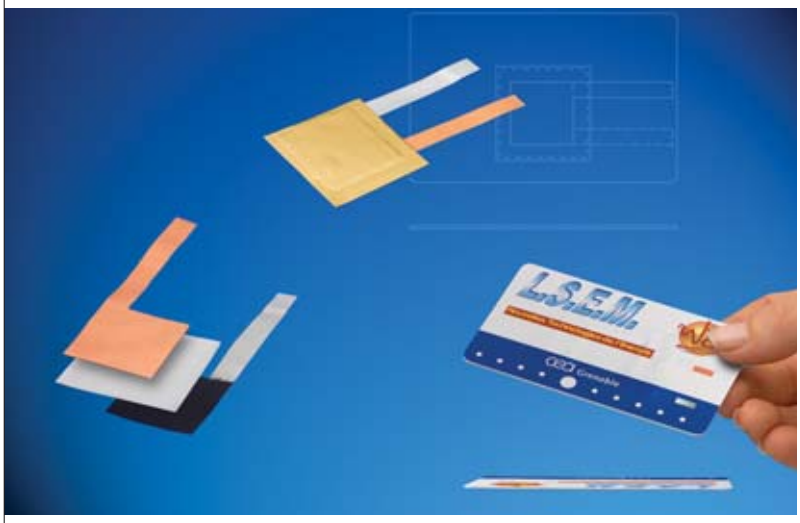
New paths in **lithium storage batteries** and **battery electrolytes**



CEA/Artechnique

Ultrathin components of a Li-ion storage battery, prior to integration into a smart card; components developed by LITEN and LETI at CEA/Grenoble.

Following the considerable growth seen in lithium storage batteries, accompanying the rise of portable devices, CEA research workers are developing, together with partners in industry and academe, original, low-cost technologies, and are investigating novel families of battery electrolytes.

Two new generations of lithium storage batteries

CEA is bringing out novel, low-cost lithium-ion storage batteries, affording high inherent safety, both for high capacities, and high power outputs.

In the years 1990–95, mainly owing to the impetus from Japanese portable device manufacturers (video-cameras, computers, then-nascent mobile telephony), two novel electricity storage pathways emerged, representing a breakthrough, compared to conventional technologies. Development of ***nickel–metal hydride*** **storage batteries**, first, followed by that of ***lithium storage batteries*** (see Box1), brought about an upheaval in the then-existing offer, taking most conventional manufacturers by surprise (see Box E, **Storage batteries, cells and batteries: constantly improving performance**).

Revolutionizing the status quo: the Japanese industry

The rise of these technologies, and mainly of the second one, further benefited, around the mid-1990s, from the sudden, and huge, expansion in the mobile telephony market (+ 1% per month in 2000, a 70% penetration rate in Europe in 2003, as against just a few percent in 1996), bringing strong demand for high energy densities, in a small volume. Thus, the market for lithium batteries topped 4.5 billion euros in 2000, while manufacturers from Japan (Sony, Sanyo, Matsushita) and Korea (LG, Samsung) take the lion's share (70%) in a market that is now over 95% dominated by companies from Asia (Japan, Korea, China), to the detriment of European firms, but equally of US businesses, these being virtually kept out of the main market, namely power supply for portable devices. A number of European initiatives are nonetheless emerging, concerning development of particular lithium battery pathways, affording specific benefits, compared with the ***lithium-ion*** pathway currently developed in Japan, and more broadly in Asia. Investigations carried out at CEA/Grenoble are being conducted in partnership with such manufacturers as SAFT, Batscap (Bolloré Group), Tadiran, and academic organizations, including LEPMI, ICMCB, and IMN. (1)
Concurrently, CEA is developing, again with a manufacturer, lithium microsources, with processes brought in from microelectronics, a first generation being brought out in 2003 (see Box 2).

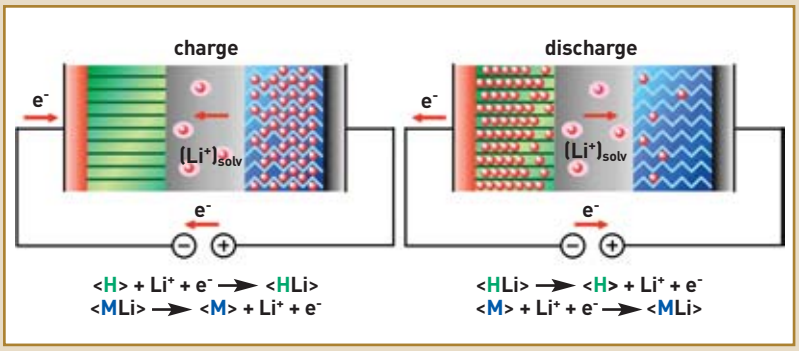
Two innovative, inexpensive solutions

Current lithium-ion storage batteries, based as they are on technology of the cobalt–graphite type, are by far those exhibiting the best performance, in terms of gravimetric and volumetric **energy density**, these stan-

(1) LEPMI: Materials and Interface Electrochemistry and Physicochemistry Laboratorry (Laboratoire d'électrochimie et de physico–chimie des matériaux et des interfaces); ICMCB: Solid-State Chemistry Institute, Bordeaux (Institut de chimie de la matière condensée, Bordeaux); IMN: Jean-Rouxel Materials Institute, Nantes (Institut des matériaux Jean-Rouxel, Nantes).

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.

ding, respectively, at 150–170 Wh/kg, and over 400 Wh/l (see Table).

However, target requirements for energy storage, in a sustainable development perspective, entail *very low battery* cost, at most €100–200/kWh, well below current prices for lithium-ion systems, standing at a minimum €500/kWh, for Chinese batteries.

CEA/Grenoble has registered a number of patents covering development of novel, low-cost materials, such as iron phosphate and titanium oxide. The organization is thus able to offer new generations of low-cost lithium-ion batteries, affording high inherent safety, one exhibiting *high energy density* or *high capacity*, the other delivering *high power*.

The high-capacity pathway

For photovoltaic applications, lead–acid storage batteries are the systems used in the overwhelming majority of cases, owing to their low cost (< €150/kWh), placing them well to the fore, compared to other technologies (NiCd, NiMH and Li-ion). Their electric performance, however, does not allow them to exhibit longevity matching that of the associated solar panels (> 10 years). CEA's Miniature Energy Source Laboratory (LSEM: Laboratoire des sources d'énergie miniatures) is proposing to use the new $LiFePO_4$–graphite technology, which in the short term involves an objective cost lower than €300/kWh, bringing four benefits, compared to lead–acid technology: higher durability, very low self-discharge, lighter systems, by a factor 5–6, and no maintenance. The materials cost for a lithium-ion battery (some 80% of battery cost) is impacted to 25% by the cost of cobalt, and 25% by the cost of safety features, required, in particular, because of the high reactivity exhibited by that compound at high temperature. A cost reduction by over 30% may be achieved with the new generations of storage batteries, through use of iron phosphate, as a result, on the one hand, of the objective cost of this compound (one third that of cobalt), and, on the other, of dispensing with safeguards, owing to its high chemical and electrochemical stability.

The main barrier, as regards this family of compounds, is low electron conductivity, raising issues with use in batteries (see Box 3). Through optimization of composition and fabrication, CEA/Grenoble was able to stabilize iron phosphate performance at ambient temperature (165 mA/g at 23 °C) (see Figure 1).

	Pb	NiCd	NiMH	Li-ion
gravimetric energy density (Wh/kg)	30	30-50	70-80	150-170
charge time (minutes)	300-600	180-300	180-300	90-120

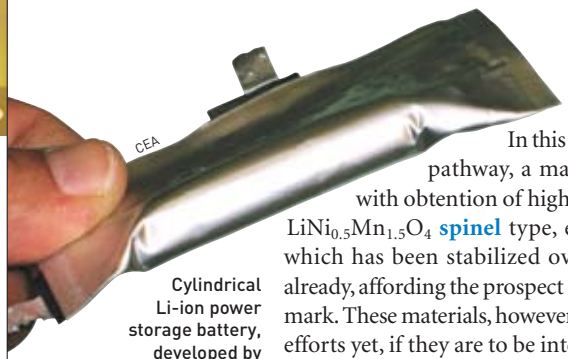
Table.
Comparative gravimetric energy densities and charge times for the main storage battery families (target values for the power Li-ion pathway).

The joint HEF–CEA laboratory: microbatteries using microelectronics processes

2

CEA and manufacturer HEF (Hydromécanique et frottement) opened in April 2003 a joint laboratory. This laboratory enables transposition of HEF's microbattery technology to the area of microelectronics, through developments in miniaturization and a collective fabrication process compatible with microelectronics processes.

Initial production of microbatteries on silicon wafers achieved the expected performance, of 100 µAh/cm² at 2–2.5 V. Current developments are addressing reliability of semi-industrial fabrication, with as low as possible reject rate, and improving performance by a factor 2–3. This technology allows integration of this type of storage battery directly onto an ASIC (application-specific integrated circuit), e.g. to power, in the near future, smart-card security systems.



Cylindrical Li-ion power storage battery, developed by CEA/Grenoble.

In this "high-capacity, low-cost" pathway, a major breakthrough came with obtention of high-voltage materials of the $LiNi_{0.5}Mn_{1.5}O_4$ **spinel** type, exhibiting performance which has been stabilized over more than 50 cycles already, affording the prospect of passing the 240 Wh/kg mark. These materials, however, do require further R&D efforts yet, if they are to be integrated into commercial storage batteries, with the ability to withstand 500 cycles.

The high-power pathway

For the **hybrid vehicle** application, constraints for batteries are highly demanding, in terms of cost and performance, with respect to power. Currently, systems being developed range from supercapacitors, having the ability to deliver a large amount of energy over a relatively short time span, to conventional lithium-ion solutions. For the time being, none of these technologies fully meet target specifications, owing to their price, in particular. The tech-

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).

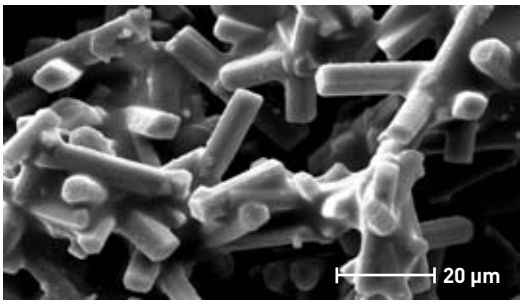
A storage battery, whichever technology is implemented, is essentially defined by three quantities. Its **gravimetric** (or **volumetric**) **energy density**, expressed in watt-hours per kilogram (Wh/kg) (or in watt-hours per liter [Wh/l]), corresponds to the amount of energy stored per unit mass (or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

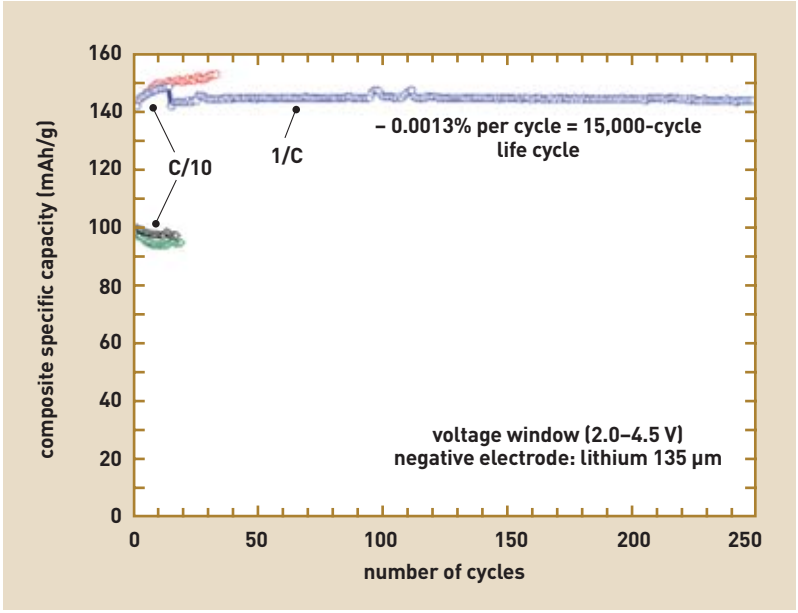
(1) One cycle includes one charge and one discharge.

Figure 1.
Stability of the $LiFePO_4$ compound, under nominal 1 C regime (charge 1 h–discharge 1 h). Losses: < 0.002% per cycle. The four curves correspond to two distinct synthesis conditions, for which they evidence impact on material performance.
Note: A current regime of C/*n* denotes a charge current such that battery nominal capacity, designated as C (in Ah), will be charged in n hours. Thus, for a 10-Ah battery, C/10 corresponds to a 1-A charge current allowing charge to be achieved in 10 hours. For fast charges, 10 C, in this case, denotes a 100-A charge current theoretically allowing charging in 1/10 hour, i.e. 6 minutes.



CEA

Photograph under scanning electron microscopy of a form of $LiFePO_4$ prepared by hydrothermal synthesis.



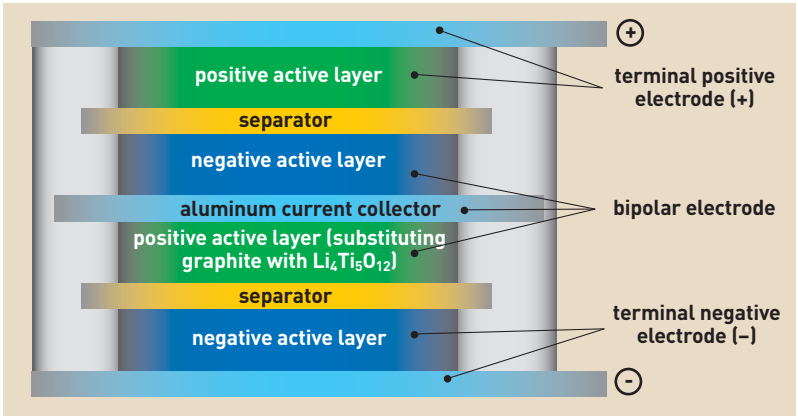


Figure 2.
Principle schematic of a 5-V storage battery using the bipolar technology patented by CEA.

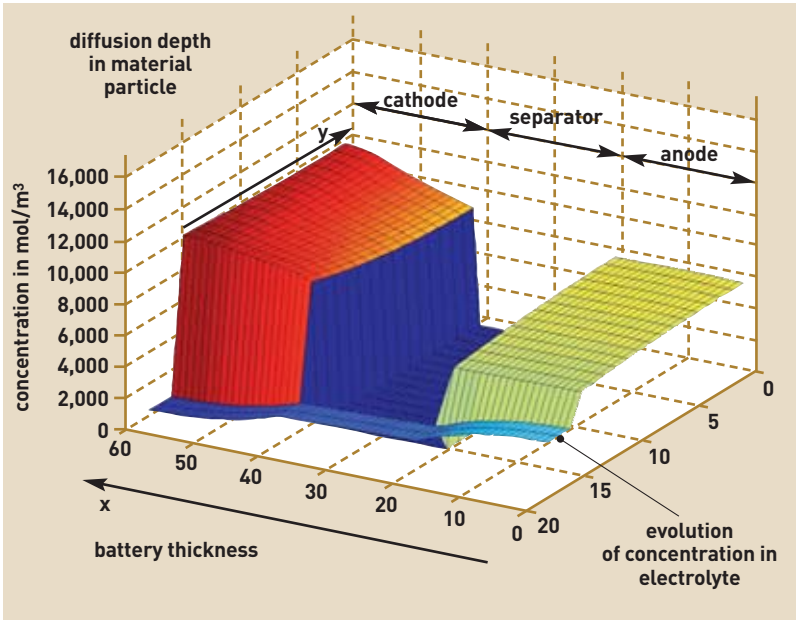


Figure 3.
Example of graphic printout from the Modal program, developed by CEA/Grenoble, showing the various lithium concentration profiles, both in the electrolyte and in the electrode active materials (battery thickness and diffusion depth in µm)

nology advocated by CEA/Grenoble combines a number of major innovations: introduction of iron phosphate at the positive **electrode**, to achieve lower costs, and ensure guaranteed safety, introduction of a titanium oxide at the negative electrode, substituting for graphite, to enable fast full charge – over less than a few minutes – and development of a bipolar technology allowing drastic reductions as regards connectors, this being a major brake on high-voltage system performance (see Figure 2). The latest findings (see Figure 3) show the stability of the storage battery, when subjected to 2,000 fast charge (70% charge capacity in 3 minutes)–fast discharge (2 minutes) cycles.

Developments concerning power storage batteries further rely on modeling their operation. For such purposes, the Modal computation program (code) has been developed, and is even now enabling prediction of the behavior of new generations of storage batteries, depending on such parameters as electrode thickness or **electrolyte** salt concentration (see Figure 3).

Prototypes exhibiting capacities ranging from 1 Ah to 5 Ah have been constructed for each of these technological pathways. Target applications (medicine, portable tools, smart cards, defense, space…) range far wider than photovoltaics and hybrid vehicles.

An initial storage battery based on the $LiFePO_4$–$Li_4Ti_5O_{12}$ couple, accommodating charging to 60% capacity in 7 minutes, has been constructed by CEA, the organization developing, at the same time, a novel polymer electrolyte favoring performance in terms of power, and allowing a 30% gain, compared to current commercial separators. Comprehensively, these lithium-ion technology developments have resulted in some ten patents or so being registered in one year.

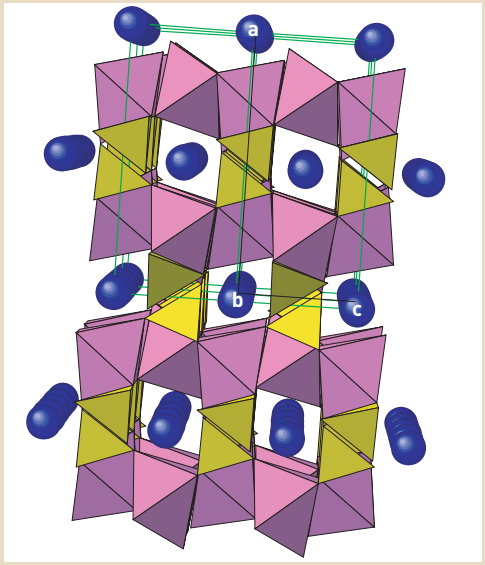
> Sébastien Martinet
Technological Research Division
CEA Grenoble Center

$LiFePO_4$, a positive electrode active material for the future

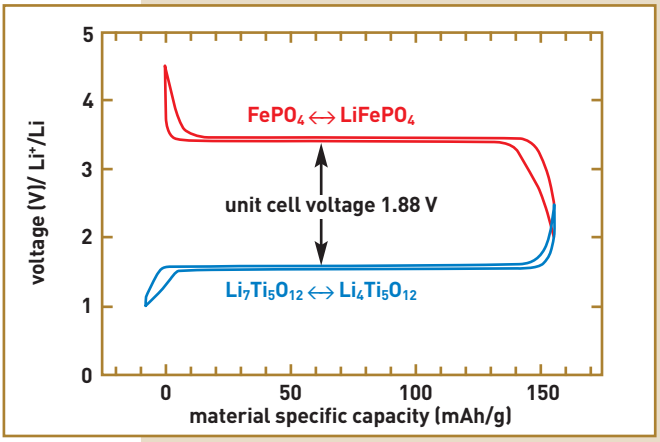
3

Lithium-ion storage batteries using the $LiCoO_2$–graphite material couple have been on the market for some twelve years or so. Nowadays, investigations are aimed at finding substitutes for these compounds, to achieve gains in terms of energy carried, power, safety, and cost. Positive electrode compounds with claims, as of now, to offer alternative solutions to cobalt oxide include the lamellar compounds $LiNi_xAl_{1-x}O_2$, $Li(Ni_xCo_{1-2x}Mn_x)O_2$ – in particular $LiNi_{0.5}Mn_{0.5}O_2$ – oxides of spinel structure $LiMn_2O_4$, and iron phosphate of structure isotypic to olivine $LiFePO_4$. Lamellar compounds (160–200 mAh/g, 3.8 V/Li^+/Li) mainly meet the requirement for increased stored energy, partial or complete substitution of cobalt making for cost reductions, while doping ensures safety. Compounds of the spinel type (110–120 mAh/g, 4.0 V/Li^+/Li) allow fabrication of power batteries, using an inexpensive material. The compound of phosphate-olivine type (165 mAh/g, 3.4 V/Li^+/Li) is a low-cost compound, for which stored specific energy is comparable to that of $LiCoO_2$.

CEA has been actively pursuing, over the past few years, optimization of $LiFePO_4$ synthesis, and of operating conditions for this compound. Indeed, the compound combines a number of useful properties, which should open up a broad range of applications to it. Its structure, isotypic of olivine $(MgFe)SiO_4$, featuring polyanionic PO_4 groups, is stable in the two extreme compositions ($LiFe^{+2}PO_4$, $\square Fe^{+3}PO_4$) involved in electrode operation. [1] Thus, practical available specific capacity, for this compound (165 mAh/g), is very close to theoretical attainable capacity (170 mAh/g), this being achieved in fully reversible fashion. The electrochemical reaction $LiFePO_4 \leftrightarrow cFe^{+3}PO_4 + Li^+ + e^-$ unfolds in accordance with a two-phase process, at a stable voltage of about 3.4 V/Li^+/Li. This working voltage lies within the electrochemical stability domain of the organic electrolytes commonly used in Li-ion storage batteries, by contrast with other compounds, operating at around 4 V. At the same time, in this compound, oxygen is strongly bound to phosphorus. Contrary to what happens in lithium-and-nickel, cobalt, manganese mixed oxides, the oxygen present in the compound (more particularly in its non-intercalated state) is not liable to react with the organic solvents included in the electrolyte composition, even if subjected to accidental heating. The two last-mentioned points mean this compound is an inherently safe electrode active material.



Crystallographic structure of $LiFePO_4$ (pink–purple octahedra: FeO_6; khaki tetrahedra: PO_4).



Curves plotting voltage over state of charge for $LiFePO_4$ and $Li_4Ti_5O_{12}$, illustrating their possible association in a Li-ion system, exhibiting stable voltage at 1.9 V.

Taken together, the characteristics exhibited by $LiFePO_4$ (outstanding cyclability, low cost, safety) mean this compound is a prime candidate for all-electric or hybrid vehicles ,electric tools, and stationary systems.

This compound being a very poor electron conductor, the material's operating characteristics (lithium insertion–disinsertion) are highly dependent on morphology, and the nature of the conducting matrix holding it within the electrode. Part of the investigations being conducted at CEA are thus addressing mastery of low-cost processes enabling achievement of defined, specific morphologies, possibly down to nanometric scale, and compositions that are better electron conductors. In a form optimized for power applications, it is thus possible to make this compound deliver a charge or discharge equal to 75% of full capacity in 6 minutes. Coupled with the oxide $Li_4Ti_5O_{12}$ – for which power-application grades are also being developed – it forms a rugged, inexpensive 1.9-V rechargeable system, a likely candidate substitute for current Ni–Cd and Ni–MH systems.

> **Frédéric Le Cras**
Technological Research Division
CEA Grenoble Center

(1) ☐ stands for the position of a Li vacancy, or empty site.

Towards new battery electrolytes

Safety and high performance are the main requirements lithium-ion battery electrolytes have to meet. CEA research workers are looking to improve the former through use of polymer–gels, and the latter by employing molten salts.

In **batteries**, the **ion conductor**, or **electrolyte**, separating the **electrodes** is a key element. On the one hand, its state (liquid, or solid) has an incidence on system safety, and, on the other, electrolyte conductivity determines the operating temperature range. CEA is involved in development of new electrolytes. Polymer–gels are used in order to ensure higher safety for lithium-ion–polymer batteries, and molten salts to sustain battery performance at low temperature.

Polymer–gels

Liquid, carbonate-based electrolytes (propylene or ethylene carbonate, dimethyl carbonate) form the ion conductor in most cylindrical or prismatic (flat) lithium batteries commercially available at present to power portable electronics. While they do exhibit good conductivity, of the order of 1 mS/cm at ambient temperature, and allow operation between – 20 °C and + 60 °C, they do not provide, however, optimum safety conditions or performance. At the same time, dry **polymers** such as polyoxyethylene, mainly investigated for the purposes of transport applications (electric vehicles), though safer owing to the absence of liquids, exhibit conductivity levels that are far too low for utilization at ambient temperature.

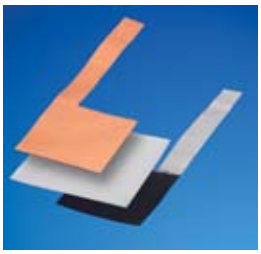
Over the past few years, investigations have addressed development of polymer–gel films, in order to achieve improved safety, higher volumetric energy densities, and greater shape flexibility, at lower fabrication costs. Such benefits are linked to the fact that the polymer–gel ensures cohesion between the positive and negative electrode films, thus allowing the rigid metallic casing to be replaced by a flexible, leakproof case. These electrolytic membranes consist in a polymer matrix, conferring mechanical stability, in which the liquid electrolyte is embedded. Liquid mass percentage lies in the 50–70% range, to achieve ion conductivity close to that of the liquid, while maintaining good mechanical stability for films having thicknesses of a few tens of micrometers (1µm = 10^{-6} m). The matrix is soluble, or fusible, to be compatible with such conventional polymer fabrication processes as casting, or extrusion. (1) CEA/Grenoble is looking into matrices of the porous PVDF–HFP (polyvynilidene difluoride–hexafluoropropylene) copolymer type, performance of which is being tested in thin, flexible batteries. Developments are particularly addressing enhanced power performance, compared to liquid-electrolyte systems.

Molten salts

Many applications require that battery operating domain be extended downward, to cover low temperatures. This entails achieving lower internal resistance, hence improved electrolyte ion conductivity. Aside from electrolytes consisting in a lithium salt, dissociated in a polar (2) organic solvent, such as the carbonates mentioned earlier, CEA is looking into ionic liquids, solely comprising **anions** and **cations**. The best-know ionic liquids are molten salts. Thus, for instance, table salt (NaCl) melts at about 800 °C, and the liquid obtained only contains Na^+ and Cl^- ions. One of the essential characteristics of such liquids, related to their structure, is their high ion conductivity. Their main limitation is their melting temperature, this being high as a rule. Molten salts melting at lower temperatures are used for specific applications: this is the case for sodium chloroaluminate ($NaAlCl^4$), melting at 153 °C (Na^+, $AlCl_4^-$), which exhibits conductivity of 0.5 S/cm at 160 °C.

Organic salts make it possible to lower the fusion points of such mixtures, down to temperatures of – 90 °C. Owing to the advantage of lithium-ion batteries operating at low temperature, these ionic liquids have seen accelerated development of late. Novel electrolytes have been suggested, in particular electrolytes having for cation EMI^+ (ethyl–methylimidazolium) or BMI^+ (butyl–methylimidazolium), and for anion BF_4^- or PF_6^-. Their main advantages consist in high chemical stability, in particular with respect to air and water, thermal stability over a range from – 90 °C to + 400 °C, depending on the electrolyte, an electrochemical window (3) of around 5 V, ability to be gelified by polymers (PVDF, for instance), and low vapor pressure. Their conductivity may reach 25 mS/cm at ambient temperature. If they are to be used in lithium-ion batteries, however, a lithium salt must be found, that is highly soluble in such electrolytes. This issue would appear to have been resolved by a US company (Covalent Associates), according to their statement announcing the forthcoming commercialization of high-conductivity electrolytes. The other barrier to development of these salts is their high cost. Consequently, new, less costly synthesis methods, in aqueous media, are currently being investigated.

> **Sébastien Martinet** and **Hélène Rouault**
Technological Research Division
CEA Grenoble Center
> **Jean-Yves Poinso**
Military Applications Division
CEA Valduc Center



CEA/Artechnique

Full complement of components for a lithium-ion–polymer battery: graphite negative electrode on copper collector, positive electrode (black) on aluminum collector, and, in the middle, electrolyte membrane. This membrane absorbs the electrolyte, thus forming a polymer–gel.

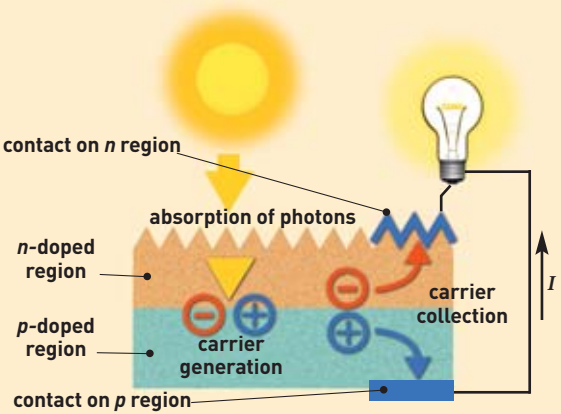
(1) Extrusion: a forming process, involving coating the solvated-polymer-based mix, then drying it in line to form a microporous membrane.

(2) Polar: featuring a dipole, i.e. a set of two closely-spaced electric charges, of equal amplitude and opposite signs.

(3) Electrochemical window: potential domain for which the electrolyte exhibits no electrochemical reactions liable to cause degradation to it.

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.

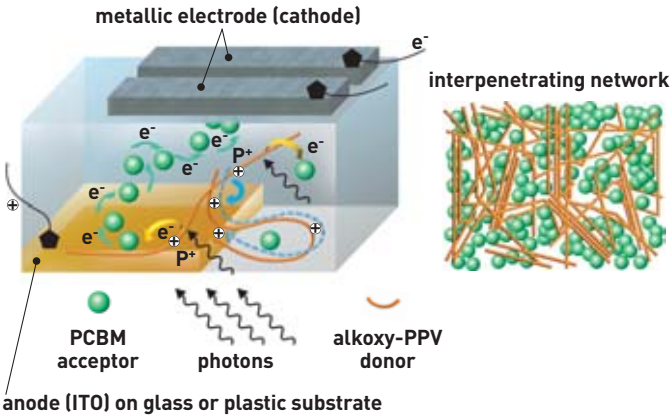


Figure from a presentation by S. Sariciftci (www.lios.at)

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