

ELECTRICITY STORAGE: BATTERIES

Lithium batteries: the scientific and technological stakes of a highly promising market

In both the portable equipment and transportation fields, the world has firmly embarked upon the path of increasing energy consumption, where the source must be capable of providing a maximum amount of energy and power for the smallest possible volume and mass. Already – and this will be confirmed over the next few years – electrochemical energy storage systems, namely batteries, are in great demand. And lithium batteries are on their way to becoming the batteries of the future. For example, lithium storage batteries count for almost 10% of today's portable electrochemical energy sources.



Bramaz/JERRICAN

The battery market is booming thanks to the considerable growth of the portable equipment market.

Technological revolution by Japanese industry

Between 1990 and 1995, mainly at the prompting of Japanese manufacturers of portable equipment (video cameras, computers, the budding mobile telephone industry, etc.), two new technological fields emerged, announcing a complete break from traditional technologies. The development, first of all, of *nickel-metal hydride* storage batteries, followed by that of *lithium* storage batteries, has totally altered the original technological landscape and taken most traditional manufacturers by surprise (see box F, *Storage batteries, cells and batteries: steadily improving performance*). The progress of these technologies, and especially of lithium storage batteries, was boosted, into the bargain, by the sudden, substantial growth of the mobile telephone market in the mid 1990's (+ 1% a month in 2000, and a 70% penetration rate in Europe in 2003 compared to just a few percent in 1996). This market is constantly in search of high **energy densities**, within a limited space. That is how the lithium storage battery market exceeded the 4.5 billion Euro mark in 2000, and how three Japanese manufacturers (Sony, Sanyo, Matsushita) are taking the lion's share (70%) of a market which is henceforth dominated by Japan (over 95%) to the detriment of not only European industrialists, but also the Americans, who are practically non-existent on the main market, namely that of supplying energy to portable equipment.

Nevertheless, a number of European ventures are emerging, with a view to develop-

ping specific types of lithium storage battery with definite advantages over the *lithium-ion* technology which is currently being developed in Japan.

Optimising performance and economic competitiveness

To appreciate the advantages of lithium batteries⁽¹⁾, we must go back to the way they work (see box). Thanks to lithium's physical properties, these batteries are able to provide high energy densities.

Research scientists have several objectives, inspired both by user needs and authorities' concerns about safety and environmental protection. Therefore, performance improvement in terms of energy density, **cyclability** and service life continues to motivate a large number of research teams all over the world. These batteries are destined to be used by the general public, which means that they will be used in all sorts of circumstances, for example at low winter temperatures. To compete with conventional batteries, they must be affordable: around 1 Euro/Wh for portable equipment and 150 Euro/kWh for the electric vehicle. They must be guaranteed safe to use and they must be reprocessed at the end of their service life, not only because they operate on lithium, which reacts strongly to air, but also because of the toxic materials they may contain.

(1) The term "lithium batteries" is used indifferently to denote lithium cells and/or storage batteries.



Different lithium storage battery prototypes. The button-type storage battery was manufactured at the CEA/Grenoble, whereas the cylindrical and spiral storage batteries were made by Tadiran Batteries Ltd., the CEA's Israeli partner. The positive electrode's active material (in powder form) was developed at the CEA.

Totem de Pierre/CEA

To help its industrial partners take up this technological challenge, the CEA is exploring a variety of research topics, mainly within the framework of European projects. It is counting on the help of all its operational divisions to do this (technological research, nuclear energy, military applications, physical sciences), as well as on its partners in fundamental research (CNRS/the National School of Chemistry in Paris...).

Developing new positive electrode materials

This is why, as part of the European Joule project, and in close co-operation with the companies Erachem Europe (Belgium) and Tadiran Batteries Ltd. (Israel), a special effort has been made to develop new positive electrode materials in order to synthesise materials capable of exchanging large quantities of cheap lithium, and which have a low level of toxicity and are usable in *lithium-ion* systems. Compounds based on manganese oxides have finally been selected as they are competitive and capable of replacing the expensive, toxic cobalt oxides currently used by Japanese manufacturers.

Developing new generations of lithium storage batteries

The CEA has also launched a research programme on new generation **electrolytes** for use at low temperatures. Indeed, battery performance is contingent, among other things, upon the electrolyte's **ionic conductivity**. Now, standard electrolytes, composed of a solvent and lithium salts, exhibit a very low level of ionic conductivity at cold temperatures. So, the CEA is trying to develop a new family of cheap, ionic liquid electrolytes, which are solvent-free and are obtained by dissolving salts at a very low melting-point. Moreover, using **polymer-gel** as an electrolyte seems to be an appropriate solution for the lithium batteries of tomorrow.

The space provided for the energy source in future portable equipment will be increasingly limited. There is no longer any question of using standard formats if the aim is to improve energy density. Under these circumstances, specific development procedures, using flexible materials such as polymer-gel, will have to be devised for the manufacture of such products. Today, the CEA is using every possible means to develop these procedures. It has therefore equipped itself with the appropriate facilities, including an anhydrous room, and has developed thin layer demonstration prototypes. It is also working on the European project,



Assembling a lithium storage battery in an anhydrous glove box, with argon scanning, at the CEA/Grenoble.



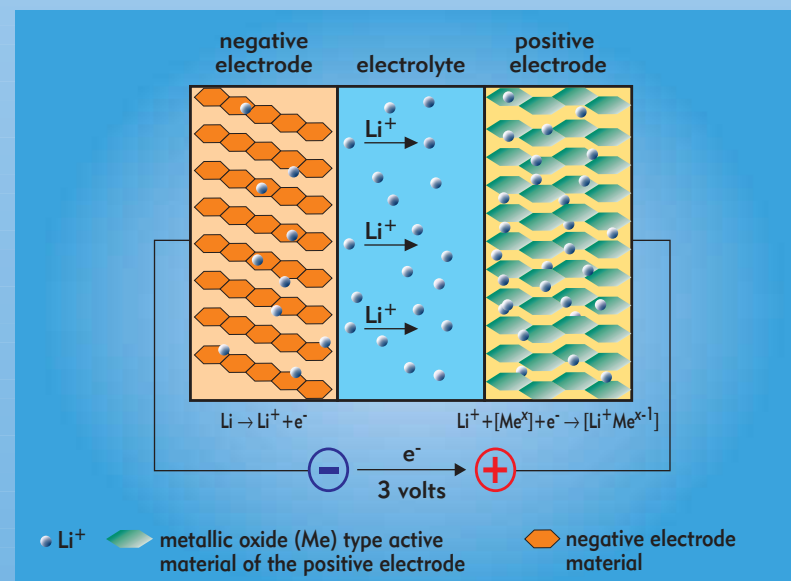
Totem de Pierre/CEA

How a lithium storage battery works

During operation, i.e. when the storage battery is discharging, the lithium released by the negative electrode in ionic form (Li^+) travels through the ionic conducting **electrolyte** and inserts itself into the crystal network of the positive electrode's active material (metallic oxide type lithium interstitial-compound). The passing of each Li^+ ion into the storage battery's internal circuitry is perfectly compensated by the passing of an electron into the external circuitry, thereby generating an electric current. The **mass energy density** released by these reactions is proportional both to the difference in potential between the two electrodes and to the quantity of lithium in the interstitial material. It is also inversely proportional to the system's total mass. Now, lithium is both the lightest of metals (with an atomic

molecular mass of 6.94 g) and the best reducer: lithium-based electrochemical systems can reach voltages of 4 V, as opposed to 1.5 V for other systems. Lithium batteries are therefore able to provide the highest mass and volume energy densities (typically 140 Wh/kg and 260 Wh/l): on average, 50% greater than those obtained by conventional batteries.

The lithium storage battery operates in the same way, whether a metallic lithium or carbon-based negative electrode is used. In the latter case, the technology used is known as *lithium-ion*, as the lithium never takes on a metallic form in the storage battery, and "yo-yos" between the two lithium interstitial-compounds to be found in the positive and negative electrodes each time the storage battery is charged or discharged.



Storage batteries, cells and batteries: steadily improving performance

Storage batteries and cells are electrochemical systems used to store energy. They reconstitute the chemical energy generated by electrochemical reactions, in the form of electrical energy expressed in **watt-hours (Wh)**. These reactions are activated within an elementary cell, between two **electrodes** immersed in an **electrolyte**, when a resistor, e.g. an electric engine, is connected to the cell's terminals. The storage battery is based on a reversible electrochemical system. It can be recharged, whereas a **cell** cannot. The term "battery" is therefore used to denote a set of elementary cells (usually rechargeable).

A storage battery, whatever the technology used, is mainly defined by three different measurements. Its **mass** (or **volume**) **energy density**, in watt-hours per kilogram, Wh/kg (or in watt-hours per litre, Wh/l) corresponds to the quantity of energy stored per storage battery **mass** (or **volume**) unit. Its **mass power density**, in watts per kilogram (W/kg), represents the **power** (electrical energy provided per time unit) that the storage battery mass unit can supply. Its **cyclability**, expressed as a number of cycles⁽¹⁾, characterises the storage battery's **service life**, or the number of times it can reconstitute the same energy level after being recharged.

Up until the late 80's, the two main technologies available on the market were *lead storage batteries* (used to start vehicles and provide a back-up supply for

telephone exchanges, etc.) and *nickel-cadmium storage batteries* (portable tools, toys, emergency lighting, etc.). The lead-based technology, more commonly known as lead battery, is also described as a *lead-acid* system. Indeed, the chemical reactions brought into play involve the lead oxide that composes the **positive electrode** (wrongly known as the cathode) and the lead that makes up the **negative electrode** (anode), both

tions must be reversed by circulating an imposed electrical current. The disadvantages of the lead technology (weight, fragility, use of a corrosive liquid) led to the development of **alkaline storage batteries**, with a greater **capacity** (quantity of electricity reconstituted on discharge), but with a smaller **electromotive force** (difference in potential at the terminals of the open-circuit system). Their electrodes are based on either nic-



SAFT/Le cocotier bleu

Range of lithium-ion storage batteries offering a wide span of performance capabilities, from high energy to high power.

of which are immersed in the diluted sulphuric acid solution which acts as an electrolyte. These reactions tend to convert the lead and the lead oxide into lead sulphate, producing water in the process. In order to recharge the battery, these reac-

tion and cadmium (*nickel-cadmium storage battery*), nickel oxide and zinc (*zinc-nickel storage battery*) or silver oxide coupled with zinc, cadmium or iron (*silver oxide storage batteries*). All these technologies use a potash solution as an electrolyte. Lead technologies, like alkaline storage batteries, are highly reliable, but their mass energy densities are relatively low (**30 Wh/kg** for *lead*, **50 Wh/kg** for *nickel-cadmium*).

In the early 90's, with the growth of the portable equipment market, two new technologies emerged: *nickel-metal hydride storage batteries* and *lithium storage batteries* (see box, *How a*



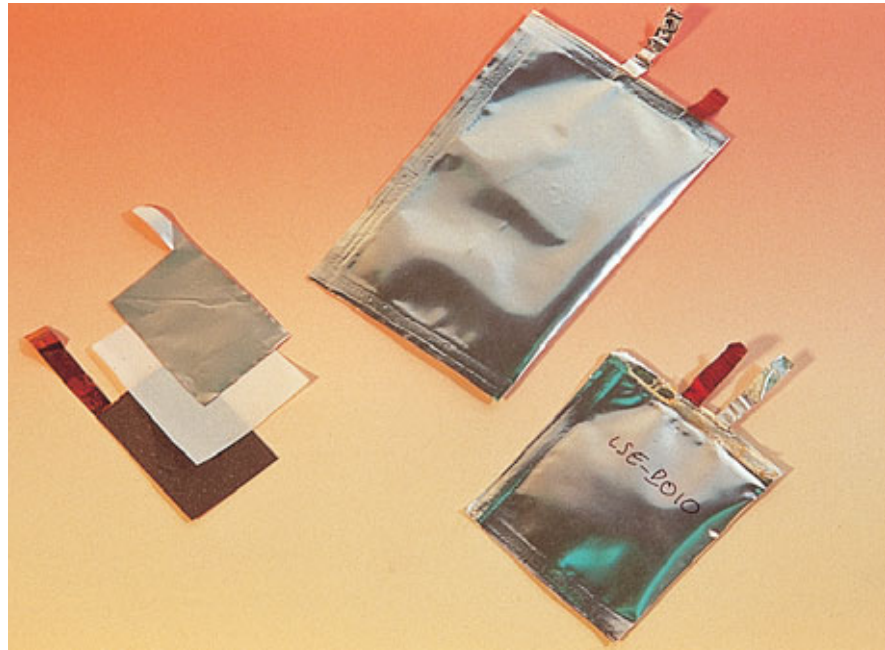
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"Very high energy range" nickel-metal hydride storage batteries, for portable tool applications.

(1) A cycle corresponds to a recharge and a discharge.

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lithium storage battery works). The first technology, which used a nickel-based positive electrode and a negative electrode composed of an alloy which absorbs hydrogen, immersed in a concentrated potash solution, provided a mass energy density of **70 to 80 Wh/kg**. The second technology had already been investigated towards the end of the 70's, with a view to finding electrochemical combinations which would perform better than the *lead* or *nickel-cadmium* storage batteries used up until then. The first models were therefore designed with a metallic lithium-based negative electrode (*lithium-metal* technology). However, this technology ran into problems linked to the poor reconstitution of the lithium negative electrode after each successive recharge. This is why, towards the beginning of the 80's, research began on a new type of carbon-based negative electrode, used as a lithium interstitial-compound. The *lithium-ion* technology had come into being. Japanese industrialists quickly became the leaders in this field. They already manufactured portable equipment and considered that the energy supply was one of the strategic components of this equipment. This is how Sony, who did not originally manufacture storage batteries, decided, during the 80's, to invest considerably in the technology's progress and industrialisation. In February 1992, Sony announced, to everyone's surprise, that the industrial manufacture of *lithium-ion* storage batteries was to begin immediately. The performance of these first storage batteries was relatively restricted (**90 Wh/kg**). Since then, however, performance has improved considerably (**140 to 160 Wh/kg** in 2000) thanks, on the one hand, to technological progress (reduction of the storage battery's redundant mass and volume) and, on the other hand, to the optimisation of material performance. Mass energy densities of **190 to 200 Wh/kg** are anticipated for around 2003.



Totem de Pierre/CEA

Thin layer lithium storage battery developed by the CEA. Thin, flexible, ideal for supplying chip cards with built-in screens, rechargeable, this storage battery is composed of a manganese oxide layer (positive electrode), a polymer film (electrolyte) and a lithium film (negative electrode).



Energy, with the mobile telephone manufacturer, Philips, the aim being to develop a new type of lithium storage battery to supply tomorrow's communication tools. Finally, specific work is being carried out on the development of *very* thin layer energy sources capable of supplying chip cards, for example, or "smart" cards that are able to communicate with their environment. A demonstration of how these micro-batteries work is planned for 2002.

Guaranteeing user safety: a priority

The safety of lithium batteries is a crucial issue which conditions their use by the general public. It is still the manufacturer's leading concern. The CEA has therefore adopted a global approach to the subject that covers thermal, mechanical and toxicological risks. It has, for example, helped to design a storage battery unit for an electric scooter, within the framework of a European project. Its role consisted in modelling thermal effects and proposing a cooling solution for the unit. Thermal runaway tests are, moreover, systematically carried out on the prototypes developed by its industrial partners (Tadiran Batteries Ltd., Bolloré Technologies, etc.).

Processing or recycling

Finally, the CEA, which is naturally concerned by environmental protection, is involved, *via* two European projects known as Brite-Euram and Growth, in the definition and design of different stages of the recycling process, aiming to re-use the components from worn lithium batteries. Thus, an innovative procedure, which has been patented, is being developed to recover manganese oxides and re-use them as the active material for positive electrodes.

Alternatives to current technologies

Since 1991, the CEA has acquired a good deal of know-how in the field of lithium storage batteries. Within the framework of the recently established New Energy Technologies programme, it is now using this know-how to actively, and contractually, support the efforts of its industrial partners in Europe to create credible alternatives to current technologies. The CEA contributes its expertise to the search for new materials, process development (material synthesis, recycling, etc.), electrochemical valuation and the development of demonstration objects.

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The promise of new positive electrodes for lithium storage batteries

Manganese, an ideal choice

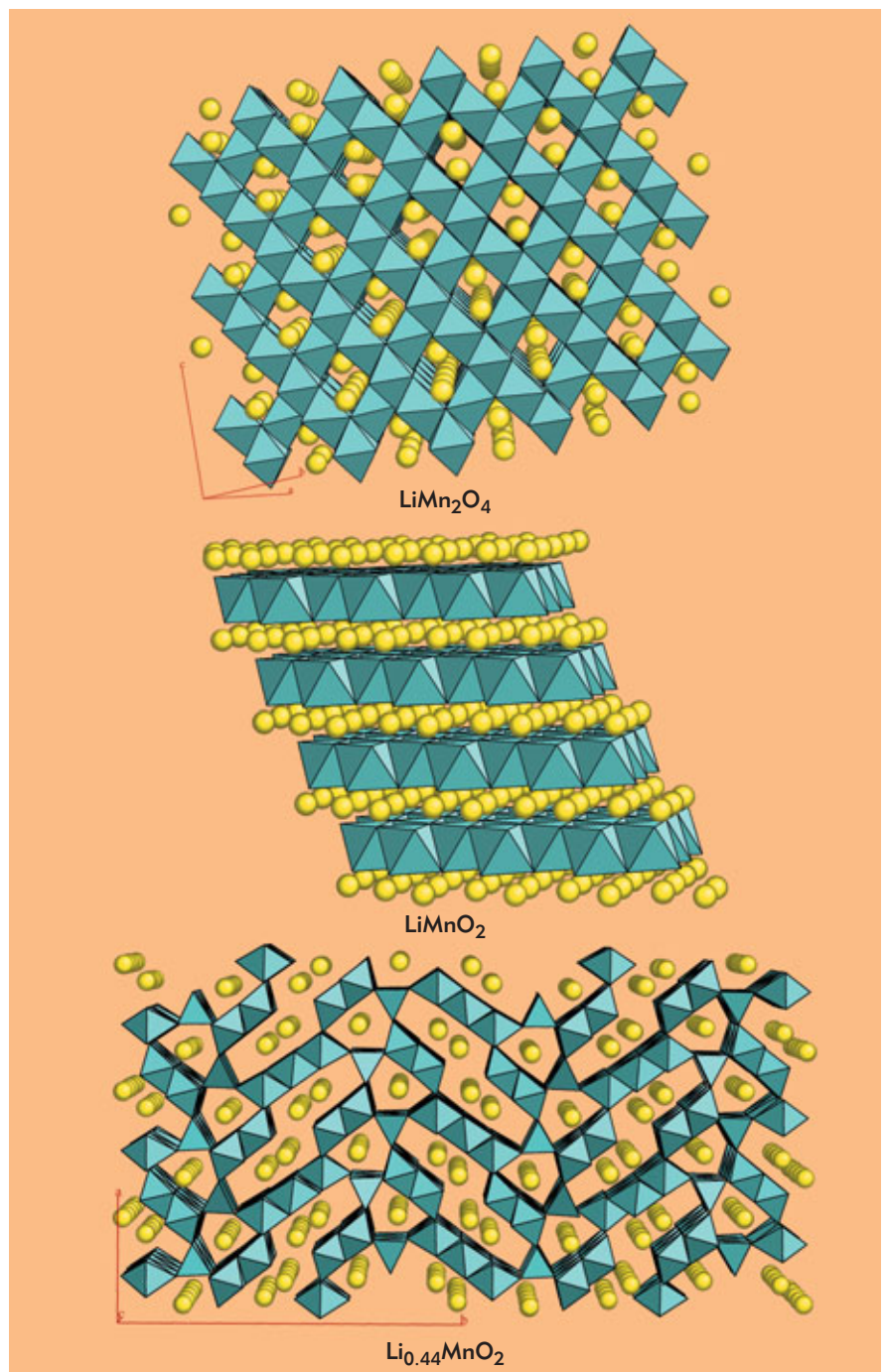
Manganese oxide has been used for many decades as **positive electrode** material in 1.5 volt (V) **saline and alkaline cells**⁽¹⁾ (of the Leclanché type). At the beginning of the 1980s, it was incorporated in the first 3 V lithium cells, still used today mainly in calculators, cameras and many other general purpose applications. The relative abundance of manganese – and its consequent low cost – and its low toxic level in comparison with other compounds currently being used in the manufacture of lithium storage batteries (cobalt, nickel, vanadium, etc.) make it an excellent choice for this booming market. On this basis the CEA has been working on this subject since 1992.

A large variety of structures for manganese oxides

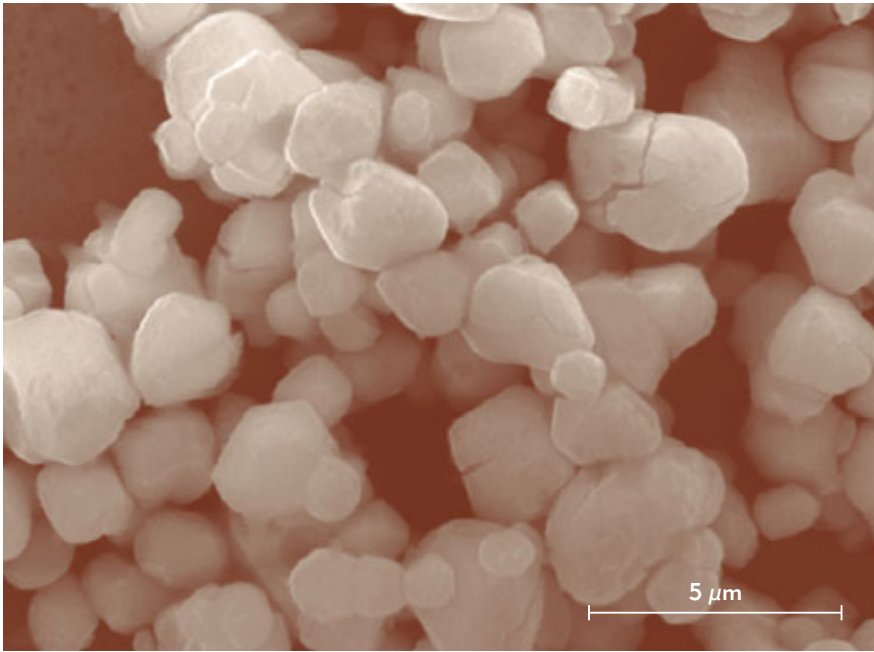
The XMnO_2 manganese oxides exist naturally in different crystallographic forms. Even more may be obtained in the laboratory by various physico-chemical processes. Their structure comes from the regular packing of MnO_6 octahedrons. In some cases, they form channels or surfaces in which the lithium is

able to enter and leave again. Because of this, the capacity for reversibility is mainly linked to the stability of the MnO_2 “skeleton” during the charge-discharge cycles that the storage battery will undergo.

(1) The manganese dioxide MnO_2 (positive electrode)-zinc (negative electrode) cell was invented around 1870 by the French engineer Georges Leclanché.



Structures of various manganese oxides studied for their capacity to exchange reversibly lithium ions represented by yellow spheres. The green polyhedra correspond to MnO_6 and MnO_5 assemblies. Different families of MnO_2 structures are illustrated: with intersecting channels for the spinel structured LiMn_2O_4 compound, with planes for the lamellar structured LiMnO_2 compound and with parallel channels for the $\text{Li}_{0.44}\text{MnO}_2$ compound obtained by ion exchange using $\text{Na}_{0.44}\text{MnO}_2$.



SEM view of a $\text{Li}_2\text{Mn}_2\text{O}_4$ powder (spinel structure LiMn_2O_4 compound chemically reduced).



Figure 1. Charge and discharge plot for the lithium-impregnated spinel structure LiMn_2O_4 compound studied in a negative electrode lithium storage battery. To obtain this material, LiMn_2O_4 is chemically converted to a biphasic mixture of 90% $\text{Li}_2\text{Mn}_2\text{O}_4$ and 10% LiMn_2O_4 ; the overall composition is therefore $\text{Li}_{1.95}\text{Mn}_2\text{O}_4$. An initial charge, during which the lithium is extracted from the positive electrode, reaches the electrochemical biphasic stage at 3 V, then the two monophasic stages of lithium extraction of LiMn_2O_4 around 4 V. The subsequent cycles involve only monophasic stages.

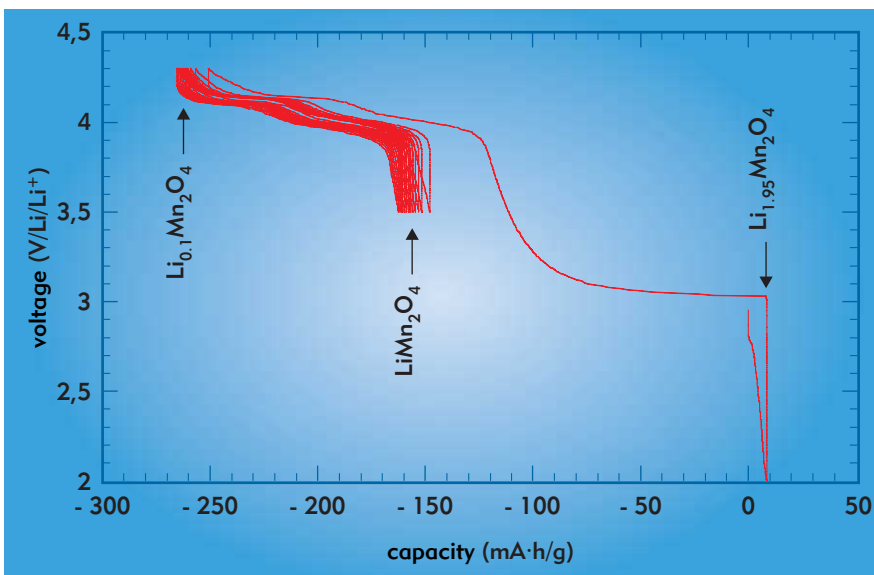
Currently, research in laboratories all around the world is focusing on LiMn_2O_4 compounds and their variants, $\text{Li}_{0.33}\text{MnO}_2$ and LiMnO_2 , as they have some interesting properties. More recently, promising studies have been made on oxides such as $\text{Li}_{0.44}\text{MnO}_2$ and the phases from sodium bronzes. In collaboration with its partners Erachem Europe and Tadiran Batteries Ltd., the CEA has until now particularly concentrated its efforts on the first two types of compounds. With a view to integrating

these products into *lithium-ion* storage batteries, sustained work has enabled these materials to be obtained in a lithium-impregnated configuration, i.e. with a composition close to LiMnO_2 , while preserving their performance. Today, there are two drawbacks that limit the use of manganese oxides:

- their chemical reactivity at high operating temperatures (typically 55 °C in laptop computers) with regard to the **electrolyte**;
- the diffusion speed of lithium is appreciably less than in cobalt oxide LiCoO_2 , currently used as constituent of the positive electrode, thus restricting the charge and discharge of the storage battery.

In the field of storage battery-powered mobile equipment, the development of micro-electronics should soon allow components to operate with a voltage lower than 2 V. Tomorrow's materials should therefore above all be capable of exchanging a large quantity of lithium and of supplying a voltage of between 2 and 3 V. Some forms of manganese oxide have such properties with a capacity⁽²⁾ of the order of 200 mA·h/g for several cycles (figure 1). The objective of future studies will therefore be to obtain a compound of this type, stable over several hundred cycles in real operating conditions.

(2) The specific capacity of electrode materials corresponds to the electrical charge (quantity of electricity) available in these materials during oxidation or reduction reactions (lithium ion exchange between negative and positive electrodes). It is expressed in milliamp hour per gram (mA·h/g) or in amp hour per kilo (A·h/kg).



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Moving towards new battery electrolytes

The key element in batteries is the ionic conductor or **electrolyte** that separates the electrodes. On the one hand, its physical state, either liquid or solid, has an impact on the safety of the system and on the other, its **conductivity** determines the operating temperature range. The CEA is involved in the development of new electrolytes. Polymer gels should give increased safety to *lithium-ion polymer* batteries and molten salts maintain the performance of low temperature batteries.

Polymer gels

Liquid carbonate-based electrolytes (propylene carbonate, ethylene carbonate, dimethyl carbonate) are the ionic conductors for most of the cylindrical or rectangular (flat) lithium batteries currently sold for portable electronics. These electrolytes provide good conductivity of the order of 1 mS/cm at ambient temperatures and can operate between - 20 and + 60 °C. However, they do not offer optimum conditions for either safety or performance. As for dry **polymers** such as polyoxyethylene, mainly studied for transport applications (electrically powered vehicles), although safer because of the absence of liquid, their conductivity levels are much too low for use at ambient temperatures.

For several years, research has therefore concentrated on developing polymer gel films with the aim of obtaining increased safety, greater **volume energy densities** and greater flexibility of shape with reduced manufacturing costs. These advantages are

linked to the fact that the polymer gel ensures cohesion between positive and negative electrode films and thus allows the conventional rigid metal container to be replaced by a flexible and waterproof packaging. These electrolytic membranes are composed of a polymer matrix ensuring mechanical stability and in which the liquid electrolyte is held. The liquid density varies between 50 and 70% so that an **ionic conductivity** is obtained close to that of the liquid while maintaining a good mechanical stability for films of several tens of micrometres thick ($1 \mu\text{m} = 10^{-6} \text{m}$). The matrix can be dissolved or melted to be compatible with classic polymer handling processes such as casting or extrusion⁽¹⁾. The CEA is interested in polyacrylonitrile type matrixes, the porous co-polymers PVDF-HFP (polyvinylidene difluoride-hexafluoropropylene) whose performance is tested in thick, flexible batteries.

Molten salts

Many applications are available that can extend the range of battery operation towards lower temperatures. This involves reducing the **internal resistance** and hence increasing the ionic conductivity of the electrolyte. In addition to electrolytes composed of a lithium salt dissociated in a polar organic solvent⁽²⁾ such as the carbonates described above, the CEA is interested in ionic liquids that are composed solely of ions of negative electrical charge (anions) and ions of positive electrical charge (cations). The most well-known ionic liquids are molten salts. For example,

table salt NaCl melts at approximately 800 °C and the liquid obtained contains only Na^+ and Cl^- ions. One of the main properties linked to their structure is their high ionic conductivity. Their main limitation is their melting point, which is usually high. Low temperature molten salts are used for specific applications: this is true for sodium chloro-aluminate, NaAlCl_4 , which melts at 153 °C (Na^+ , AlCl_4^-) and whose conductivity is 0.5 S/cm at 160 °C.

Organic salts allow the melting point of these mixtures to be reduced to - 90 °C. Considering the interest in *lithium-ion* batteries functioning at low temperature, these ionic liquids have recently been the subject of accelerated development. New electrolytes have been proposed, particularly with EMI^+ (ethyl-methyl imidazolium) or BMI^+ (butyl-methyl imidazolium) as the cation and BF_4^- or PF_6^- as the anion. The main advantages lie in a great chemical stability, particularly with regard to air and water, a thermal stability between - 90 and 400 °C depending on the electrolyte, an electrochemical window, i.e. a field of potential where the electrolyte shows no electrochemical reactions likely to cause degradation, of the order of 5 V, a capacity for becoming gelled by polymers (PVDF for example) and a low vapour pressure. Their conducti-

(1) Formation process consisting of forcing the polymer-based mixture in its melted state using a specially shaped tool.

(2) With a dipole, i.e. a pair of electrical charges of the same amplitude and opposite sign in close proximity.

Components of a lithium-ion polymer battery: on each side the current collectors (copper and aluminium grids), the negative electrode (green), the positive electrode (black) and in the centre the electrolytic membrane. This membrane absorbs the electrolyte and so makes a polymer gel.



Glove box for the study of the molten salts, at the CEA/Le Ripault.



CEA/DAM

velocity may reach 25 mS/cm at room temperature. However, to be used in *lithium-ion* batteries it is necessary to find a lithium salt that is very soluble in these electrolytes. This difficulty seems to have been overcome by an American company (Covalent Associates) who has announced the forthcoming commercialisation of high conductivity electrolytes. The other obstacle to development of these salts is their high cost. New, easier methods of synthesis in aqueous environments are also currently being studied at the moment.

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Lithium batteries and their safety of use

A global approach for improved safety

Lithium batteries are increasingly present in our environment. They already supply energy to many battery-powered appliances and involve new fields of application everyday (household appliances, do-it-yourself equipment, etc.) not to mention the electrically powered car application, which is still an attractive area. In any case, their safety remains the main concern of manufacturers, because these products may be the cause of incidents such as internal short circuits, abnormal overheating or current or voltage instability, causing *thermal*, *mechanical* (rupture of the housing) and *toxicological* (inhalation of toxic gas) risks. In fact, if the battery behaves abnormally, the physico-chemical processes of degradation initiated in the electrochemical system are likely to lead to the formation of gas, hence increasing the internal pressure of the battery. The housing is then at risk of bursting, suddenly exposing the components to the air, resulting in possible combustion and even the emission of toxic substances in certain types of battery.

Nowadays, most commercial products offer safety guarantees of a high level. For

example, some are equipped with a thermal resistor which cuts out the **conduction** processes if the battery heats up abnormally. The metal housings are designed to split rather than burst, while an expansion space is systematically included in the container to prevent risk of explosion. A safety vent is also intended to free gases that are over-compressed. Several technologies use an **electrolyte** that **polymerises** in the case of overheating, blocking all irreversible degradation phenomena.

Even if the new solutions provide ever increasing safety and even if all products available to the public are systematically subjected to a draconian series of tests, the zero risk factor does not exist. This is why a global approach to the subject has been undertaken at the CEA to lead an experimental programme where teams specialised in materials, electrochemistry and thermohydraulics collaborate. The various thermal, mechanical and toxicological aspects are thus studied comprehensively and simultaneously.

Thermal aspects

Four years ago, voluntary flashpoint tests were carried out at the CEA/Grenoble on high **capacity** prototypes (100 Wh), in order to

ascertain the sometimes very reactive conditions that lead to the discharge of large quantities of flames and smoke, but without the projection of particulate material. Flame temperatures reached 600 °C while the fire could continue to burn for ten minutes. The total amount of energy released was estimated to be 20 kW.

Now, technology has evolved and the quantities of lithium used in batteries have been reduced, obviously altering their thermal behaviour. The Laboratory of System Thermohydraulic Studies in Grenoble has therefore designed and produced an original experimental device, FeuLi, to analyse the behaviour in case of overheating.

As a complement to this equipment, mainly aimed at relatively large elements, other tests are planned by the LPIC (Innovative Conditioning Processes Laboratory) at CEA/Valrhô-Marcoule on smaller components. Indeed, incineration is one of the methods being considered to re-treat used lithium cells and batteries. In any case, the procedure must be set up under maximum safety conditions. This is the reason for performing temperature tests. They consist of testing the battery behaviour under thermal stress simulated by progressive heating on a hotplate or by more violent heating using a welding torch. These experiments will be

The Feuli loop installed at the CEA/Grenoble studies the flashpoint of one or more lithium storage batteries in a high temperature chamber (left) with a volume of about 40 litres. The transitory measurements of the thermocouples installed in a copper heat absorber with a mass of approximately 140 kg situated above the reaction chamber allows the flashpoint and the instantaneous power produced to be more accurately known. The gases generated are analysed and cleansed before being discharged.



CEA



Figure 1. The Thermomechanical Limit Test (LTT) is used to determine the behaviour laws of a sample (height equal to or less than 15 mm and diameter equal to or less than 10 mm) subjected to a pressure corresponding to a mass of 3.5 metric tons and a maximum temperature of 500 °C. The pressure of generated gases is measured and then the gases are analysed by mass spectrometry and/or infrared absorption spectrophotometry.

carried out in a laboratory belonging to the Military Applications Division at the CEA/Le Ripault, which is well equipped with remote control and discharged product analysis devices.

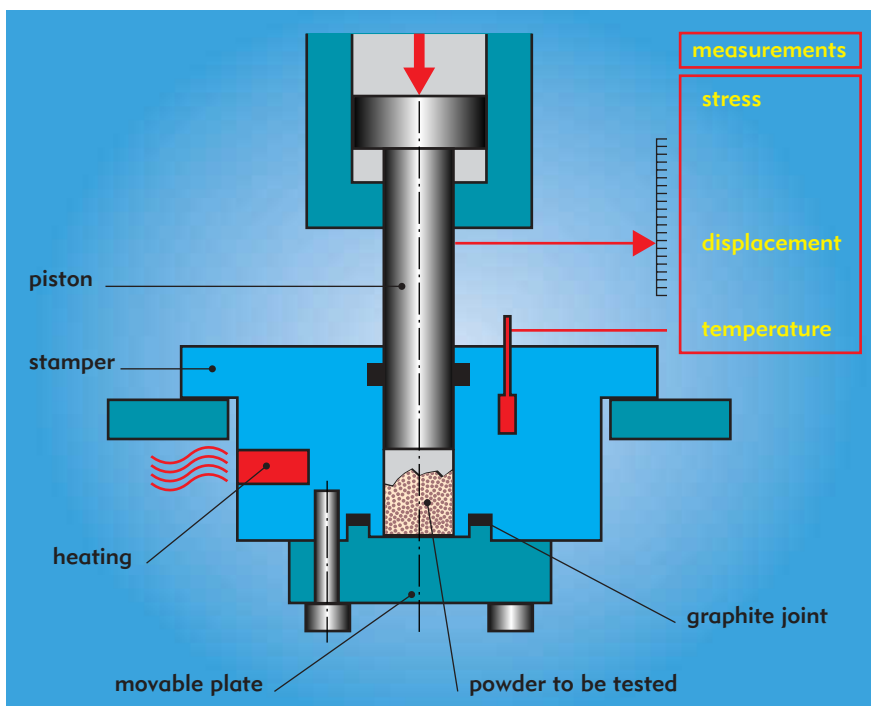
Mechanical aspects

To anticipate the inherent risks of an accidental explosion of a battery housing, and also to evaluate its reactivity during an opening operation (crushing, for example), which

is an inevitable stage in a recycling process, knowledge of the mechanical behaviour of the product is imperative. This is the reason that the CEA will carry out a programme of systematic tests subjecting batteries to diverse mechanical stress (drilling, stamping, cutting off, etc.) such Thermomechanical Limit Test (LTT) (figure 1).

Toxicological aspects

It is possible that the materials (or their sub-products) used in the manufacture of some types of lithium batteries and cells are irritants or corrosive. Their release may be caused by opening the housing during accidental thermal or mechanical stress or during recycling operations. The tests carried out to study the thermal and mechanical aspects will therefore be equipped with specific analysers allowing the maximum amount of information to be obtained on products likely to be formed in the case of degradation of the battery housing.



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Processing and recycling lithium batteries

French law recently ratified the European directive of 1991 regarding collection and elimination or recycling of **cells** and **storage batteries** containing heavy metals⁽¹⁾. These operations have been already practised in France for all types of storage batteries from the publication date of the decree, i.e. 16 May 1999. It now also rules them to all types of cells, with or without toxic components, since January 2001, as it has been in the Netherlands since 1995, in Belgium since 1996, and in Germany and Sweden since 1998.

In France, these requirements therefore apply immediately to lithium storage batteries, particularly since they contain toxic products such as fluorine-based salts. However, for lithium cells, the law took effect on 1 January 2001. While awaiting processing, the storage of used cells can be quite a risk since the metallic residual lithium reacts strongly with air and humidity at ambient temperature. Professional organisations have therefore been set up to support industrial companies having to meet the new legal requirements (figure 1).

Possible methods of processing

In France, the legal requirements are being implemented in two ways for dead **batteries**: destroying or recycling some of the materials in them following sorting and container opening (figure 2).

Destruction

The destruction of lithium batteries is performed in France by Citron SA, a subsidiary of the Swiss company Citron AG, and by Valdi, a subsidiary of the French company Tredi SA. They both specialise in the recovery of metals such as zinc, cadmium and lead from cells and storage batteries. The procedure involves treating the cells in a heat-reducing atmosphere (called pyrolysis).

Lithium batteries have been introduced into the pyrolysis load, which mainly contains zinc-carbon and aluminium-manganese cells. The risk of these batteries violently reacting with the others is prevented by previous sorting the large components and

(1) Metals with a density greater than 4.5: these include zinc (7.14), cadmium (8.6), lead (11.35), etc.



Alain Buu/GAMMA

After collection, used cells and storage batteries are sorted and their containers opened. They are then processed on one of two ways: destruction by pyrolysis or recovery of the re-usable materials contained in them.



restricting the number of lithium batteries included in the batch.

Recovery, recycling and re-use

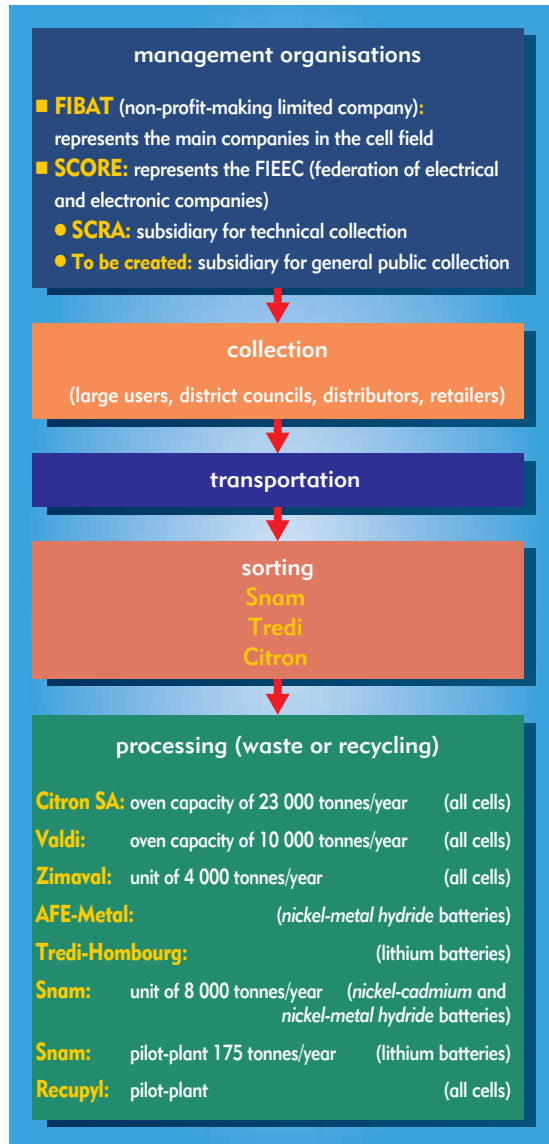
Procedures are already in place in several countries. The practice is different for *lithium-metal* batteries and for the most recent generation of *lithium-ion* batteries (box F, **Storage batteries, cells and batteries: steadily improving performance**).

Lithium-metal batteries are processed in only two places: one in Canada and the other in the USA, both close to the Pacific coast and belonging to the American companies Toxco Inc. and BDC Inc. respectively. These companies use either liquid argon equipment or a highly ventilated oven to reduce the risk of a violent reaction between lithium and air or water. In Europe, these types of battery are not processed and their transportation is strictly regulated. The current stock consists of non-rechargeable batteries from military or industrial applications.

Lithium-ion batteries contain much less lithium than earlier batteries. Snam in France and AEA Technology Batteries in the United Kingdom have developed processes to recover certain materials: particularly cobalt which, in its oxide form (LiCoO_2), is mainly used today to form the **positive electrode**. AEA Technology Batteries in particular provides separation of the cobalt from the lithium by selectively dissolving the lithium through reduction of the LiCoO_2 powder (patented process). This process also allows lithium fluorides and organic solvents constituting the **electrolyte** to be recovered with the high degree of purity necessary for re-use in the manufacture of new lithium batteries.

These *lithium-ion* batteries are generally sold to the general public (particularly because they are much safer to use than previous batteries) in a wide variety of models and constituents. In particular, liquid electrolyte is being proposed now to be replaced by a new generation using a polymer electrolyte (allowing improved safety of use).

Figure 1. French professional organisations involved in the recovery and recycling of cells and storage batteries.



reactivity have been overcome: in particular, opening the containers. In other respects, the significant rise in use of *lithium-ion* batteries raises the question of how to adapt current pyrolysis technologies.

With regard to the recovery of new recyclable materials from *lithium-ion* batteries, the separation techniques required are complicated by the great variety of types (and composition) of batteries now marketed and by ongoing improvements to battery design. There are currently two ways of overcoming this additional difficulty: either a separation technique that would be appropriate for the mixture of all substances arising from non-differentiating collection, or early sorting specific to a separation technique adapted to a homogenous group of components. This latter method can only work if battery manufacturers and industrial organisations engaged in sorting technologies co-operate.

On the basis of this, the CEA has offered its expertise and know-how in waste processing so that these objectives can be reached. As part of a first stage, the methods based on the thermal destruction in complete safety of all *lithium-ion* type batteries sold to the general public can thus be studied.

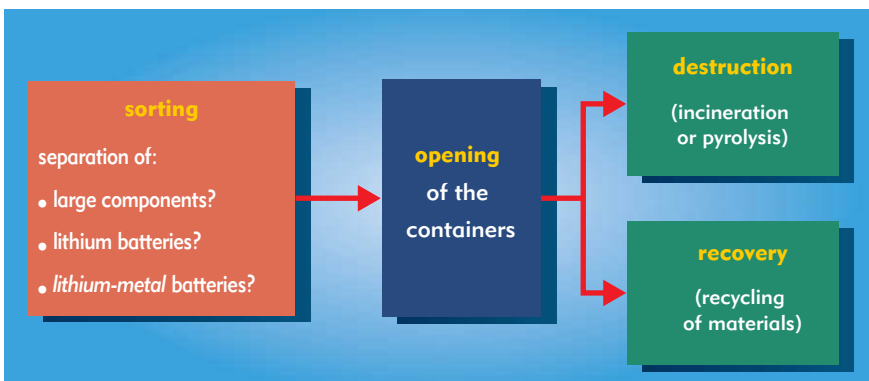
Finally, through two European projects, Brite-Euram and Growth, the CEA is directly involved in the design and installation of a certain number of processes: crushing and passivation of lithium and recovery of the active components of the positive electrode. For example, the CEA is involved with the Grenoble company, Recupyl, in the development of an innovative process allowing manganese oxides to be recovered from used lithium batteries for re-use as active positive electrode material.

Developing new processes

Processing or recycling of lithium batteries has certainly got off to a good start in France. However, today in Europe there is no process capable of destroying *lithium-metal* batteries (large types or large quantities of small models) in complete safety. The treatment of current stocks will only be possible when the main steps for stabilising their



Figure 2. Cell and storage battery processing and recycling methods.



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