Storage of **intermittent** energies

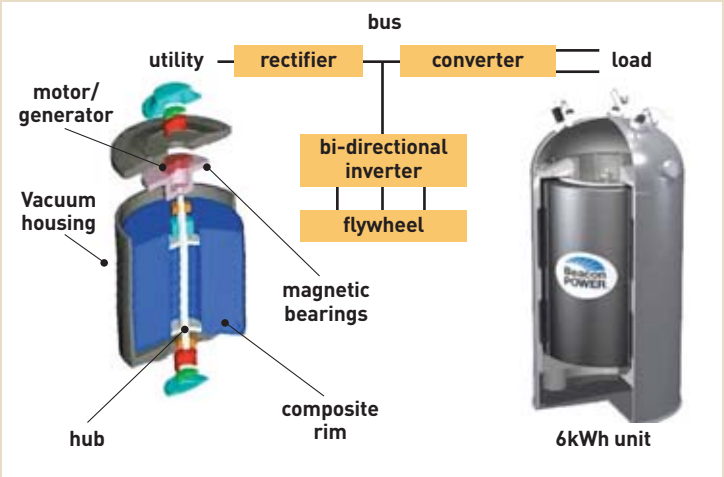
The growth in renewable energies, with respect in particular to integration into the distribution grid, entails new energy storage requirements. Best-suited technologies vary, depending on applications.

F. Vigouroux/CEA

GENEC staff, at CEA/Cadarache, putting batteries through charge–discharge cycles, thus simulating a variety of utilizations, controlling efficiency and investigating component aging.

Flywheel storage 1

Modern flywheel energy storage systems comprise a massive rotating cylinder, supported by magnetic levitation, coupled to a motor/generator. Maintenance requirements for such systems are slight, and longevity is considerable (> 20 years). A device such as that shown here (2 kW, 6 kWh) is a low-cost system for telecommunications applications. Large installations, comprising 40 ¥ 25-kW/25-kWh systems, for instance, have the capability to store 1 MW, which may be delivered in 1 hour.



Beacon Power

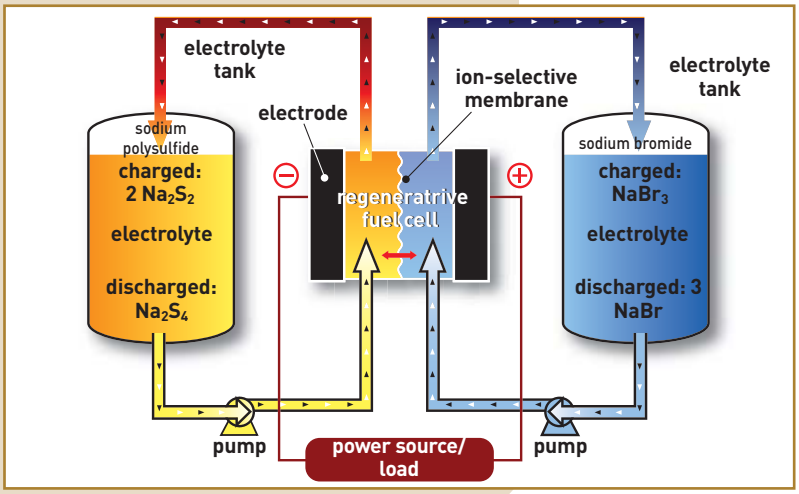
Storage, the weak point on the energy scene, is nonetheless one of the keys to the rise of **renewable energies**. When the energy source is intermittent, and utilization occurs in a remote location, which may not be connected to a distribution grid, storage, of course, is a requisite. Such a requirement is not so obvious, when the source is connected to the grid – as is the case for wind power or **photovoltaics**, in industrialized countries – however storage will be found to be indispensable in the future. Indeed, with the liberalization of the energy market, numerous decentralized sources, mostly of renewable, intermittent origin, will be connected to the grid, and may give rise to imbalances on the network. To remedy this disadvantage, storage, and intelligent management of these diverse sources are the best solution.

Currently, electricity production is highly centralized. The balance between consumption and production is primarily ensured by daily, and seasonal, predictive management of requirements, but equally, when basic production is found to be insufficient, by calling on complementary resources, including hydroelectric and thermal power stations. Such plants in effect also use a form of stored energy: water, for pumped-storage plants, or **fossil energies**, for thermal plants.

Optimum type of storage is closely related to nature of application and type of production: a small system in a remote location will need to store energy

The high potential of redox batteries 2

Redox batteries are electrolyte-flow batteries, in which the chemical compounds involved are in solution (see Figure). A number of associations involving bromine have been looked into: with zinc, sodium, vanadium, and, most recently, sodium polysulfide. The electrochemical reaction, occurring through a membrane inside the cell, is reversible (charge and discharge). Through use of large tanks, and coupling of many cells, large amounts of energy may be stored, and delivered. By way of example, Regenesys Technologies constructed a storage system using this process, having a 15 MW–120 MWh capacity, in the United Kingdom in 2003; however this technology nowadays is dominated by all-vanadium-based electrochemistry. Overall electrical efficiency for this type of storage stands at around 75%.



of a few tens of watt–hours (Wh), while a large power station will call for storage of several megawatt–hours (MWh). Consequently, the storage technologies meeting the relevant technical and economic criteria will necessarily be of diverse kinds. Technologies abound, however comparison between them is made difficult, among other considerations, owing to the diversity of the stages of maturity they have reached.

In this respect, CEA took on coordination of a European thematic network, INVESTIRE, having the set goal of comparing a variety of storage technologies, according to their utilization, with a view to evaluate performance, costs, and environmental impact. This network, including as it did research centers, manufacturers, small and medium enterprises and non-profit associations, brought together 33 partners.

Nine technologies were selected for that survey: lead–acid batteries, lithium batteries, supercapacitors, nickel-based batteries (NiCd, NiMH), combined electrolyzer–hydrogen storage–fuel cell systems, flywheels (see Box 1), redox batteries (see Box 2), compressed air, and metal–air batteries.

Applications were classified into four categories: (1) low-power applications in remote locations, mainly for the purposes of powering sensors or emergency call boxes; (2) medium-power applications in remote locations (personal home electric power systems, village power supply); (3) grid-connected applications, with peak leveling; and (4) power quality control (see Table).

To allow performance comparisons between the various technologies involved, for the categories thus defined, a schedule of 22 criteria was drawn up, including, e.g., cost, energy efficiency, energy density, specific power, number of cycles, recyclability, and ease of determining system health. The energy efficiency of each technology may thus be compared

category	1	2		3	4	
autonomy	10–30 days	1–10 days		0.25–10 hours	2 seconds–10 minutes	
typical discharge current	< 0.01 * C_{10} (1)	0.02 * C_{10}–0.1 * C_{10}		0.25 * C_{10}–2 * C_{10}	100 * C_{10}	
typical charge current	0.05 * C_{10}	0.05 * C_{10}–0.2 * C_{10}		0.2 * C_{10}–0.5 * C_{10}	100 * C_{10}	
power range	1 Wh–100 kWh	10 Wh–1 MWh		10 kWh–1 MWh	1 Wh–1 MWh	
typical number of full cycle equivalents per annum	20	50–100	100–400	300–1,000	3,000	100,000
per cycle	5%	10–30%		50–80%	50–80%	
electricity generation	photovoltaic	hybrid, with diesel generator	photovoltaic	photovoltaic wind power		
typical applications	sensors, data recorders, telecommunications	heavy power demand: rural electrification of the village type	light power demand, IES type (individual electrification system)	load leveling	pump start-up	grid current quality control units

(1) *C_{10} denotes the maximum amount of energy that may be drawn from a storage unit in 10 hours, at constant discharge current.

Table.
Specifications for the four categories covering storage technologies, according to applications.

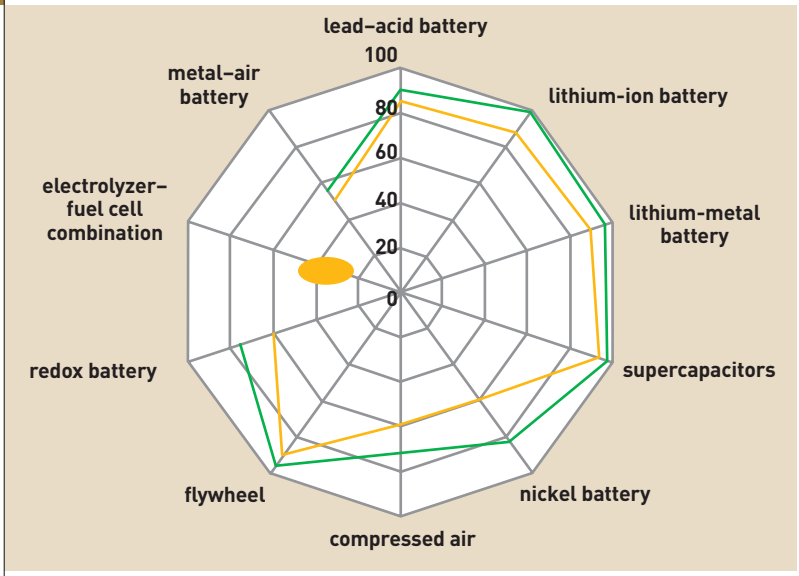


Figure 1.
Example diagram showing the energy efficiency of each technology for a given application category.

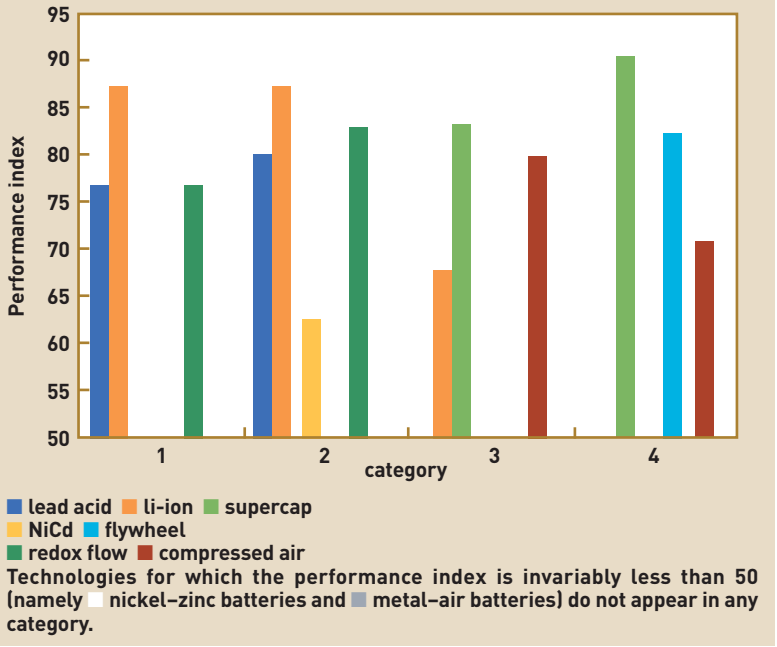


Figure 2.
Performance indexes for the nine storage technologies, according to each of the four application categories.

(see Figure 1). The ensemble of these criteria allows evaluation of a performance index, according to the four categories set out (see Figure 2).

Some general trends may be identified, as a result of this review. (1)

For the low-power stationary application category, the crucial point is achieving as low as possible self-discharge. (2) On the sole basis of the technical criteria alone, lithium-ion then turns out to be the best candidate.

For the small system (a few kilowatt–hours), remote location, intermittent energy-based category, the crucial criterion is autonomy; lead–acid batteries provide the best tradeoff between cost and performance. Lithium-ion delivers higher performance, at a cost however that is still too high. For larger requirements (several hundred kilowatt–hours), lead–acid still leads lithium, while alternative solutions either exhibit poorer performance, or involve excessive cost: compressed air (excessive self-discharge), fuel cells (very high cost, poor energy efficiency), redox batteries (maintenance costs).

In the third category, for peak power leveling, involving large energy storage capacities (several megawatt–hours), compressed air and redox batteries are the most suitable, with a major advantage to the former, in terms of cost. These technologies, however, have yet to be proven on the ground.

For the fourth category, for power quality, the crucial criteria are ability to deliver energy, and **cycling**. Flywheels and supercapacitors are the best-suited technologies, together with lithium-ion batteries.

Of the nine technologies considered, lead–acid batteries meet the technical criteria for all categories, but are disadvantaged, however, by their limited durability, and poor reliability. Nickel-based batteries and metal–air batteries are never ranked in lead positions, for the criteria selected (poorer performance, slightly higher costs). Fuel cell–hydrogen systems are disadvantaged by their lack of maturity. Finally, a number of technologies not considered by this review have the ability to provide solutions for intermittent energy storage: hydropower storage, heat storage, for large-scale applications, superconducting magnetic energy storage (SMES) for smaller scales.

To meet the future requirements of increasingly decentralized production, storage, in the short and medium term, will call for technological improvements. Lithium-ion batteries exhibit outstanding performance, however the cost involved is prohibitive for off-grid system applications in developing countries. Recycling, and end-of-life disposal of such batteries call for R&D efforts.

Lead–acid batteries still represent the best cost–performance tradeoff, remaining a weak point, however, with respect to off-grid, remote location systems; improved performance, in terms of durability, must be developed, if they are to meet more effectively the requirements of populations still cut off from access to electricity. A number of research efforts are being conducted at CEA by GENEC (Service Photovoltaique et stockage: "Components for PV and storage" group), in these areas, with support from **Ademe** and manufacturers in France and other countries.

For grid-connected applications, in the medium term, requirements are set to increase steadily: the most suitable technologies (redox batteries, compressed air, supercapacitors, flywheels) have reached varying stages of maturity, and may yet be optimized in terms of cost, reliability, and efficiency.

> **Pascal Couffin** and **Marion Perrin**
Technological Research Division
CEA Fontenay-aux-Roses and Cadarache Centers

(1) A major part of the findings may be found on the website: http://www.itpower.co.uk/investire/index.html

(2) Self-discharge is that part of the energy initially held in the storage unit which is dissipated over a given time span, in the absence of any use.

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).

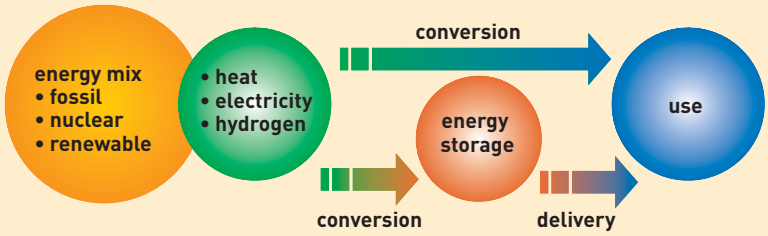


Figure 1.
The energy scheme.

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.

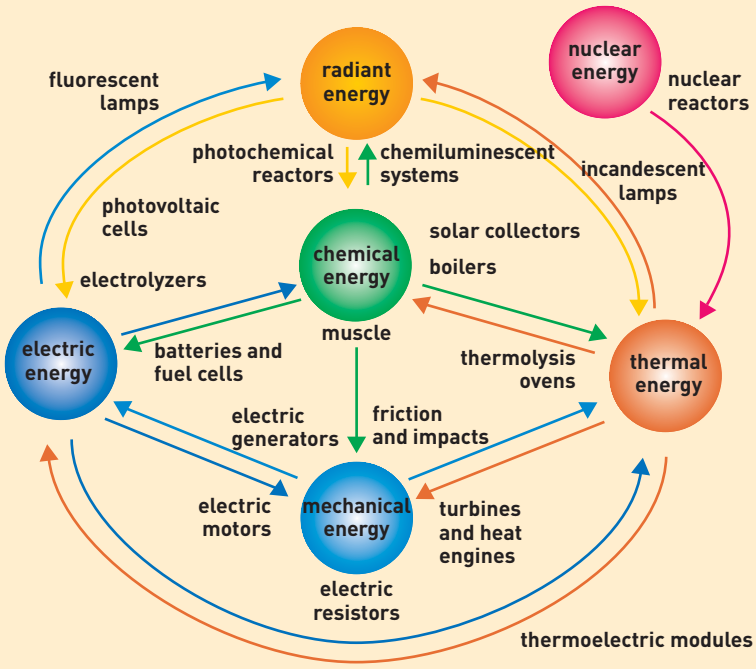
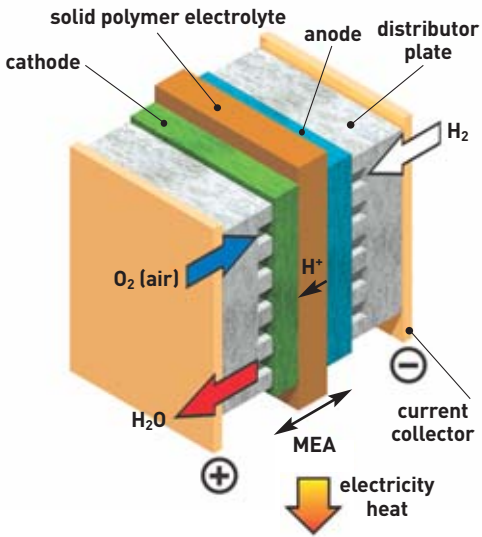


Figure 2.
Conversions of the six main forms of energy, with a few examples of energy converters.

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).

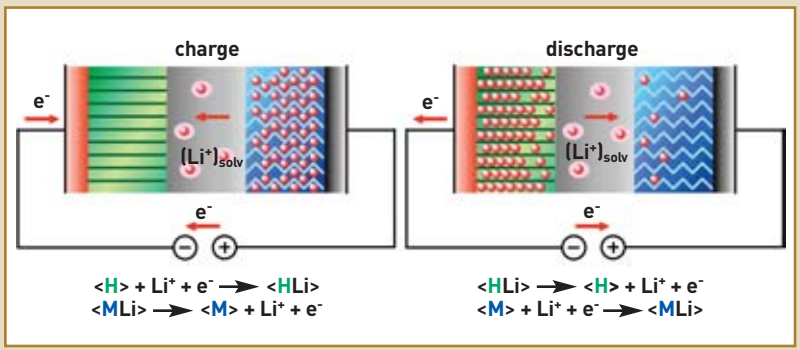
A storage battery, whichever technology is implemented, is essentially defined by three quantities. Its **gravimetric** (or **volumetric**) **energy density**, expressed in watt–hours per kilogram (Wh/kg) (or in watt–hours per liter [Wh/l]), corresponds to the amount of energy stored per unit mass (or 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.

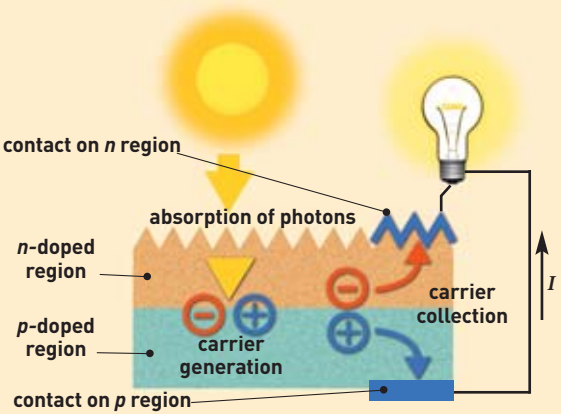
Operating principle of a lithium storage battery



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.

D How does a photovoltaic solar cell work?

The photovoltaic effect used in solar cells allows direct conversion of light energy from the Sun's rays into electricity, by way of the generation, and transport inside a semiconductor material, of positive and negative electric charges, through the action of light. This material features two regions, one exhibiting an excess of electrons, the other an electron deficit, respectively referred to as *n-type doped*, and *p-type doped*. When the former is brought into contact with the latter, excess electrons from the *n* material diffuse into the *p* material. The initially *n*-doped region becomes positively charged, and the initially *p*-doped region negatively charged. An electric field is thus set up between them, tending to force electrons back into the *n* region, and holes back into the *p* region. A junction (so-called *p-n* junction) has been set up. By placing metallic contacts on the *n* and *p* regions, a diode is obtained. When the junction is illuminated, photons having an energy equal to, or higher than, the width of the forbidden band, or band gap, yield their energy to the atoms, each photon causing an electron to move from the valence band to the conduction band, leaving behind it in turn a hole, also able to move around the material, thus giving rise to an electron-hole pair. Should a load be positioned at the cell's terminals, electrons from the *n* region will migrate back to the holes in the *p* region, by way of the outside connection, giving rise to a potential difference: an electric current passes (see Figure).



The effect thus involves, basically, the material's semiconducting properties, and its doping, to improve conductivity. Silicon, now used in most cells, was selected for the presence of four valence electrons in its outermost shell (column IV of the Mendeleyev periodic table). In solid silicon, each atom - termed a tetravalent atom - is bound to four neighbors, and all electrons in the outermost shell participate in the bonds. Should a silicon atom be substituted for by an atom from column V (a phosphorus atom, for instance), one of its five valence electrons is not involved in the bonds; as a result of thermal agitation, it soon moves to the conduction band, thus becoming free to move through the crystal, leaving behind it an immobile hole, bound to the doping atom. There is electron conduction, and the semiconductor is designated as an *n-type doped semiconductor*. If, on the other hand, a silicon atom is substituted for by an atom from column III (boron, for instance), carrying three valence electrons, one electron is missing, if all bonds are to be maintained, and an electron may quickly move in to fill this gap, taking up the vacant orbital, as a result of thermal agitation. A hole thus arises in the valence band, contributing to conduction, and the semiconductor is said to be a *p-type doped semiconductor*. Atoms of elements such as boron or phosphorus are thus doping agents in silicon. Photovoltaic cells are assembled into modules.

Note: In *Organic photovoltaic cells: towards an all-polymer path...*, you will find the operating principle of organic photovoltaic cells (Box, p. 122).

Operating principle of an organic photovoltaic cell

Following absorption of photons by the polymer, bound electron-hole pairs (excitons) are generated, subsequently undergoing dissociation. Owing to inherent limitations in organic materials (exciton lifetime, low charge mobility), only a small fraction of photon-generated electron-hole pairs effectively contribute to the photocurrent. One of the main ideas is to achieve volume distribution of the photogeneration sites, to enhance exciton dissociation. This approach is based on increasing junction surface area, through deployment of an interpenetrating network of the donor-acceptor (D-A) type, effecting transport of holes (P^+) to the anode (indium-tin oxide [ITO]), and of electrons (e^-) to the metallic cathode (made e.g. of aluminum [Al]). While quantum separation efficiency, for photoinduced charges in systems associating a semiconducting polymer (of PPV or polythiophene type) with a fullerene derivative (PCBM), is thus close to unity, the challenge now is to restrict recombination and trapping processes limiting charge transport and collection at the electrodes, to improve overall device efficiency, this currently still being low (less than 5%). The rise of the pathway is also heavily dependent on mastery and understanding of cell aging mechanisms, but equally on mastery of thin-film technologies, to achieve protection of the device against atmospheric oxygen and water vapor.

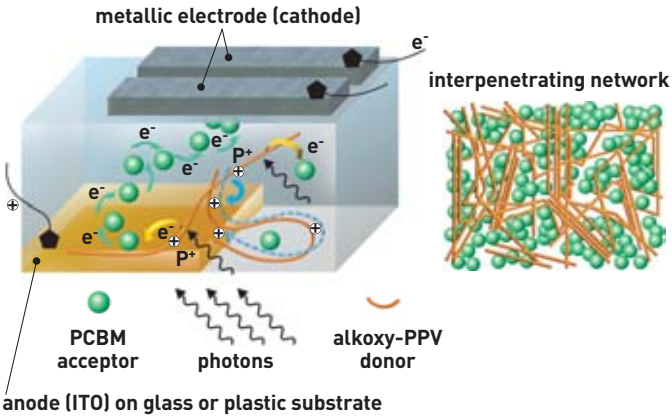


Figure from a presentation by S. Sariciftci (www.lios.at)

The blue dotted line shows the trajectory of holes inside the material.