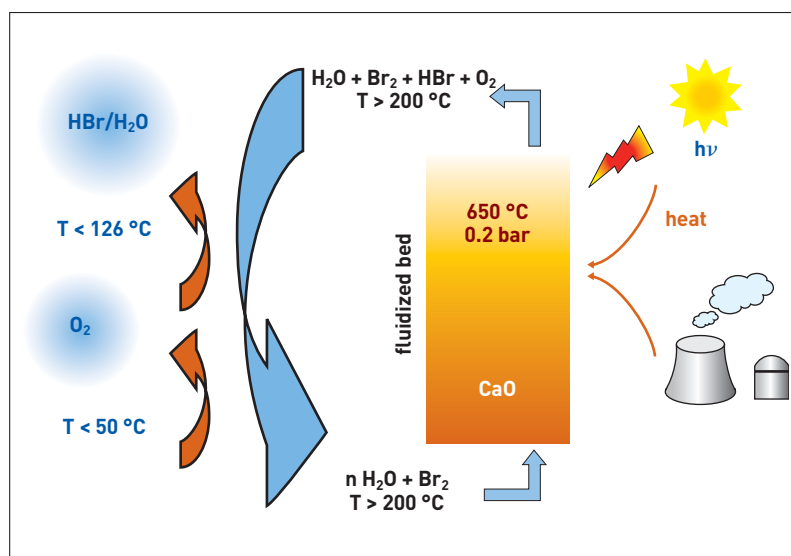
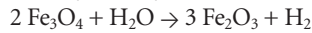


Figure 3. Example of a simplification of the Japanese process. Reactions (5) and (6) are carried out in a single fluidized-bed reactor.



tite (Fe_2O_3)-magnetite (Fe_3O_4) transitions allow hydrogen generation through reduction of water, in accordance with the following quite simple scheme:

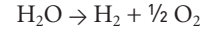


Simple trials carried out at CEA have demonstrated the chemical feasibility of this cycle, together with actual hydrogen production. Such oxidation-reduction cycles require as a rule very high temperatures, incompatible with those a nuclear reactor may yield, but which might yet be envisaged with a solar oven.

Net overall result: a simple dissociation reaction

Use of thermochemical cycles for hydrogen production has been widely investigated since the 1960s, since they offer the major benefit, theoretically, of lowering the temperature level required for water splitting, while ensuring release of oxygen and hydrogen in separate locations. Indeed, use of intermediate chemical reactants that might be termed - were this not an abuse of language - thermodynamic catalysts allows, for each of these reactants, some part to be covered, at lower energy levels, along the way required to achieve split-

ting of the water molecule, and thus release of hydrogen. The benefit of operating such cycles takes on its full significance if all of these chemical intermediates are truly fully regenerated over a production process, so that the net result may boil down to the simple dissociation reaction:

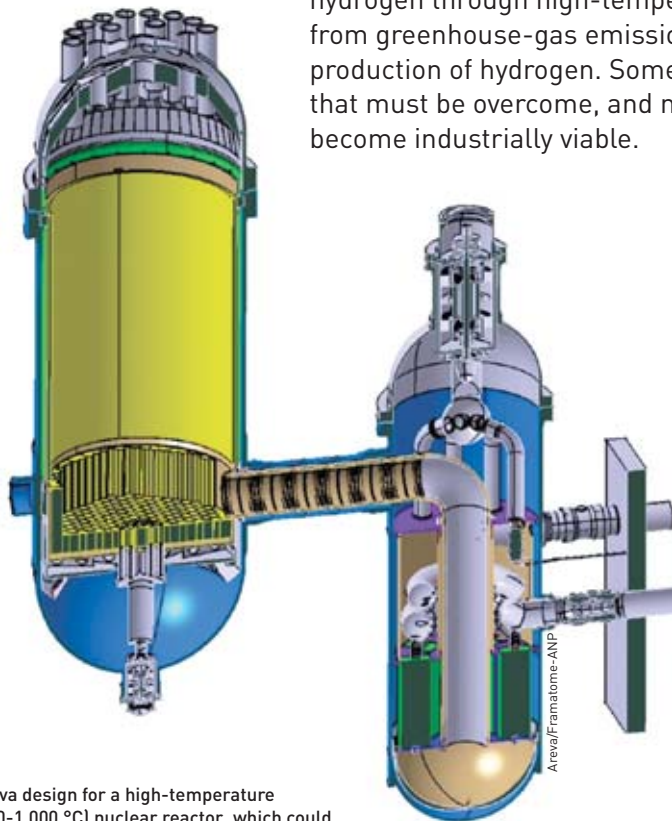


The ensemble of investigations carried out to date have enabled assessment of the feasibility of various cycles, on a laboratory scale rather than on an industrial scale. Initial findings for some of these cycles might be termed promising, were the ideal concept of reactant regeneration conformed to, and extrapolation to the industrial scale possible. Such are the challenges taken up by a number of teams at CEA. They will have the task of defining production systems making possible mass production of hydrogen at acceptable costs, while meeting a number of environmental criteria. The aim is to prepare for the options of tomorrow, that will condition the energy landscape for the coming decades.

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High-temperature electrolysis

Steam, heat and electricity. Such are the sole ingredients required to produce hydrogen through high-temperature electrolysis. This process, potentially free from greenhouse-gas emissions, is a serious candidate as regards mass production of hydrogen. Some technological barriers do still remain, however, that must be overcome, and major cost savings must be achieved, if it is to become industrially viable.



Areva design for a high-temperature (850-1,000 °C) nuclear reactor, which could be used for cogeneration of electricity (300 MWe) and hydrogen.

High-temperature electrolysis (HTE) consists in splitting the water molecule into **hydrogen** and oxygen, at temperatures between 700 °C and 1,000 °C. This process for mass production of hydrogen was the subject of some investigation, particularly in Germany in the 1980s. At the time, it was deemed to be not sufficiently economical, compared to competing technologies, and research work came to a stop. Since then, significant advances have occurred, making it possible to look to new developments.

Compared to conventional water electrolysis processes, high temperature brings benefits in three respects (see [Production by water electrolysis](#)). As regards energy requirements, first of all: the total energy to be supplied is smaller, owing to the greater kinetics of high-temperature reactions (3.1 kWh/Nm³ are required for HTE, as against 4.1 kWh/Nm³ for conventional electrolysis). Secondly, in terms of compactness: HTE allows operations at high current densities, resulting in large production capacity for a small volume (smaller by half). In terms of economics, finally: supplying a signi-

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).

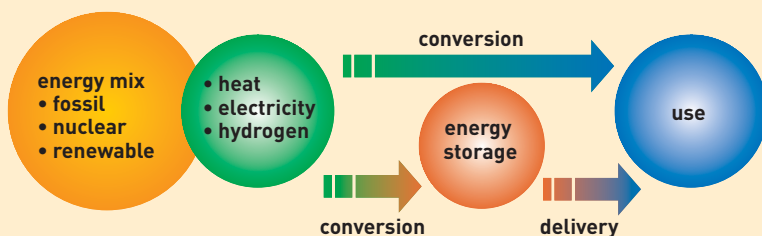


Figure 1. The energy scheme.

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.

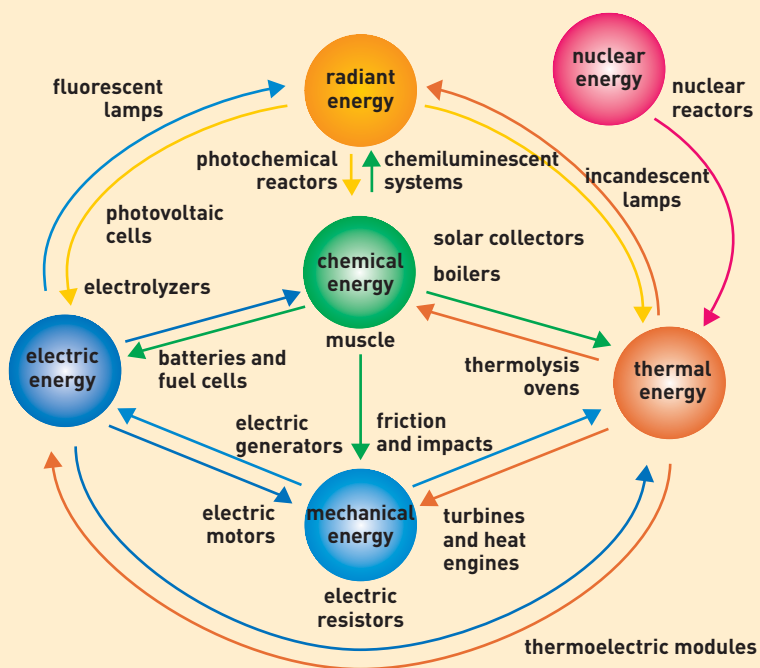
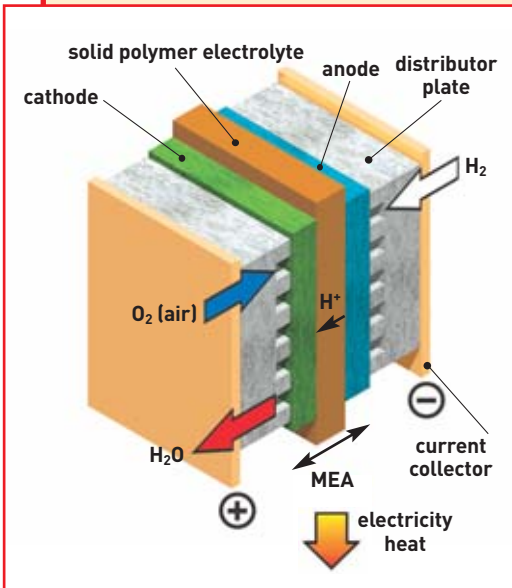


Figure 2. Conversions of the six main forms of energy, with a few examples of energy converters.

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/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.

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

