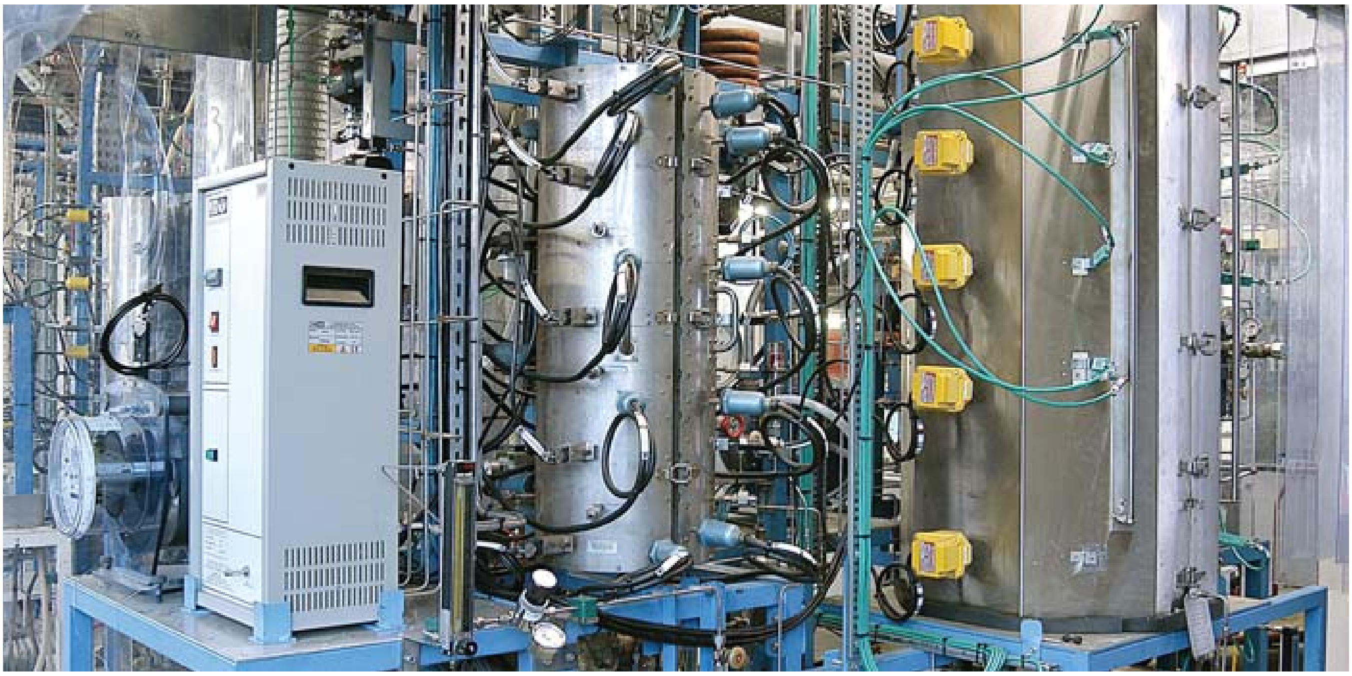
To achieve the switch from the status of mere chemical commodity to that of energy carrier, hydrogen is to experience an upheaval as regards its production methods. The goal? To eschew, ultimately, use of fossil energies, and, as of now, to avoid as far as possible release of greenhouse gases - though transitional solutions will probably be resorted to, still involving use of hydrocarbons. Just as long as it takes to bring to maturity innovative solutions (high-temperature electrolysis, thermochemistry, chemical transformation of biomass), and paths still at the fundamental research stage, such as production "from Sun and water," or water photolysis.

How is **hydrogen to be produced**?

Production from fossil fuels

If hydrogen is to become an energy carrier, it will most certainly be generated, initially at any rate, from fossil energies, as is already the case presently, for industrial applications of hydrogen.



IFP

Biopac pilot unit at Institut français du pétrole (French Petroleum Institute) producing high-purity hydrogen from ethanol to power a fuel cell.

The reason why **hydrogen** is so attractive is that this molecule - chemically active as a **reducer** - easily combines with atmospheric oxygen, yielding energy and water as sole end products. The other side of the coin is that hydrogen production, conversely, requires large amounts of energy, since it is based on hydrogen-rich molecules that are essentially stable, such as water (H_2O) or **methane** (CH_4).

In the past, industrial production of hydrogen from **hydrocarbons** has gone for the options showing the best returns, in economic terms. Unsurprisingly, the dominant feedstock in use is, by far, **natural gas**, having methane as it does for its main constituent. Other **fossil energies** are sometimes employed, since they also include some hydrogen, which may be generated by means of a partial oxidation reaction.

All such solutions taking fossil energies (or possibly **biomass**) as their starting point involve going through the synthesis gas stage, this being a mixture of carbon monoxide (CO) and hydrogen (H_2). However, optimum process configuration depends on the end use of that **synthesis gas**: produced in integrated units, this may go into production of ammonia and ammonia derivatives, or **methanol**, or, by means of the Fischer-Tropsch (FT) process, synthetic diesel fuels .

The dominant technologies in use nowadays for synthesis gas production from hydrocarbons are **steam reforming** (reaction 1), partial oxidation, and

autothermal reforming, a mix of these two processes, mainly used for the production of synthetic liquid hydrocarbon fuels.

The dominant technologies, to maximize output of hydrogen from available synthesis gas, are (reaction 2) water-gas shift, this effecting the conversion of CO into H_2 (and CO_2) by addition of water; and, for final purification purposes, purification through a molecular sieve (1) of the pressure swing adsorber (PSA) type, purification by methanation, and membrane purification.

Steam reforming of hydrocarbons

Steam reforming consists in transforming feeds of light hydrocarbons into synthesis gas (a mixture of H_2, CO, CO_2, CH_4, H_2O and further impurities) by reaction with steam over a nickel catalyst. This transformation occurs at high temperature (840-950 °C) and for a moderate pressure (of the order of 20-30 bars). This may be followed by various operations, leading to hydrogen production, and thus, further, to synthetic hydrocarbon fuel manufacture. In every case, the feed for a steam reforming unit may consist in natural gas (the reference feedstock), methane, or even naphtha. (2)

Technip/Syncrude

The steam reforming unit built by Technip for Syncrude Canada. Over a single line, this has an output of 223,000 **Nm³**/h hydrogen, and a further 75 MW electricity.

Steam reforming of natural gas

Natural gas is essentially methane. However, it must as a rule undergo desulfurization before being fed to the steam reforming unit. To maximize hydrogen output, the two main chemical reactions that need to be set up are synthesis gas production and CO conversion.

reaction 1:

1 $CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad \Delta H = 206 \text{ kJ mol}^{-1}$

reaction 2:

2 $CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41 \text{ kJ mol}^{-1}$

net result from the two reactions:

3 $\mathbf{CH_4 + 2\,H_2O \rightarrow CO_2 + 4\,H_2} \qquad \Delta H = 165 \text{ kJ mol}^{-1}$

The first reaction constitutes the reforming step proper. This is an **endothermic** reaction, and is characterized by an H_2/CO ratio of about 3. The second reaction corresponds to CO conversion (*water-gas shift*). This is a slightly **exothermic** reaction, and is more or less complete, depending on whether it is effected in one or two steps. Overall, the balance of the two reactions is endothermic. The two final steps consist in separation of CO_2 and hydrogen, then in elimination of the last remaining traces of impurities.

Partial oxidation of hydrocarbons

Partial oxidation may be carried out with a much broader range of compounds, from natural gas to heavy residues, and even coal. Economically speaking, processing of heavy feedstocks is justified when the additional capital outlay involved is compensated for by lower feedstock prices, as with petroleum coke, for instance. On the other hand, capital costs and operating conditions are more demanding.

Carried out at high temperature (1,200-1,500 °C) and elevated pressure (20-90 bars or more), in the presence of an oxidizer (air, or more commonly oxygen) and a temperature moderator (steam), partial oxidation of hydrocarbons leads to hydrogen production, as does steam reforming. By contrast, however, this reaction is exothermic, and occurs (as a rule) without a catalyst. The two main technologies, in industrial terms, are the Shell and Texaco processes.

Partial oxidation of vacuum residues

The two main reactions involved are synthesis gas production (simplified overall reaction shown as equation **6**) and carbon monoxide conversion (equation **2**b).

A typical vacuum residue (3) comprises over 50 carbon atoms. It is symbolized here as the hydrocarbon chain CnHm, corresponding to an H/C ratio of m/n.

reaction 1:

6 $C_nH_m + (n/2)\,O_2 \rightarrow n\,CO + (m/2)\,H_2$

$\Delta H = -36 \text{ kJ mol}^{-1}$ (pour $n = 1$, $m = 4$)

reaction 2:

2b $n\,CO + n\,H_2O \rightarrow n\,CO_2 + n\,H_2$

$\Delta H = -41 \text{ kJ mol}^{-1}$ (pour $n = 1$)

net result from the two reactions:

7 $C_nH_m + n\,H_2O + (n/2)\,O_2 \rightarrow n\,CO_2 + (n + m/2)\,H_2$

$\Delta H = -77 \text{ kJ mol}^{-1}$ (pour $n = 1$, $m = 4$)

The first reaction (taking place at a temperature in the 1,300-1,500 °C bracket) constitutes the partial oxidation step proper. This is an exothermic reaction, and is characterized by an H_2/CO ratio of about 0.75 (for an H/C ratio of around 1.5). It stands for the overall outcome from a large number of reactions, resulting in formation of CO and H_2, but equally of H_2O, C (soot) and CH_4. Mention may be made of a few of the secondary reactions:

$CO + 3\,H_2 \rightarrow CH_4 + H_2O$, $CO + H_2O \rightarrow CO_2 + H_2$ et $C_nH_m + n\,H_2O \rightarrow n\,CO + (n + m/2)\,H_2$.

It should also be noted that the synthesis gas generated in this manner often contains sulfur compounds. Indeed, the sulfur initially carried in the feed - in the case of heavy petroleum residues, in particular - is not separated upstream, and is thus also converted, mainly into H_2S and to a small extent into COS. Which is why these two compounds are to be found in the synthesis gas, which must consequently undergo desulfurization. Depending of the partial oxidation process adopted, this is effected before (Shell) or after (Texaco) the CO conversion step (reaction 2).

---

(1) Molecular sieve: a selective-adsorption material which, featuring pores of equivalent dimension to that of the molecules to be trapped, allows separation and capture of such molecules.

(2) Naphtha: the main raw material of petrochemistry.

(3) Residual product from the processing, in a *vacuum* distillation unit, of the residue from the *atmospheric* distillation of petroleum.

With respect to the first reaction, both technologies feature a burner, a heat-recovery stage (a steam-generator boiler in the Shell case, a quench-cooling scheme for the Texaco process), and a soot-scrubber stage. Depending on the process, the synthesis gas obtained varies with respect to water content and temperature. Regardless of the technology adopted, the second, CO conversion, reaction is virtually complete, and similar to that described in the steam reforming case.

The overall balance of the first two reactions is exothermic. Further, the maximum mass efficiency for hydrogen, relative to vacuum residue, is equal to:

$2*(n + m/2)/(12n + m) = 3.5/13.5 = 26\,\%$.

Autothermal reforming

The autothermal reforming process is probably the most interesting among coming developments in hydrogen production processes from hydrocarbons. Its main benefit lies in compensating (in a single fixed-bed reactor) for the endothermic reactions of steam reforming with the exothermic reactions of partial oxidation.

This process is arousing much interest for large-capacity applications, particularly with regard to the gas-to-liquids (**GtL**) path, since the CO/H_2 ratio may be adjusted prior to entry into the FT reactor. As in partial oxidation, oxygen cost is an important parameter in this case. Which is why extensive R&D efforts are being devoted to the membrane reactor concept. By means of ceramic membranes, which have yet to be validated in industrial production, it should be feasible to do away with the costly air-separation step. The GtL path is promising, since it provides a very-high-quality source as an alternative to conventional petroleum-derived hydrocarbon fuels, and equally an alternative to the liquefied natural gas path for the bringing on stream of gas deposits.

Hydrogen purification

The two main paths for hydrogen purification are purification over a molecular sieve of the PSA type, and purification by methanation. In the latter path, two distinct steps occur successively: decarbonation, and methanation itself. For the first step, consisting in removal of CO_2, ethanolamine or carbonate processes are employed. Residual CO_2 then only amounts to 0.005-0.1% by volume. In the second step, methanation of the residual CO and CO_2 is carried out. Final contents are then less than 0.001%, for a final hydrogen purity of 95-98%.

CO methanation:

4 $CO + 3\,H_2 \rightarrow CH_4 + H_2O(4) \quad \Delta H = -\,206\ \mathrm{kJ\ mol^{-1}}$

CO_2 methanation:

5 $CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \quad \Delta H = -\,165\ \mathrm{kJ\ mol^{-1}}$

The PSA path does not involve a decarbonation step. In other words, hydrogen purification (by **adsorption** of impurities on beds of molecular sieves) is carried out directly on synthesis gas - this having a content of 65-70% hydrogen - once CO conversion is effected. Hydrogen purity achieved, after passing through the PSA unit, is of the order of 99.9%.


Air Liquide/Voets and Van Leeuwen

Unit for the cogeneration of hydrogen and carbon monoxide operated by the Air liquide Group in Rotterdam (The Netherlands).

New economies of scale

On such well-established technological foundations, mass production of hydrogen has developed. The requirement, however, to improve the offer by achieving cost reductions continues to bear heavily. The major industrial gas producers have thus resorted to outsourcing, to a number of pooled resources, to meet the demand from their customers. The latter are supplied by pipeline, from large production units.

If hydrogen is to become, on the other hand, an **energy carrier**, it will certainly be generated, initially at any rate, from fossil energies, essentially for economic reasons. Nevertheless, such production will have to go hand in hand with CO_2 capture and geological storage, to restrict the impact of this output on climate evolution.

> **Colin Baudouin, Stéphane His**
and **Jean-Pierre Jonchère**
Institut français du pétrole (IFP)
Rueil-Malmaison (Hauts-de-Seine département)

FOR FURTHER INFORMATION:

S. His, *L'Hydrogène : vecteur énergétique?* Fiche Panorama 2004:
http://www.ifp.fr/IFP/fr/fichiers/cinfo/IFP-Panorama04_11-HydrogeneVF.pdf

J.-P. Arlie, S. His, with contributions from CEA, Total and the French Hydrogen Association (AFH2), "Étude technico-économique prospective sur le coût de l'hydrogène", *Mémento de l'hydrogène*, AFH2, December 2003:
http://www.afh2.org/archive/etude_eco_11_2003.pdf

J.-P. Jonchère, " Production d'hydrogène à partir de combustibles fossiles", *Mémento de l'hydrogène*, AFH2, October 2003:
http://www.afh2.org/archive/fiche_3_1.pdf

G. Bourbonneux, chapter on hydrogen production ("Production d'hydrogène"), in P. Leprince, *Procédés de transformation*, Technip, 1998.

C. Raimbault, "L'hydrogène industriel: synthèse, purification", *L'Actualité chimique*, May 1997.

"L'hydrogène, maillon essentiel du raffinage de demain", *Pétrole et Technique*, No. 390, September-October 1994.

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).

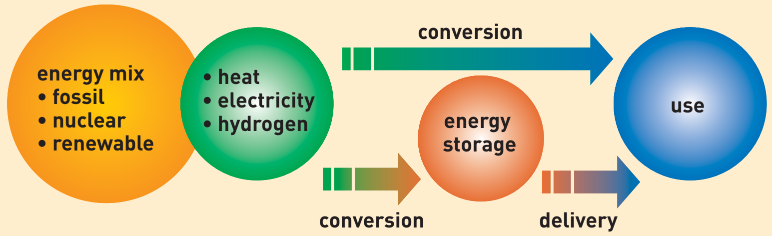


Figure 1.
The energy scheme.

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.

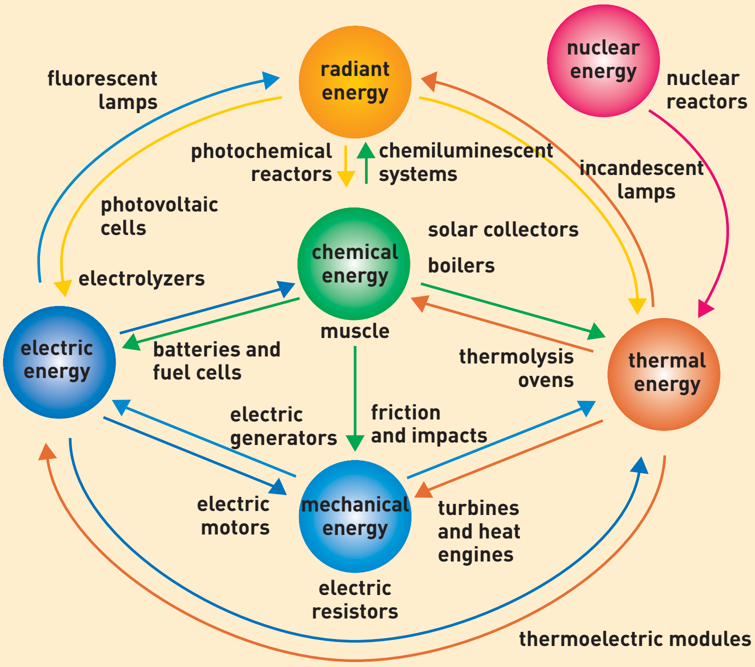
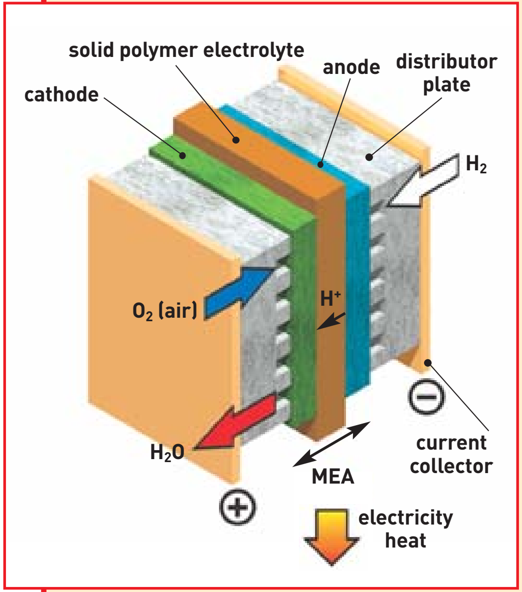


Figure 2.
Conversions of the six main forms of energy, with a few examples of energy converters.

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^2. 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).

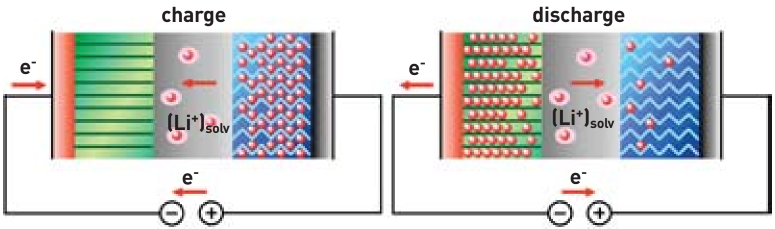
In the early 1990s, with the growth in the portable device market, two new technological pathways emerged: nickel–metal hydride storage batteries, and lithium storage batteries (see Box on *Operating principle of a lithium storage battery*). The first-mentioned pathway, involving a nickel-based positive 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.

Operating principle of a lithium storage battery

1



$$\langle H\rangle + Li^+ + e^- \longrightarrow \langle HLi\rangle$$
$$\langle MLi\rangle \longrightarrow \langle M\rangle + Li^+ + e^-$$

$$\langle HLi\rangle \longrightarrow \langle H\rangle + Li^+ + e^-$$
$$\langle M\rangle + Li^+ + e^- \longrightarrow \langle MLi\rangle$$

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.