INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

SMR.704 - 31

Workshop on Materials Science and Physics of Non-Conventional Energy Sources

(30 August - 17 September 1993)

"Batteries"

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BATTERIES

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Summary

After a brief illustration of the hystory and of the characteristics of the most common primary and secondary batteries, their impact on the present technology and on the enviromental control, will be discussed and evaluated.

1. INTRODUCTION.

When at the beginning of the 1880s, Alessandro Volta, Professor of Natural Philosophy at the University of Pavia, announced at the Royal Society of London the way of obtaining electric energy by combining copper and zinc disks with interposed a felt imbebbed by a salt solution, he certainly could not imagine the tremendous impact that his invention would have exherted on the modern technology. Effectively, the discovery of Volta has disclosed to the scientific world the route for energy conversion a,nd storage by electrochemical means, with the related important fallout in various aspects of our present industrial societies. In fact, although batteries are known since the early 19th century, the emergence of the microelectronics and the consequence of the evolution of large-scale integrated circuit with the growing popularity of portable electronic devices (from digital watches to audio and video recorders and to cordless telephones) have today enormously expanded the battery manufacturer industries and the entire field is still object of extensive and worldwide development and research. In addition, secondary batteries, such as the well-known lead-acid batteries, have been used for decades as power sources for car engine ignition and, in present days, their production has reached tonnage levels with annual sales which only in the United States exceed $ 1billion. Finally, the recent concerns in energy saving and in urban pollution, also promoted the development of special batteries capable of storing the energy produced by intermittent alternative sources or of providing the power needs for the traction of electric cars and vehicles. However, if from one side the present battery production has provided a satisfactory response to the energetic request of the consumer electronic and car market, from the other has also posed some serious problems, mostly related to ecological and safety aspects. In this paper we will first illustrate the present status of development of the battery technology, to then attempt to discuss the expected future improvements and, finally, outline the present concern on the collection and recycling management of exhausted batteries which are disposed every day by tons in the urban waste streams.

2. BASIC OPERATIONAL PRINCIPLES.

A battery is based on an electrochemical cell which enables the direct conversion of chemical energy into electricity. As schematized in Figure 1, an electrochemical cell is in its essency formed by two electrodes, one negative or *anode* and the other positive, or *cathode*, which are separated by an *electrolyte*, i.e. a medium containing mobile ions, generally being a liquid, aqueous or non-aqueous, salt solution or a ion-conducting solid. When the external circuit is closed through a load, namely when the cell is *discharged*, the overall electrochemical reaction, i.e. the redox process which is representative of a given battery system, proceeds essentially in two steps occuring at each of the cell's two electrodes: electrons are released at the anode (promoting the oxidation semi-reaction), flow through the external circuit and are consumed at the cathode (promoting the reduction semi-reaction). The circuit is closed by the ion transport through the electrolyte. Therefore, the electrochemical reaction can be represented as the sum of the anode and cathode semi-reactions. Accordingly, the *electromotive force*, E, or *open circuit voltage*, OCV, of the battery is given by the difference between the potential of the positive electrode and that of the negative electrode:

$$E = E_{+} - E_{-} \qquad [1]$$

A given electrochemical reaction can be characterized by the equilibrium free energy change ΔG, which, in turn, is related to the electromotive force E of the battery by the relation:

$$\Delta G = -nEF \qquad [2]$$

where n is the number of electrons involved in the reactions and F is the Faraday constant (96491 coulombs or 26.8 Ah). This equation provides the thermodynamic evidence of the direct relation between chemical energy, expressed by ΔG, and electric work, expressed by nEF.

The maximum amount of electricity which a given battery is capable to deliver is referred to as the *capacity* C and is measured in Ampere-hour, Ah. Correspondingly, the maximum deliverable energy is given by the product ExC and is expressed in watt-hours, Wh. Both the values of Ah and Wh are related through the Faraday's Law to the amount of reactants, *w*(in kilogram): the greater is this amount the longer the discharge current is sustained and thus, the higher are the Ah and the Wh delivered by the battery. In this way, the maximum (theoretical) capacity is given by:

$$C\ (\mathrm{Ah}) = \frac{nF\ (\text{coulombs mole}^{-1}) \times w\ (\mathrm{kg})}{M\ (\text{kgmole}^{-1}) \times 3600} \qquad [3]$$

where M is the molecular weight of the reactants.

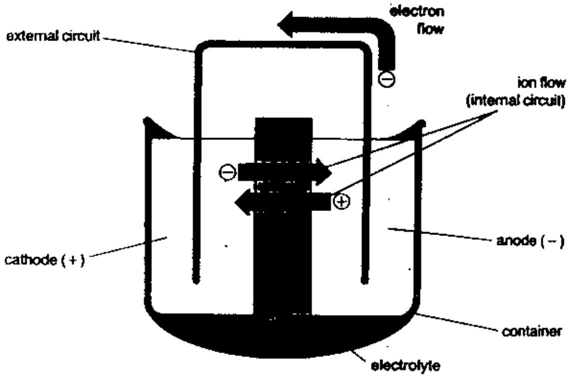


Figure 1 - Scheme of an electrochemical cell.

Under practical discharge conditions, both the operational voltage and the efficiency of the electrochemical reaction diminuish, this resulting from kinetics and mass transport limitations (charge transfer and mass diffusion overvoltages), and, thus, both the delivered practical capacity and energy depend upon cell construction and discharge characteristics. Therefore, rated energies and capacities, namely values referring to rated discharge modes, are generally reported and guaranteed by the battery manufacturer. The ranges of available values is extremely variable, passing from the 0.1 Wh of single cell batteries used for data retention in integrated circuits of computer memories to the 3 million Wh of batteries consisting of many cells in series and parallel arrays designed for propulsion of submarines and the 100 million Wh batteries planned for the electric power industry

Other important distintive parameters for batteries are the *specific power* Ps, and the *specific energy*, Es, namely the power or energy for unit weight *w* (kilogram) of reactants, which are measured in $\mathrm{Wkg^{-1}}$ and in $\mathrm{Whkg^{-1}}$, respectively. The maximum, theoretical value of E_S is given by:

$$E_S\ (\mathrm{Whkg^{-1}}) = \frac{E(\mathrm{V}) \times C\ (\mathrm{Ah})}{w\ (\text{kg of reactants})} \qquad [4]$$

and that of P_S by :

$$P_S\ (\mathrm{Wkg^{-1}}) = \frac{E\ (\mathrm{V}) \times I\ (\mathrm{A})}{w\ (\text{kg of reactants})} \qquad [5]$$

Obviously, also the practical values of P_S and E_S depend on the practical discharge regimes, being always lower that the theoretical ones and directly related one to each other: an increase in the former usually reflects in a decrease of the latter and the direct comparison between the two, displayed as a plot of P_S versus E_S (Ragone plot), is commonly reported as a figure of merit for a given battery. As an illustrative example, Figure 2 shows Ragone plots for few well-known types of batteries.

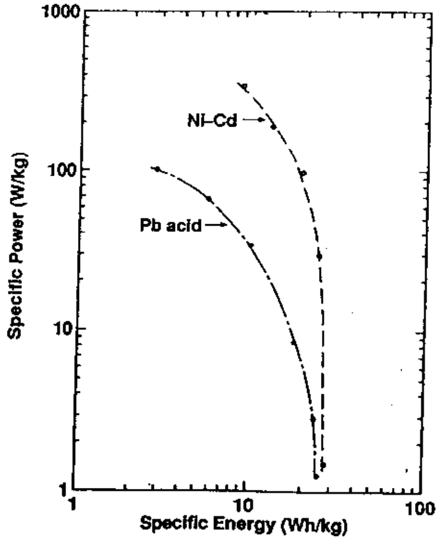


Figure 2 - Specific power vs. specific energy (Ragone Plot) of some common primary and secondary batteries at 25 °C.

A battery which cannot be reused when its amount of reagent has been totally consumed in discharge, is called a *primary* battery. Typical examples of primary batteries are the ordinary flash light or radio receiver zinc-carbon and the alkaline batteries. Once hexausted, these batteries must be disposed, and this may creates considerable enviromental concern (see following sections). A battery, which once discharged, can be made to go reverse, namely which can be *recharged* by an external source of electricity to its initial chemical energy content, is called a *secondary* battery. Such a batteries, which include the common lead-acid car battery, can be put through many charge-discharge cycles (the number of which determines their *cycle life*) and thus they can be used to store electric energy that had been generated by some other means. However, the life of secondary batteries is not indefinite and, therefore, also in this case the problem of safe disposal may eventually become crucial. In addition, an efficient exploitment of the secondary batteries especially in view of their use either as emergency power sources in fixed installations or as power storage for renewable natural energy sources or again as load-levelling systems in power plants or , and especially, as traction power for electric vehicles, requires values of specific energy which are far from those provided by the existing systems. Therefore, advanced secondary batteries, where the ratio between energy and weight is at least two times higher than that of the lead-acid battery, are urgently needed and, accordingly, consistent research efforts are presently devoted to reach this goal.

3. PRIMARY BATTERIES.

3.1 - Dry batteries.

Following the discovery of Volta, the French scientist Georges Leclanché introduced in 1860 his zinc-manganese dioxide cell, which, a part from some structural and design modifications, still provides the operational basis for the modern and popular dry cells produced by tonnages for the consumer electronic market in a varieties of sizes and capacities.

The Leclanché *carbon -zinc* cell is based on the following sequence:

$$\underset{(anode)}{Zn} \ / \ \underset{(electrolyte)}{ZnCl_2,\ NH_4Cl\ acq.} \ / \underset{(cathode)}{MnO_2,\ C} \qquad [6]$$

with an associated electrochemical reaction of the type:

$$Zn + MnO_2 + NH_4Cl \Longrightarrow MnO(OH) + Zn(NH_3)Cl \qquad [7]$$

and an open circuit voltage (OCV) varying at ambient temperature between 1.55V and 1.74V.

Although with a basic chemistry virtually identical to that proposed by Leclanché, the modern version of the battery involves the immobilization of the liquid electrolyte in a paste or gel (hence the denomination *dry* for this and similar batteries) which is mixed with the manganese dioxide cathode, as well as the replacement of the zinc anode rod by a zinc can that serves both electrode and container purposes. Figure 3 illustrates in comparison the original form of the Leclanché zinc-manganese dioxide with that the modern zinc-carbon variant and Figure 4 shows in scheme the most common sizes in which these batteries are today produced.

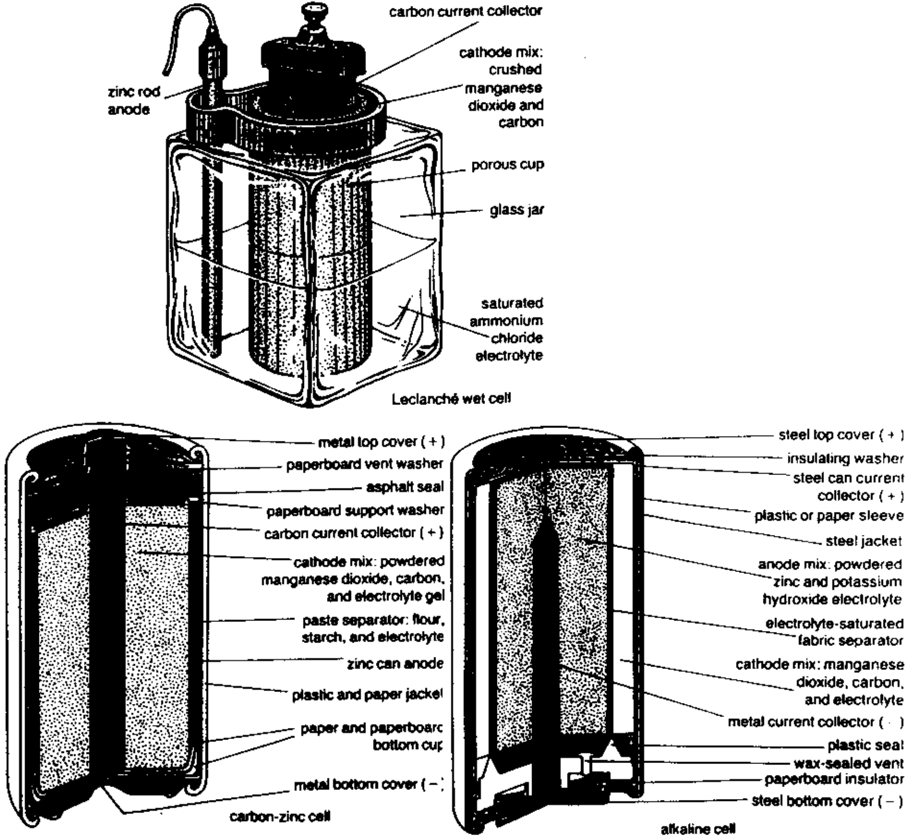


Figure 3- The original form of the Leclanché zinc-manganese dioxide compared with two modern versions, the carbon-zinc and the alkaline cells.

(From : C.A. Vincent, "Batteries-a technology recharged", Encyclopaedia Britannica, 1986, YB 126.)

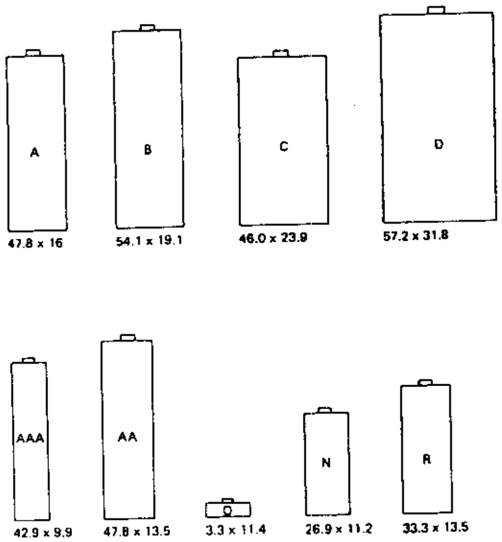


Figure 4- The various sizes of dry cells today in the market.
(*From: C.A.Vincent, F.Bonino, M.Lazzari and B.Scrosati,"Modern Batteries", Arnold Pu.,London, 1987*)

Another increasing popular variant of the Leclanché zinc-manganese dioxide cell is the so called alkaline cell which is based on the scheme:

$$\underset{(anode)}{Zn} \;/\; \underset{(electrolyte)}{KOH\ acq.} \;/\; \underset{(cathode)}{MnO_2,\ C} \qquad [8]$$

with an associated electrochemical reaction:

$$2Zn + 2MnO_2 + H_2O \Longrightarrow 2MnO(OH) + 2ZnO \qquad [9]$$

and an OCV = 1.55V at ambient temperature.
The modern structure of this cell (Fig. 3) uses the carbon-zinc design turned inside out, namely a core of powdered zinc and an alkaline electrolyte separated by a fabric separator from an outer layer of manganese dioxide and electrolyte. Since the electrolyte is based on potassium hydroxide,i.e. a strong corrosive agent, the cell necessitates of an expensive steel case and of a well-engineering sealing assembly.

Another commercially important aqueous system is the *zinc-mercury oxide* battery, invented in 1945 by the American scientist Samuel Ruben. This battery, sometime also named *mercury* or *Ruben-Mallory* battery, is based on the following scheme:

$$\underset{(anode)}{Zn\ (Hg)} \;/\; \underset{(electrolyte)}{KOH\ acq.} \;/\; \underset{(cathode)}{HgO,\ C} \qquad [10]$$

with the associated electrochemical reaction:

$$Zn + HgO \Longrightarrow ZnO + Hg \qquad [11]$$

and an OCV equal to 1.36 V at ambient temperature.
The battery is mainly fabricated as low-drain, button cell, with a construction realized by piling in an stainless-steel container a pellet of amalgamated zinc, a concentrated potassium hydroxide aqueous solution immobilized in a felt and a pellet of a mercury oxide-carbon mixture (Figure 5).

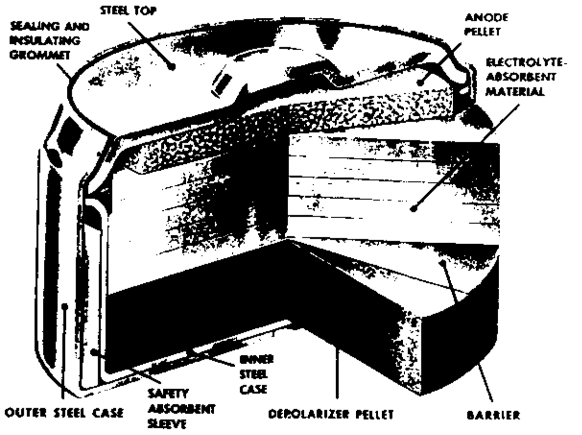


Figure 5 - Typical configuration of a button-size, pressed-powder zinc-mercury oxide cell.
(*From: G.V.Heise and N.C.Cahoon , "The Primary Battery", John Wiley & Sons, New York, 1971*).

The main specific characteristics of this battery is that the electrolyte is not consumed during the discharge (see scheme [11]). This, together with the high density of HgO, makes possible very compact cell structures with resulting batteries having high *volumetric energy* *density* (expressed in $Whcm^{-3}$) and discharge voltages which remain constant during almost all of their useful life, as illustrated by the typical, low-rate discharge curve illustrated in Figure 6.

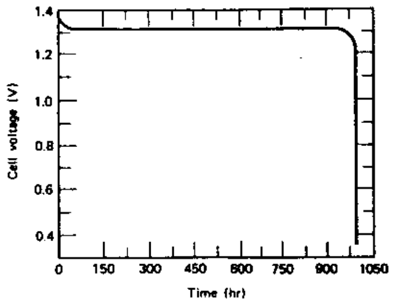


Figure 6- Typical low-rate (1350 ohm load) discharge curve at room temperature of a zinc-mercury cell of 1Ah nominal capacity. (*From: G.V.Heise and N.C.Cahoon , "The Primary Battery", John Wiley & Sons, New York, 1971*).

However, the high cost and, especially, the enviromental risk associated to the large quantity of mercury content have progressively limited the diffusion of this battery in favour of other high energy, compact and cleaner systems.

3.2 -Metal-air batteries.

In view of the growing popularity of microelectronics, the prime objective of the today battery industry is that of producing miniature batteries with a design capable of packing as much energy as possible. A convenient way of reaching this goal is that of using atmospheric oxygen by making it to diffuse into the cell as the cathode reactant. Oxygen has a high specific capacity , is obviously an abundant and cheap reactant and its direct use from the atmosphere eliminates the need for the cathode container (which remains restricted to the sole current collector (usually a porous carbon impregnated by a suitable catalyst), this resulting into an increased volume available for the anode, most commonly zinc. All this translates in a considerable increase of the overall energy density.

Cells using this principle, named *metal-air* batteries, have been effectively known for more than a century, since originally developed for railway use and for operation radio sets in areas where power lines had not yet penetrated, and, in more modern

times, for mine, off-shore and on-shore markers, buoys, telephone, telegraph and radio operations.

The most common version utilizes a zinc anode and a concentrated sodium hydroxide aqueous solution, to obtain a general scheme of the type:

$$\underset{(anode)}{Zn\ (Hg)}\ /\ \underset{(electrolyte)}{NaOH\ acq.}\ /\underset{(cathode)}{O_2,\ C} \qquad [12]$$

The electrochemical reaction is the result of the sequence of somewhat complicated steps that can be summarized as follows:

at the cathode:
1) reduction of oxygen adsorbed on the active electrode surface with the formation of hydroxyl ions:

$$O_2 + 2H_2O + 4e^- ==> 4\ OH^- \qquad [13]$$

at the anode:

oxidation of zinc to zinc oxide :

$$2Zn + 8OH^- ==> 2Zn(OH)_4^{2-} + 4e^- \qquad [14]$$

$$2Zn(OH)_4^{2-} ==> 2ZnO + 4OH^- + 2H_2O \qquad [15]$$

with an overall cell reaction:

$$2Zn + O_2 ==> 2ZnO \qquad [16]$$

and a nominal OCV of about 1.4 V at room temperature.

The above outlined discharge mechanism evidences the key role of the carbon current colector cathode since the optimization of its composition and morphology is crucial for favouring the absorption of the atmospheric oxygen and its diffusion at the interface (role of the porosity), to favour the cathodic reduction of oxygen to hydroxyl ions at the active interface (role of the catalyst) and to facilitate the removal of these ions from the interface. Figure 7 shows the cross section of a common zinc-air battery which evidences the multilayer constraction of the cathodic side

The production of zinc-air cells is today mostly directed to button-size, dry (electrolyte immobilized by starch) batteries using a high performance oxygen electrode consisting of a teflon-bonded catalyst composite covered with a gas-permeable waterproof membran. These batteries, which have a very high energy density, are particularly suitable for powering medical devices such as hearing aids.

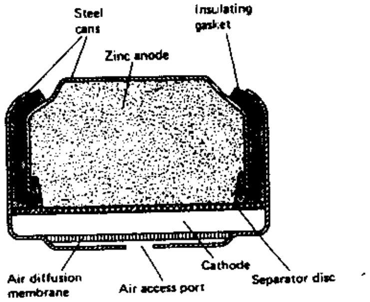


Figure 7- Cross section of a zinc-air button cell.
(From: C.A.Vincent, F.Bonino, M.Lazzari and B.Scrosati,"Modern Batteries", Arnold Pu.,London, 1987)

3.3 - Lithium batteries.

In the development of advanced high-energy, small-size batteries since the microelectronic market, a leading position has been today attained by lithium batteries. While having discharge characteristics as good as those of best mercury miniature batteries, lithium batteries offer the extra bonus of higher specific energy and capability of operating at lower temperature ranges. Lithium is the lightest metal element with a very high specific capacity (3.86 Ahg^{-1} and 7.23 $Ahcm^{-3}$), so that individual lithium cells supply about 3V compared with the common 1.5V delivered by the mercury and other dry-cells, this resulting in an immediate advantage in terms of packageable energy. Furthermore, lithium is a relatively abundant metal of contained toxicity and this gives expectations of moderate cost and of enviromental tolerance. On the other hand, the high energetic potentialities pose lithium among the most reactive metals. For instance, lithium reacts vigorously with water so that lithium cells must use nonaqueous electrolytes, both in the liquid (e.g., solutions of lithium salts in aprotic organic solvents) or in the solid (e. g., defective lithium salt crystals) state and must be assembled in humidity-free enviroments (dry rooms).

Among the most successful lithium batteries figures the *lithium-iodine* battery assembled by posing in direct contact metallic lithium (anode) with a compound formed by the combination of poly-2-vynilpyridine (thereafter simlpy abbreviated as P2VP) and iodine, in the $P2VP.8I_2$ composition (cathode). The compound is capable of releasing iodine and thus, at the contact between the two electrodes, lithium reacts with iodine to form a

separating layer of lithium iodide, LiI, which also serves as the electrolyte since cabable of carrying current by migration of lithium-ion vacancies through its crystal lattice.

Therefore, the scheme of the battery is:

$$\underset{(anode)}{Li} \; / \underset{(electrolyte)}{LiI\ solid.} / \underset{(cathode)}{P2VP.8I_2\ ,\ C} \qquad [17]$$

with the following electrochemical reaction:

$$14\ Li + P2VP.8I_2 \Longrightarrow 14\ LiI + P2VP.I_2 \qquad [18]$$

to which is associated an OCV of 2.8V at room temperature.

Lithium iodine solid-state cells, which are housed in ermetically sealed containers, have excellent storage life, i.e. exceeding ten years; however, the high electric resistance of the electrolyte confines their use to low current drain applications. On the other hand, the high reliability (absence of electrolyte leakage or gas generation) makes the lithium-iodine batteries ideal for powering implantable medical devices (Figure 8).

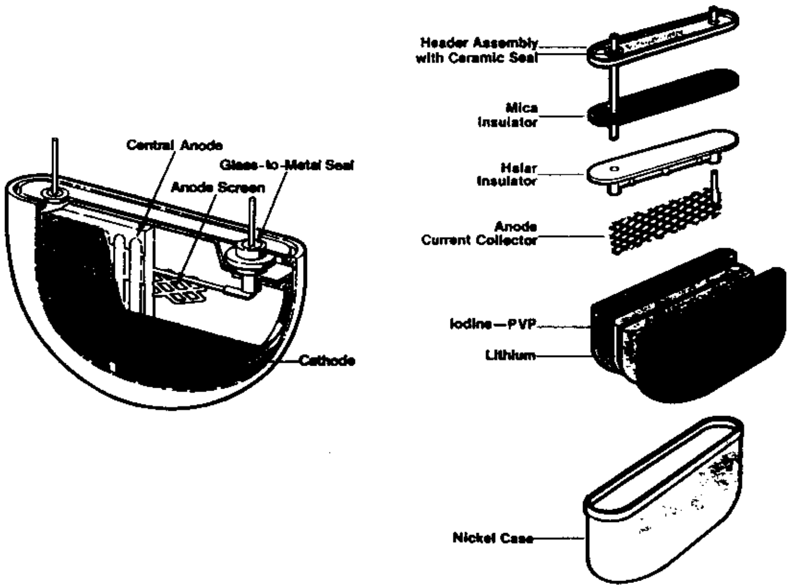


Figure 8- Scheme and exploded view of a solid-state lithium-iodine battery designed for pacemaker use.
(From: Batteries for Implantable Biomedical Devices, B.B.Owens Ed., Plenum Press, New York, 1986.

Today, almost the totality of pacemakers are powered by this type of batteries, which, in a suitable, low-volume (about six cubic centimeters) design (Figure 8) and under typical "demand" conditions (i.e., operation only under detection of irregular heartbeats), assures a lifetime of a decade .

Beside lithium-iodine, many are the primary lithium batteries currently under production for a variety of applications in the consumer electronic market. All these batteries employ lithium as the anode but differs for the cathode material and for the electrolyte used . A popular example is the *lithium-manganese oxide* battery, initially introduced in the market in 1975 by the Sanyo Japanese industry and today produced and commercialized by various European and American industries. The battery may be schematized as:

$$\underset{(anode)}{\mathrm{Li}} \;/\; \underset{(electrolyte)}{\mathrm{LiBF_4\ in\ PC\text{-}DME\ liquid}} \;/\underset{(cathode)}{\mathrm{MnO_2}\ ,\ \mathrm{C}} \qquad [19]$$

where PC= propylen carbonate and DME=1,2-dimethoxyethane are the aprotic organic solvents used to dissolve the lithium tetrafluoro borate salt to form the liquid electrolyte. The electrochemical reaction may be written as:

$$\mathrm{Li + MnO_2 \Longrightarrow LiMnO_2} \qquad [20]$$

with an associated OCV around 3.0.V

The lithium-manganese dioxide batteries are generally produced in various button-size types (Figure 9) as ideal power sources for digital watches, automated photographic equipments, pocket calculators and tape recorders.

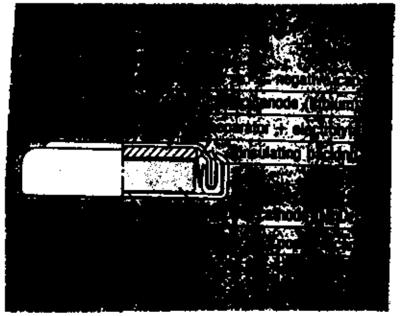


Figure 9 - Scheme of a button-size lithium-manganese dioxide battery.
(*From.:.Sanyo Electric Co. Bulletin, 1992*)

Other types of lithium batteries are based on a variety of solid, liquid, and soluble cathodes . The latter uses both gases, such as sulfur dioxide dissolved in a suitable electrolyte, or liquids, such as thionyl chloride which acts both as the active cathode material and the solvent for the electrolyte salt (e.g. lithium aluminum chloride, $LiAlCl_4$). These liquid-depolarizer lithium batteries have outstanding performance in terms of temperature range of operation and of discharge rates. Despite the fact that lithium is in direct contact with aggressive cathode materials, the formation of a protective film (passivation layer) at the lithium interface prevents significant self-discharge assuring long shelf life (Figure 10). The lithium - thionyl chloride and lithium-sulphur oxide batteries are generally fabricated in cylindrical sizes with rated energies as high as 75 Wh. However, the realibilty of these batteries is limited; for instance, under abuses (prolonged short-circuiting, reverse polarity, etc.) the batteries may explode or vent toxic gas. Therefore, the penetration of liquid depolarizer lithium batteries has been limited to the military market where high power density is the highest request and the major advantage, while the civil use has been almost inexistent due to safety considerations.

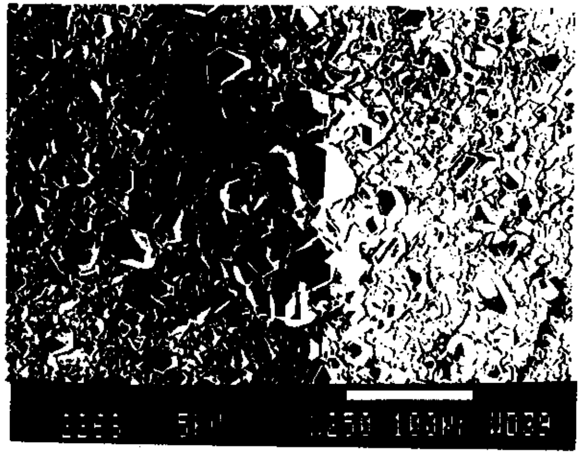


Figure 10 - Scanning Electron Microscope photograph of the passivation layer (formed by LiCl crystals) covering the lithium electrolde in thionyl chloride batteries.

In general, and as already stressed, the specific energy of lithium batteries is considerably higher than that of the common aqueous dry cells. For instance, a typical lithium-thionyl chloride D-size (see

Fig. 4 for dimensions) has a rated energy output of 34 Wh, compared to the average 5 Wh for a standard Leclanché zinc-carbon cell and the 12Wh for an alkaline cell of the same size. However, although progressively falling as the production rises, the cost of lithium batteries is still comparatively high and this still limits their widespread diffusion. On the other hand, the toxic nature of mercury and the present concern on the ecological risks associated to the disposal of the dry-batteries constantly reduces their competitiveness in favour of alternative systems, such as the lithium batteries, which give expectation of better enviromental tolerance.

4. DISPOSAL AND WASTE OF EXHAUSTED PRIMARY BATTERIES.

The production of dry batteries, directed to household portable electronic devices, has reached impressive levels. Only in Italy, the dry battery market is estimated to be approximately 383 millions units per year (Figure 11). The most used are the zinc-carbon and the alkaline/manganese dry cells, which alone contribute to more than 90% of the total national market. While these two cells are used for mass consumption, the mercury and the silver-zinc cells are directed to a somewhat more specialized market, namely as power sources for sophisticated devices, such as expensive cameras, medical and military equipment.

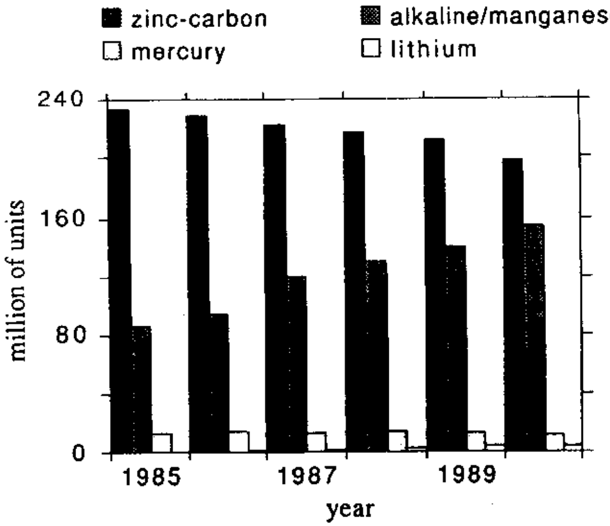


Fig. 1- Evolution of the Italian market of dry batteries during recent years.
(*From: M.Barbenni et.al., ECO IX (5) (1991) 26*)

As well known and also clearly shown in Table 1, which summarizes the characteristics of the most common commercial dry cells, all the traditional dry batteries use zinc as negative electrode. In fact, this metal offers a serie of advantages as electrode material, which include a favourable electrochemical factor (i.e. a favourable ratio between potential and mass), a relatively low cost and versatile processability. However, to prevent corrosion and to increase the mechanical resistance of the zinc (which in the case of zinc-carbon cells, acts both as electrode and as the container), it is necessary to amalgate its surface with mercury and to add to the system small quantities of cadmium. Therefore, these heavy metals are inevitably present, even if at different levels and concentrations, in all the dry cells of the current production (see Table 1).

TABLE 1-Characteristics of the most common commercial dry cells.

type	negative electrode	positive electrode	electrolyte (aqueous immobilized)	OCV (V)	content in heavy metals (wt%) Hg	Cd
Zinc-carbon	Zn	MnO_2/C	$NH_4Cl, ZnCl_2$	1.50	0.01	0.005
Alkaline/ manganese	Zn	MnO	KOH	1.50	0.025	
Mercury	Zn	HgO	KOH	1.3	30	
Silver-zinc	Zn	AgO	KOH	1.5	1	

The related enviromental hazard is well known: mercury and cadmium are very toxic metals and thus liable to induce serious risk for the health of the population and for the equilibrium of the territory. Therefore, in the most recent years there has been an increasing concern on the enviromental risk associated to the uncontrolled disposal of the exhausted batteries.

The major battery producing companies have responded to the ecological concern by progressively reducing the content in heavy metals from their commercial products and, indeed, consistent improvements have been achieved in the latest years. In fact, passing from 1988 to 1990 the mercury and cadmium content in dry batteries sold for mass consumption has been reduced of almost 50% both in the case of zinc-carbon (Figure 12) and in that of alkaline/manganese(Figure 13) cells.

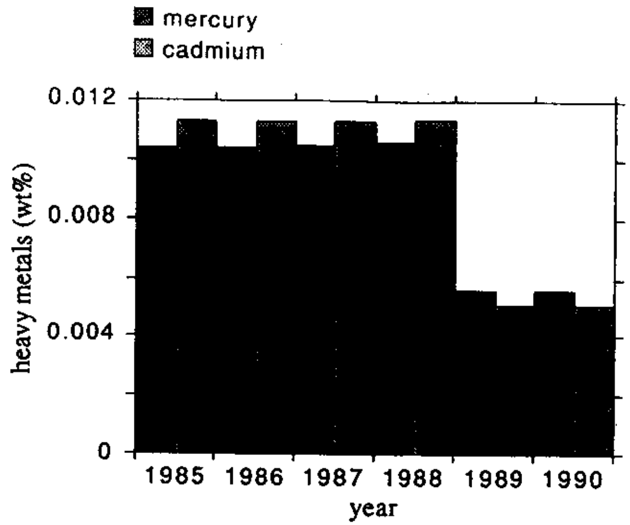


Fig. 12-Variation during the 1985-1990 period of mercury and cadmium content(weight percent, wt%) in zinc-carbon dry cells.

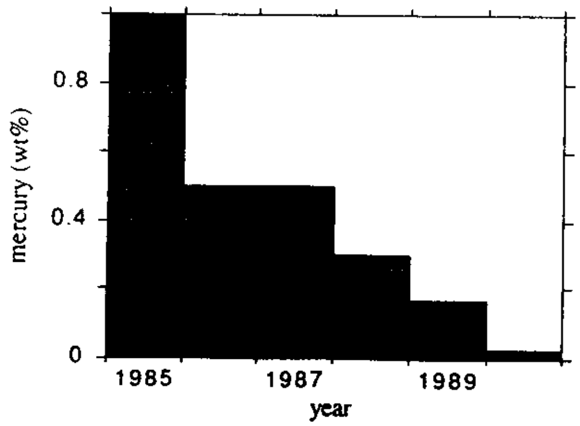


Fig.13- Variation during the 1985-1990 period of mercury content (weight percent, wt%) in alkaline/manganese dry cells.

Today most of the leading dry battery manufacturers label their products as "mercury-free" or as "green" batteries, this effectively meaning that the content in the heavy metal has been reduced below 0.025 weight percent (w/o). This has been confirmed by a spotted analysis which gave the results reported in Figure 14.

PILA	Mn	Zn	Hg	Cd	Pb	Ni
1	19,96	18,16	0,047	0,0059	0,0246	0,32
2	11,25	34,3	0,08	0,0043	0,0265	0,006
3	4,35	27,91	0	0,006	0,065	0,0096
4	11	46,075	0,015	0,024	0,26	0,0165
5	10,07	23,03	0	0,02	0,064	0,0132
6	6,47	27,05	0	0,0057	0,06	0,04
7	6,36	18,5	0	0,0077	0,114	0,029

I dati sono espressi in % (w/w)

Figure 14 - ICP analysis of the heavy metal content in a series of seven commercial dry batteries produced by different manufacturers.
(*From: M.Achilli, E.Cardarelli and B.Scrosati, unpublished results*).

This is certainly a promising result which, however, has to be taken with some care since deduced from average figures and without considering batteries arriving from countries where control in the content in heavy metals may not be a major effort and which may still represent a significant fraction of the total sale in Europe.

4.2- Present efforts in Europe for assuring the controlled disposal of exhausted dry batteries.

The above considerations suggest that, although in average containing a limited amount of heavy metals, the exhausted batteries cannot be simply damped in common landfills. A proper enviromental control requires an appropriate disposal, such as that which can be obtained with a separate collection of the exhausted batteries.

Accordingly, in 1991 the European Communities passed directions to the member Countries for issuing a legislation on the valorization and on the disposal of batteries containing hazardous materials. In synthesis, the draft imposed to the members the elaboration of a common programme for the achievement of the following main goals:

i) reduction of the heavy metal content in dry and rechargeable household batteries;

ii) promotion and commercialization of new batteries with reduced amount of hazardous materials and/or based on non-polluting components;

iii) promotion of research activities directed to the reduction of the content of hazardous materials in batteries and on their replacement with non-polluting materials, as well as on the development of appropriate recycling systems;

iv) progressive reduction of the amount of exhausted batteries which may be directly included in the total urban waste;

v) separate collection and disposal of the exhausted batteries having content in mercury, cadmium and lead exceeding the fixed limits.

TABLE 2- Activities on selective collection and disposal of exhausted dry batteries in some Italian cities.

City	inhabitants (millions)	number of containers	amount collected (tonnes/year)	percentage total consumption (%, estimated)	disposal procedure
Milan	1.5	537 (street) 600 (others)	78	18	N.SAMIM
Padua	0.3	527 (street) 407 (others)	40	43	N.SAMIM
Modena (+ suburbs)	0.5	97 (street) 337(others)	25	27	N.SAMIM SORARO
Bologna	0.5	112 (street) 1,234(others)	46	30	N.SAMIM SORARO
Rome	2.5	900(street)	58	8	N.SAMIM
Naples	1.3	separate collection planned			
Palermo	0.8	250 (street) 400(others)	planned to start in October 1991		

Source: local municipalities., 1992

Earlier than this EEC draft, namely in 1984, the Italian Government had already passed a law which listed the exhausted dry batteries in the category of hazardous wastes and which required their separate collection from the other solid urban waste. However, despite the fact that the low is in force since few years , the results have not been very encouraging: the separate collections amounts only to 20-30% of the total battery consumption in Italy(Table 2). Comparable low success has also been experienced by other Countries where similar separate collection programmes have been established(Table 3).

TABLE 3- Status of exhausted battery disposal and recycling in various countries.

Country State	type of battery collected	diversion rate (% of units sold)
Germany	mixed	15 (by weight)
Italy	mixed	20-30
Netherlands	mixed	25
Sweden	mercury NiCd alkaline	96 37 30
Switzerland	button mixed	80 35
Japan	mixed cylindrical button NiCd	7 12 2

Source : 2nd and 3rd International Seminar on Battery Waste Management (1990,1991). S.Wolsky Ed., Florida, USA

There are various reasons, mainly related to promotional and economic aspects, which may account for such a discouraging result. In fact, a successful treatment of the exhausted batteries requires the promotion of an adequate and persistent campaign to solicit the public opinion on the opportunity of the separate disposal, as well as a consistent investiment for assuring both a widespread collection and efficient disposal.

Not all the municipalities are capable of sustaining these efforts. For instance, in Italy the promotion campaign is still very limited; furthermore, the feeble attempts to convince the public opinion to take a little extra effort to dispose the used batteries in separated containers, are vigourously contrasted by an opposite campaign from the battery manufacturers.

Another and perhaps more crucial apect for the success of the separate collections is the cost of the entire operation, which includes the purchasing and the installation of special street containers and all the related management expenses. Consequently, only the richest municipalities have had so far the possibility of affording an efficient and widespread battery collection policy. In fact, it is not surprising that the most successful results have been achieved in the North and in the Center of Italy, namely in the regions which are traditionally the wealthest in the Country. In the South, where most of the cities are still affected by serious economical and social problems, the separate collection of batteries is still an action to be started or even to be programmed.

4.2 Collecting and recycling procedures in Europe.

One of the major problems which presently prevents the satisfactory completion of the battery waste cycle, is the lack of operating treatment and recycling plants. As evidenced by Table 2, almost the totality of the Italian cities uses the Nuova Samim Company, as preferred partner for the disposal of the exhausted batteries. The Company collects the batteries from the various with the intention to recycle them in a treatment plant which should have a capacity of 3 tonnes/year in a continuous cycle, with a maximum treatment capacity of 20,000 tonnes/year. Unfortunately, the plant is still in the planning stage and the dates of its construction and operation are not yet certain; thus, at the present the Nuova Samim is acting only as a main point of stockage of the battery waste.

The situation is not particularly encouraging also in other European countries. Only few battery recycling plants are at the moment in operation in Europe, mostly concentrated in Switzerland. The location is not casual since Switzerland is one of the few Countries where it is forbidden by law to landfill or incenerate the collected battery waste, and this circumstance has certainly played a crucial role in promoting the starting of large-scale recycling processes. .

Another battery recycling plant is apparently under construction in Austria with full operation planned by 1993. Again, the construction has been motivated by local government laws; in fact, since July1991 is mandatory in Austria to return the exhausted batteries to the buying points (shops or supermarkets) which in turn calls for the urgent availability of means of disposing the stocked wastes.

To our knowledge, no other plants are presently under development in Europe and since the Swiss and the Austrian plants will be barely capable of treating the battery waste of the two

home countries, the future of battery disposal in overall Europe is certainly not bright. The key question is what will it happen in the next years when, according to the EEC Directory, the separate collection of the exhausted batteries will became mandatory in all the member Countries. The answers are either a continuous accumulation of hazardous materials with unpredictable impact on the ecological equilibrium or the urgent development of efficient, high capacity, recycling plants throughout the European countries. It is sad to observe that at the present there are no signs indicating that the second will be the winning answer.

5. SECONDARY BATTERIES.

5.1- Common aqueous systems.

5.1.1- The lead-acid battery..

The history of secondary, rechargeable batteries begun in 1859 with the discovery by the French scientist Gaston Planté of the *lead-acid battery*, namely of the still the most popular electrochemical storage system, currently used as starting, lighting and ignition (SLI) battery in any type of vehicle.

The lead-acid battery is basically formed by a lead negative electrode, a lead dioxide positive electrode and an aqueous sulfuric acic electrolyte solution:

$$\underset{\text{(negative)}}{Pb} \;/\; \underset{\text{(electrolyte)}}{H_2SO_4\ \text{acq}} \;/\; \underset{\text{(positive)}}{PbO_2} \qquad [21]$$

with the following, reversible electrochemical reaction:

$$Pb + PbO_2 + 2H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{<===>}} 2PbSO_4 + 2H_2O \qquad [22]$$

and an OCV varying from 2.15 V in the charged state to 1.98V in the discharged state.

The most common configuration has six cells connected in series in order to obtain batteries with a nominal voltage of 12V, i.e. the automobile operational voltage. The six cell array is realized by interleaving groups of negative and of positive electrodes, kept in position by spacers and fabric separators. The array is then housed in a polypropylene container, filled with the electrolyte and top-sealed (Figure 15).

In the old versions the top part was also equipped with feed-through openings for periodical water tappings to compensate losses during charge cycles . Consistent improvements have been achieved in the last 20 years: the use of low-antimony, calcium-lead electrode grids has practically eliminated the water loss and today lead-acid batteries are fabricated in sealed, maintanence-free configuration. Figure 16 compares this configuration with the original Planté's cell and with an early 1950s 6V battery.

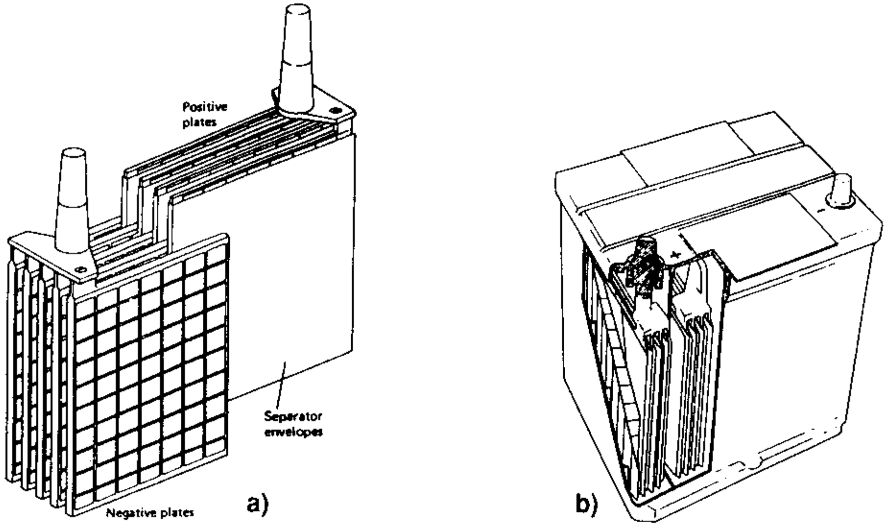


FIGURE 15 - Scheme of lead-acid battery assemblage. a)Interleaving of positive and negative electrode groups. b) Cutaway of a typical SLI battery.
(From: C.A.Vincent, F.Bonino, M.Lazzari and B.Scrosati,"Modern Batteries", Arnold Pu.,London, 1987)

Figure 16- Evolution of the lead-acid battery: the original Planté lead-acid cell is compared with an early 1950s 6V version and with a modern, 12V, maintanance-free version.
(From : C A. Vincent, "Batteries-a technology recharged", Encyclopaedia Britannica, 1986, YB

5..1.2- The nickel-cadmium battery.

Another important event in the development of storage batteries is the discovery of the *nickel-cadmium battery* by the Swedish scientist Waldemar Junger. Also this battery, which is often shortened as *nicad* battery, after some constructive improvements, is still a very popular storage system especially as power source for cordless consumer electronics, such as power tools, personal computers and portable telephones.

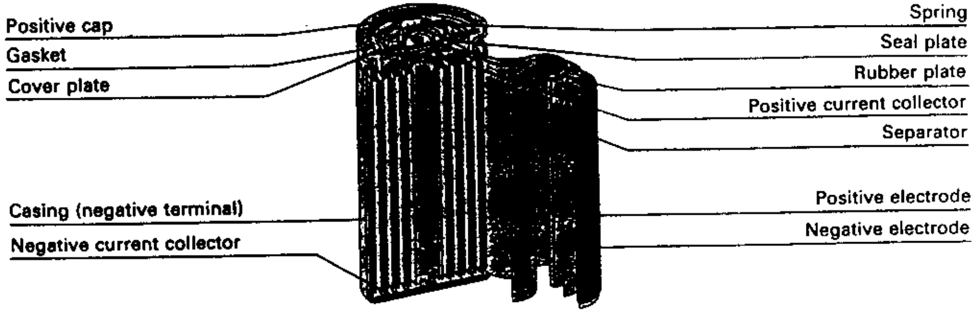


Figure 17 - Structural design of the nicad battery in the most common version.
(From: Sanyo Electric Co. Bulletin, 1991)

The basic scheme of the battery is:

$$\underset{\text{(negative)}}{Cd\,/}\quad \underset{\text{(electrolyte)}}{KOH\ acq}\quad \underset{\text{(positive)}}{/\,NiO(OH)} \qquad [23]$$

with the following, reversible electrochemical reaction:

$$Cd + 2\,NiO(OH) + 2H_2O \underset{\text{charge}}{\overset{\text{discharge}}{<===>}} Cd(OH)_2 + 2\,Ni(OH)_2 \qquad [24]$$

and an associate average OCV of 1.30V at room temperature.

The today versions of the battery are mostly in sealed, maintainance-free C or D sizes (Figure 17). These batteries are widely diffused in the market; however, the growing concern on the cadmium toxicity raises some questions on the opportunity of keeping their production at the actual levels.

5.2 - Advanced rechargeable batteries.

Quite important expectations are today posed in electrochemical batteries and in their role for the solution of various crucial problems which affects our technological societies, such as improvements in the quality of life and optimization of the energy management. In fact, in addition to the enviromental attention, also increasing concern with global energy resources require the sustaining action of batteries. Renewable natural sources, such as solar and wind, may consistently contribute to reduce pollution and to decrease the dependence from fossil fuels. However, these are intermittent sources which require a mean of storing energy during the active periods to reused it during the inactive hours. Requirement for ancillary energy storage is also growing in traditional power plants, where the demand varies during the 24-hours cycle, peaking in day time and decaying at night. The efficiency and the economy of the plant may be improved by a load-leveling action, namely by operating above minimum demand at night and storing the surplus to meet the daylight peak demand. Although various methods of storing energy , such as water pumping, gas compression, etc, are in principle available, electrochemical batteries appear ideal for both sustaining intermittent energy resources and load leveling operations. In fact, batteries are silent, versatile and modular in design. The today available prototypes, however, are unable to meet the energy density and cycle life levels for being successfully adopted for these operations.

Batteries are also urgently requested to favour the large penetration of electrically powered car in urban areas to replace the inefficient and polluting internal combustion vehicles. illustrative in this respect is the case of the city of Los Angeles which has recently passed an act according to which 2% of the total circulating vehicles must pass by 1998 from internal combustion (i.e. gasoline) to zero emission (i.e., electric) engine, with this fraction to extended up 10% by 2003.

Unfortunately, a major drawback limits the performance of the present batteries in view of their application in the electric vehicle field, namely the low value of the specific energy (see eq.[4]). For instance, the specific energy of the lead-acid battery does not exceed the 20-30 Whkg^{-1} (see Table 3), a far too low value to compete with that of fuel: to deliver the same energy supplied by a liter of gasoline would require a lead-acid battery weighing about 40 kilograms. The immediate results is that the direct use of this battery can provide only very limited authonomy: lead-acid powered electric car of the same size of the common passenger vehicles may run only for 40-60 kilometers, a too short range for being of interest for the average custmer.

Table 3- Characteristics of some storage batteries.

battery	temperature of operation	average voltage(V)	specific energy (Whkg^{-1})	
			theoretical	achievable
Lead-acid	room	2.0	161	30-40
Nicad	room	1.3	209	40-60
Ni-MH	room	1.3	216	50-60
sodium-sulfur	350°C		790	100-140
LiAl-FeS$_2$	400-450°C	1.4	650	80-100
Li-TiS$_2$	room	2.3	480	80-100
Li-MoS$_2$	room	1.8	300	50
Li-ion (C-LiCoO$_2$)	room	3.6		80
Li-polim(Li-V$_6$O$_{13}$)	100°C	2.4	860	100-150

In addition to high specific density, also long cycle lifetime, high cycling efficiency and high peak power output, are the requirements for a suitable electric vehicle battery and, therefore, the competitivity of the electric transport relies on the availability of advanced electrochemical systems. This is again clearly demonstrated by the Los Angeles case, where the key role of this availability has been fully recognized by the establishment in 1992 of a consortium between three major car companies (i.e., Chrysler, Ford and General Motors) and two Governement Agencies (Department of Energy and Electric Power Research institute), named USABC (United States Advanced Battery Consortium) to promote with massive financial support the large scale development of four systems identified as the most promising for the fabrication of advanced, electric vehicle batteries (see Figure 18) . Some of the most interesting examples of advanced batteries will be illustrated in the following sections.

Table I
US ABC Battery Criteria

Characteristic	Mid-Term*	Long Term**
Specific energy, Wh/kg	80-100	200
Specific Power, W/kg	150-200	400
Power Density, W/l	250	600
Lifetime, years	5	10
Cycle Life (at 80% DOD)	600	1000
Recharge Time, hours	<6	3-6
Ultimate Price, $/kWh	<150	<100

*Mid-term means a battery that demonstrates the above criteria in vehicle road tests, using prototype production batteries from a pilot plant by mid-1994.

**Long term means a battery that demonstrates the above criteria in vehicle tests using full-scale experimental batteries by mid-1994.

Sodium/Sulfur Battery

Specific Energy (cells), Wh/kg	120-180
Specific Power (cells), W/kg	80-160
Lifetime (cells), years	1-2
Cycle Life (cells)	500-2000
Recharge Time, hours	<6

These cells operate at 350 °C, and use a ceramic ($Na_2O \cdot 11Al_2O_3$, beta alumina) electrolyte.

The above data are for individual cells. Data for complete batteries are much less well-established. A number of electric vehicles powered by Na/S batteries have been demonstrated, but performance, cost, and lifetime data are generally unavailable.

Lithium/Polymer/Organosulfur Battery

Specific Energy (projected), Wh/kg	200
Specific Power (projected), W/kg	400
Lifetime (projected), years	several
Cycle Life (lab cells)	300+

These cells are in an early stage of development, and this is but one example of a whole family of cells that use lithium or a lithium alloy or intercalate as the negative electrode, a polymeric electrolyte, and any number of reactants at the positive electrode (eg. V_6O_{13}, TiS_2, organosulfur polymers, MnO_2, graphite). This family of cells has the advantage of being all-solid-state, and relatively safe. They are thin-film cells, and many would be assembled together to produce multi-layered modules.

Lithium/Iron Disulfide Battery

Specific Energy (cells), Wh/kg	180-200
Specific Power (cells), W/kg	~200
Lifetime (cells), years	~1
Cycle Life (cells)	>1000
Recharge Time, hours	<6

These cells use a molten salt mixture as the electrolyte and operate at 400 °C. The above data are for individual cells. No vehicle-sized batteries have been tested, though limited testing of the related LiAl/FeS has been performed. This system is in an earlier state of development than the Na/S system.

Zinc/Nickel Oxide Battery

Specific Energy, Wh/kg	60-80
Specific Power, W/kg	200-300
Cycle Life (100% DOD)	>500
Recharge Time, hours	<6

These cells have shown recent progress in terms of longer cycle life, operation as sealed and maintenance-free. Various manufacturers have tested electric vehicles powered by these batteries with the finding that the performance was excellent, but the cycle life (then, ~300 cycles) was too short.

Figure 18-The four USABC-selected advanced batteries and their expected performances;
(*From: E.J.Cairns,ECS Quarterly, Jan 1992, pag. 24*)

5.2.1- The nickel-metal hydride battery.

In addition to the electric car market, this battery s also and prevalently directled to the consumer electronic market to replace the enviromental hazardous nicad battery. The *nickel-metal hydride battery* is based on a nickel oxide electrode coupled with a 'hydrogen storage' alloy (e.g., $LaNi_5$, $Tr(Zr)Ni_2$) in an alcaline electrolyte:

$$\underset{\text{(negative)}}{\text{NiOOH}} \;/\; \underset{\text{(electrolyte)}}{\text{KOH acq}} \;/\; \underset{\text{(positive)}}{\text{MH}} \qquad [25]$$

The alloy can reversily adsorb and release hydrogen, thus acting as a metal hydride (MH) " sink" electrode capable of exchanging hydrogen with the nickel oxide counterelectrode according to the following, reversible electrochemical reaction:

$$\text{NiO(OH)} + \text{MH} \overset{\text{discharge}}{\underset{\text{charge}}{<===>}} \text{Ni(OH)}_2 + \text{M} \qquad [26]$$

having an operating voltage similar to that of the nicad battery.

Select alloy materials can store large amounts of hydrogen per volume and the higher is this amount the higher is the capacity and thus the speciific energy of the battery. For instance, in the case of the $LaNi_5$ alloy a practical specific energy of about 50-60 Whkg^{-1} can be easily achieved (see Table 3). This property, combined with safety of operation, combatibility with the enviroment and high power output capability, place the nickel-metal hydride (Ni-MH) battery(Figure 19) among the most promising advanced storage systems.

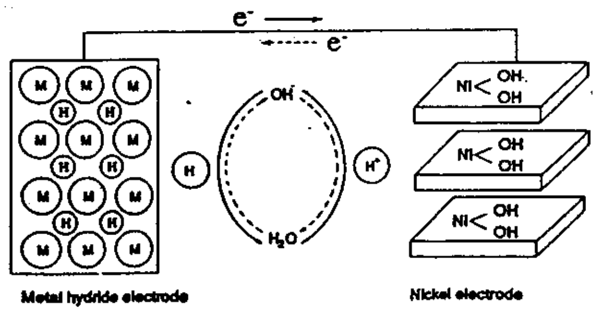


Figure 19- Scheme of a typical Ni-MH battery.

5.2.2 - The sodium-sulfur battery.

The *sodium-sulfur battery* is today the advanced system most closed to reach the large scale production for load leveling and electric vehicle applications. Various European, American and Japanese industries are currently engaged in the production of commercial prototypes. The battery is based on an electrochemical cell using two unconventional electrode materials, i.e. a sodium negative and a sulfur positive. The battery operates at high temperature, namely around 350°C, at which both electrode components are in the liquid state, this being another uncommon characteristic which requires the design of proper electrode compartments. The unique solution adopted, which sees the two electrodes kept in place by a sintered ceramic vessel which also acts as the electrolyte separator, is the distinctive feature of the sodium-sulfur battery.The vessel is made of β"-alumina, a ceramic material having a crystal structure (Figure 20) which allows fast sodium ion transport, especially at the high operational temperature, and thus the proceeding of the overall electrochemical reaction:

$$xNa + S \underset{\text{charge}}{\overset{\text{discharge}}{<\!\!===\!\!>}} Na_xSy \qquad [27]$$

During discharge sodium is oxidized at the negative to form Na^+ sodium ions which migrate through the wall of the β"-alumina vessel to reach the positive where they combine with sulfur to form sodium polysulfides of various nature. During the opposite charging process sodium ions move back through the ceramic wall to reach the negative where they are reduced to metallic sodium. The associated OCV is 2.08 V at 350°C.

Two opposite configurations are today used for the production of commercial sodium-sulfur (Na-S) batteries, namely one (A) with sodium and the other (B) with with sulfur kept inside the ceramic container (Figure 21). In both cases, since sulfur is intrinsically a poor conductor, the positive electrode compartment is coiled with a conductive graphite felt. The most common between the two is the inner-sodium configuration, so that the sodium-sulfur battery may be most generally schematized as:

$$\underset{\text{(negative)}}{Na} \ / \ \underset{\text{(electrolyte)}}{\beta''\text{-alumina}} \ / \underset{\text{(positive)}}{S,C} \qquad [28]$$

To reach full performance the Na-S battery must be heated to the operational 350 °C temperature prior to use. This is not a too serious problem since, once brought at 350°C, the Joule losses are sufficient to keep the temperature, especially if the battery is provided by an efficient thermal insulation. The crucial aspect is rather confined in the fragility of the ceramic container whose walls are made thin in order to reduce ohmic drops during current flow.

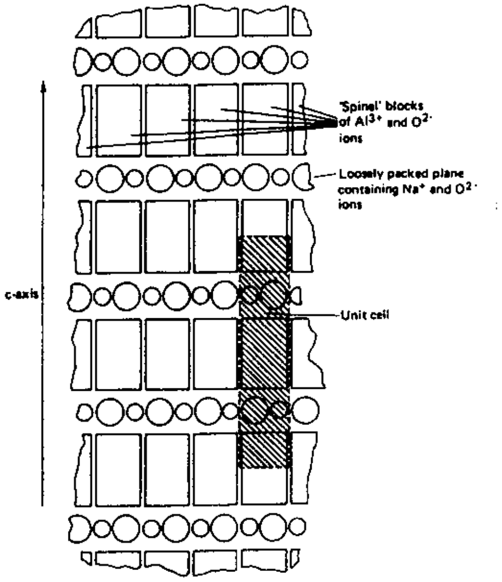


Figure 20- Model of the β"-alumina crystal structure: the space between the spinel blocks allows two-dimensional sodium ion transport

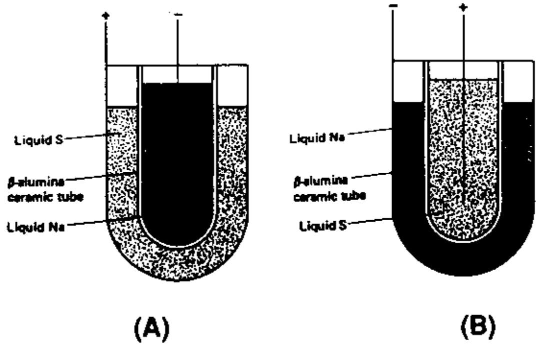


Figure 21- The two most common configurations (inner or outer sodium) of the sodium-sulfur battery.
(From: C.A.Vincent, F.Bonino, M.Lazzari and B.Scrosati,"Modern Batteries", Arnold Pu.,London, 1987)

Also difficult to solve are materials problems, related to the severe corrosive nature of the electrode components, and safety problems, related to the reactivity of the involved large amounts of liquid sodium. On the other hand, the high values of the energy density (see table 3) , the optimization of the ceramic sintering processes and the identification of highly realiable insulating ancillary materials, have opened the route for the large scale development.Today sodium-sulfur .modules are installed in vehicles of different sizes, currently under road test by various automobile companies.

In view of alleviating the materials problems met at 350 °C, alternative systems still based on the liquid electrode-solid electrolyte combination but running at somewhat lower temperature, are also under development and test. A typical example is the sodium-antimony trichloride cell, where sulfur is replaced by $SbCl_3$ dissolved in a melt of sodium chloride (NaCl) and aluminum chloride ($AlCl_3$). The scheme of the battery, which operates at 220 °C is :

$$\underset{\text{(negative)}}{\text{Na}}\ /\ \underset{\text{(electrolyte)}}{\beta\text{''-alumina}}\ /\underset{\text{(positive)}}{\text{SBCl}_3\text{, NaCl,C}} \qquad [29]$$

and its electrochemical reaction is:

$$3Na + SbCl_3 \underset{\text{charge}}{\overset{\text{discharge}}{\text{<===>}}} Sb + 3NaCl \qquad [30]$$

The OCV is approximately 2.85 V at 210°C and the theoretical specific energy is 820 $Whkg^{-1}$. The cell is constructed in a similar mannerto the sodium-sulfur cell with the β"-alumina ceramic tube and central antimonium trichloride electrode.

5.2.3. The lithium-iron sulfide battery.

The other high-temperature systems selected by the USABC for electric vehicle applications, is the *lithium-iron sulphide battery*, which, opposite to the Na-S, uses solid electrodes- i.e. a lithium-aluminum(Li-Al) or lithium-silicon(Li-Si) alloy as the negative and iron sulfide(Fes or FeS_2) as the positive- and a molten electrolyte. The original version used a LiCl-KCl eutectic liquid operating in the 450-500 °C range. Modern development is concentratedc on a LiCl-LiBr-KBr electrolyte which permits operation at 400-425 °C where thermal management and corrosion problems are reduced. The most recent configuration is then:

$$\underset{\text{(negative)}}{\text{Li(Al)}}\ /\ \underset{\text{(electrolyte)}}{\text{LiCl-LiBr-KBr}}\ \text{molten}\ /\underset{\text{(positive)}}{\text{FeS}_2\text{, C}} \qquad [31]$$

The electrochemical reaction is:

$$4LiAl + FeS_2 \underset{\text{charge}}{\overset{\text{discharge}}{\text{<===>}}} 2Li_2S + 4Al + Fe \qquad [32]$$

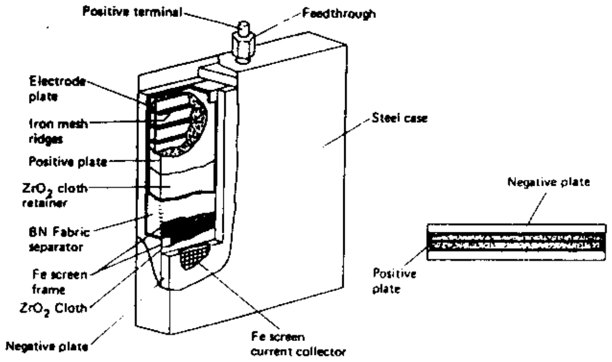


Figure 22- Schematic of a lithium iron-sulfide battery.
(*From: C.A.Vincent, F.Bonino, M.Lazzari and B.Scrosati,"Modern Batteries", Arnold Pu.,London, 1987*)

Figure 22 shows a scheme of the Li-FeSx battery. In common with the generalities of high temperature systems, the main problem of this battery lies in the extremely corrosive nature of the cell components which precludes the use of common, low-cost insulating and and separator materials. In fact, the reactivity of lithium excludes the use of common ceramics, such as silica and alumina, and the corrosion of the iron sulfides excludes the use of steel current collectors in favour of expensive molybdenum alloys. The most critical, however, is the task of finding a suitable separator material; the most successful so far has been a boron nitride (BN) felt, which, however, is very expensive and contributes only by itself to as much to the 75% of the total cell material cost.

Although the commercial success of this battery is obviously dependent on the identification of low-cost material components, few Li-FeSx vehicle prototypes have been fabricatedt and tested, primary at the Argonne National Laboratory in association with a group of American battery companies.

5.2.4. Ambient temperature secondary lithium batteries.

The development of a practical ambient temperature lithium battery has been one of the main tasks of the battery research. The most successful attempts have been obtained by using a lithium metal negative, a liquid electrolyte solution -i.e. a solution of a lithium salt in an aprotic, organic solvent- and an ' lithium intercalation' positive electrode. The latter is formed by compounds having an opened structure which allows the reversible insertion-deinsertion of lithium ions into spaces within the crystalline lattice. Examples of successful intercalation elevctrodes are the layer-structure titanium sulfide ($\mathrm{TiS_2}$) or the tunnel-structured vanadium oxide ($\mathrm{V_6O_{13}}$). The electrochemical process of these lithium-intercalation batteries is schematized in Figure 23. In discharge lithium dissolves at the negative as lithium ions which migrate through the electrolyte to be inserted into the host positive compound causing minor and reversible changes in its crystalline structure. On charge, lithium ions leave the insertion positive, reenter into the electrolyte to be plated as lithium metal at the negative. Therefore, in the case of Li-$\mathrm{TiS_2}$ cells, the process may be written as:

$$x\mathrm{Li} + \mathrm{TiS_2} \underset{\text{charge}}{\overset{\text{discharge}}{<===>}} \mathrm{Li_xTiS_2}\ (0<x<1) \qquad [33]$$

The lithium-intercalation batteries have high specific energy (485 $\mathrm{Whkg^{-1}}$ theoretical in the case of Li-$\mathrm{TiS_2}$) and, in principle, an efficient operation. Various are the battery companies in Europe, United States and, especially, in Japan , which have attempted the development of commercial prototypes of different nature and size. An apparently successful product was announced in the late 1980s by the Canadian Company MOLI Energy lmt. In its initial version the battery was based on the combination between lithium and amorphous molybdenum sulfide:

$$\underset{\text{(negative)}}{\mathrm{Li}} \ / \underset{\text{(electrolyte)}}{\text{liquid LIX solution}} / \underset{\text{(positive)}}{\mathrm{MoS2,\ C}} \qquad [34]$$

and its electrochemical reaction is again an intercalation process:

$$x\mathrm{Li} + \mathrm{MoS_2} \underset{\text{charge}}{\overset{\text{discharge}}{<===>}} \mathrm{Mo_xTiS_2}\ (0<x<1) \qquad [35]$$

The Li/$\mathrm{MoS_2}$ was fabricated, mostly in AA and in few C versions (Figure 24a) by overposing in sequence a thin layer of lithium metal (backed on a metal grid negative substrate), a micoporous separator felt and a mixture of molybdenum sulfide with carbon

and a binder (backed on a metal film positive substrate). The three contacted layers are coiled one on each others to a obtain a spiral configuration having a high surface area (Figure 24b). This assembly is then housed in a nickel-plated steel container having the dimensions (50.5x13.5 mm) and the capacity (0.6Ah) typical of the AA size (see Fig. 4). After tapping with the liquid electrolyte the external container is sealed and the battery is ready for use.

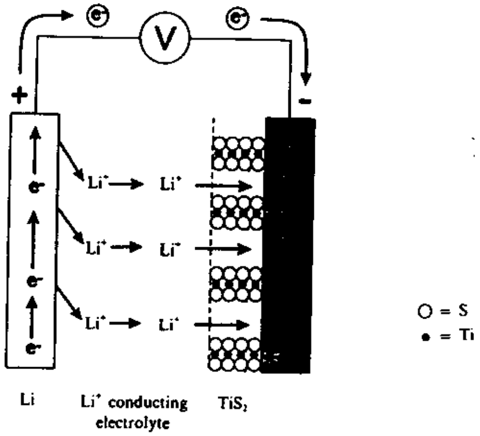
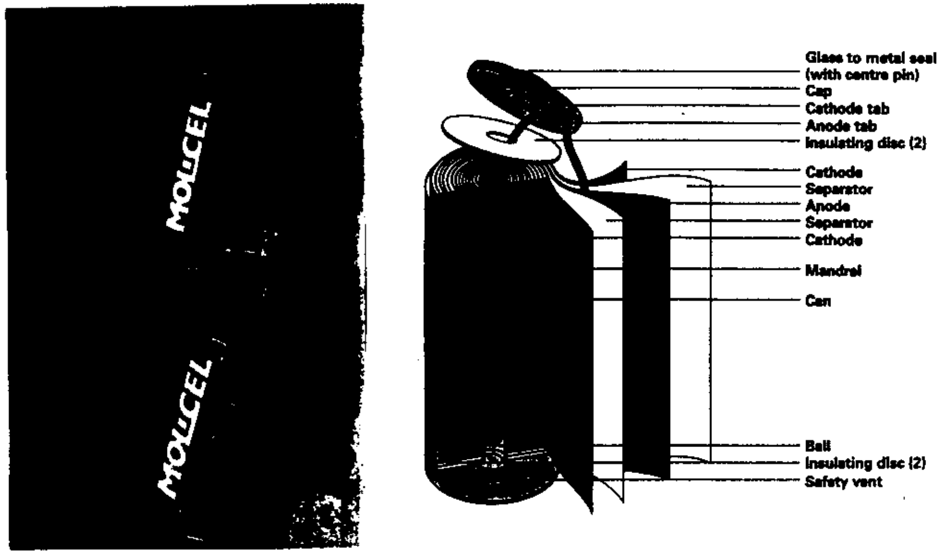


Figure 23- The electrochemical intercalation process.

Under standard operating conditions (namely at temperatures ranging between -20°C and 50 °C and at current rates of the order of 50-150 $\mathrm{mAcm^{-2}}$) the battery provides quite interesting performance, i.e., about 500 deep, high efficiency, charge-discharge cycles and a practical specific energy of the order of 50 $\mathrm{Whkg^{-1}}$.

These characteristics made the Li/$\mathrm{MoS_2}$ battery competive with the nicad and thus, its utilization in the consumer electronic market was promoted. The MOLI cell was in fact used in Japan to power portable telephones, with initial favourable response.

The main problem still plaguing these, as well as the generalities of liquid electrolyte lithium batteries, is the poor cyclability of the lithium anode. As discussed in section 3.3, lithium metal reacts with components of the electrolyte solution to form a passivation layer. The formation of this layer, which in the case of primary cell operation is beneficial since it assures long shelf life, in the case of secondary cells is greatly detrimental since it affects and restricts the cycling characteristics. Disuniformities at the interface may result in dendrite growth which may eventually short and kill the cell. In addition, due the high reactivity of lithium, abuse in handling lithium batteries may result in unsafe behaviour which ultimately can induce cell gassing of even explosions. Therefore, cyclability and safety have become the major concerns in lithium battery technology. Two are the strategies commonly followed to improve cell efficiency and reliability, namely the devolopment of electrochemical systems where the lithium metal is replaced by a lithium-rich, non-metal compound (lithium rocking-chair batteries) or where the liquid organic solutions are replaced by inert, polymer electrolytes (lithium polymer batteries). The results so far obtained alo,ng these two approaches will be described in the following sections.



(a) (b)

Figure 24. The AA and C versions of the Li/MoS_2 battery (a) and its fabrication scheme.
(*From: MOLICEL Technical Bulletin,Moli Energy Lmt, 1987*)

5.2.4.1- Lithium rocking-chair batteries.

The main concept of a *rocking-chair battery* is the replacement of the lithium electrode with a non-metal compound, say $Li_yM_nY_m$, capable of storing and exchanging large quantity of lithium ions. In this way, rather than lithium plating and stripping as in the conventional systems, the electrochemical process at the negative side would be the uptake of lithium ions during charge and their release during discharge. If another non-metal Li-accepting compound, say AzBw, is used at the positive side, the entire electrochemical process would then involve the cyclic transfer of x equivalents of lithium ions between the two electrodes:

$$Li_yMnYm + AzBw \underset{\text{charge}}{\overset{\text{discharge}}{<===>}} Li_{(y-x)}MnYm + Li_xAzBw \qquad [36]$$

Therefore, these electrochemical systems may be described as concentration cells where, as schematically illustrated in Figure 25, the lithium ions 'rock' or 'shuttle' from one side to the other. Accordingly, the term "rocking chair" batteries.

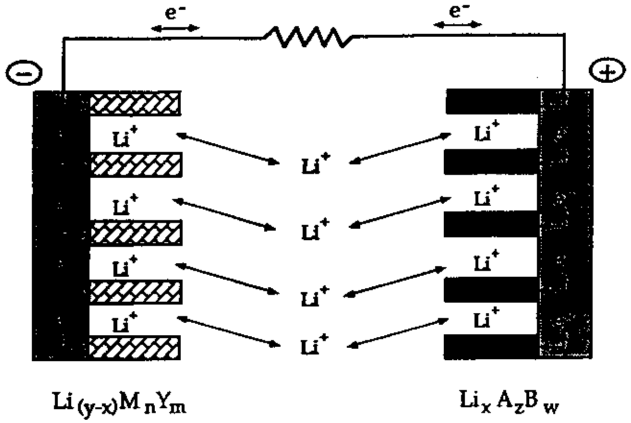


Figure 25. Model of a rocking chair battery.

Considering the nature of the electrochemical driving process, a successful operation for a rocking chair battery and its effective compeetion with a pure lithium system require some crucial conditions, namely:

i) The lithium activity in the negative electrode LiyMnYm must be close to 1 in order to assure open circuit voltages approaching those obtainable with the pure lithium ;
ii) the equivalent weight of both electrodes must be low in order to assure specific capacity values of practical interest;
iii) the diffusion coefficient of Li^+ ions in the ion-source Li_yMnYm negative electrode must be high in order to assure fast charge and discharge rates;
iv) tho changes in lithium ion chemical potential must be small in both electrodes so that to limit fluctuations during charge and discharge cycles;
v) both the ion-source and the ion-sink compounds must be easy to fabricate and based on non-toxic compounds, in order to assure low cost and enviromental tolerance.

If all these conditions are satisfactorily met, the rocking chair concept may assume practical interest since it does offer concrete potentialities for extended cycling and safety. In fact, by in principle avoiding any metal plating process and thus eliminating the conditions for the growth of irregular or dendritic lithium, the chances of shorting and of overheating the battery system may indeed be considerably reduced.

Although the rocking chair concept is not new, its application for overcomimg safety problems in lithium battery technology has recently gained renewed attention and today many industries, especially in Japan, are involved in its development.

The most popular example is the rocking chair in production at the SONY Company and which is alreafdy in the market place under the name of 'lithium-ion battery'. This battery has a basic cell structure of the type:

$$\underset{\text{negative}}{Li_xC_6} \;/\; \underset{\text{electrolyte}}{LiX \text{ in } PC\text{-}EC} \;/\; \underset{\text{positive}}{Li_{(1-x)}CoO_2} \qquad [37]$$

where the negative 'lithium sink' electrode is lithiated petroleum coke Li_xC_6 , the positive 'lithium source is lithium cobaltite, $LiCoO_2$ and the electrolyte is a solution of a lithium salt LiX (e.g. $LiClO_4$), in a propylene carbonate (PC) - ethylene carbonate (EC) solvent mixture.

As typical of rocking chair systems, the electrochemical reaction is the transfer of lithium ions across the cell:

$$Li_yC + Li_{(1-y)}CoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{<===>}} Li_{(y+x)}C + Li_{(1-(y+x))}CoO_2 \qquad [38]$$

where y is about 0.2 Faraday per mole and the cyclable charge x is around 0.5 Faraday per mole.

Although the rocking chair concept impmlies some sacrifices in terms of voltage (the Li activity in the L_xC_6 negative is less than unity) and in specific energy (the specific capacity of Li_xC_6 is one order of magnitude lower than that of Li metal), proper design and cell geometry have lead to the fabrication of D-size Li_xC_6 / $LiCoO_2$ batteries featuring a cycle life of 1,200 deep cycles and a practical specific energy higher than that of the nicad battery (see Table 3).

The success of the Sony lithium ion battery has triggered the worldwide interest and rocking chair batteries using the Li_xC/ $LiMO_2$ (where M=Co, Ni or Mn) couple are currently under development in many countries.

5.2.4.2 -The lithium polymer battery.

The *lithium polymer battery* (LPB) is an all-solid state system which in its common form combines a lithium ion conducting polymer membrane with two lithium reversible electrodes. The key component of LPBs is the polymer membrane which acts both as the lithium ion conducting elctrolyte and as the separator for the two electrodes. The polymer electrolyte membrane is typically a high molecular weight, heteroatom containing polymer (e.g., poly(ethylene oxide), PEO) with a dissolved lithium salt LiX (e.g., $LiClO_4$, $LiAsF_6$, $LiBF_4$, $LiN(CF_3SO_2)_2$, ...). The anode is commonly a lithium metal foil. The cathode is formed by a reversible intercalation compound (e.g., TiS_2, V_6O_{13}, LiV_3O_8 $LiMn_2O_4$, ...) blended with the PEO-LiX electrolyte and with arbon in order to obtain aplastic composite which is backed by a metal foil current collector. The basic structure of a LPB is then:

$$\underset{\text{negative}}{Li} \;/\underset{\text{electrolyte}}{PEO\text{-}LiX}\;/\underset{\text{positive}}{IC,\ PEO\text{-}LiX,\ C} \qquad [39]$$

where IC is the selected intercalation compound. Figure 25 illustrates the sequence of the three cell components.

The electrochemical discharge reaction is the dissolution of lithium at the negative as Li^+ ions, their migration across the PEO-LiX electrolyte and their insertion within the structure of the hosting intercalation compound:

$$xLi + IC \underset{\text{charge}}{\overset{\text{discharge}}{<===>}} Li_xIC \qquad [40]$$

namely, the typical, already discussed intercalation process (Fig. 23).

Basically, LPBs can be described as lithium concentration cells where the metal negative acts as lithium source and the intercalation positive acts as lithium sink, and where the cyclability and reliability of this process is favoured by the specific plastic (which accomodates electrode volume changes) and inert (which controls passivation phenomena) characteristics of the polymer electrolyte.

The most common ICs employed by LPBs are vanadium oxide, V_6O_{13}, vanadium bronze, LiV_3O_8, and titanium disulfide, TiS_2. of The amount of lithium which can be reversibly intercalated in the various cited ICs, namely the value of x in equation [B], varies from case to case. Accordingly, the value of x, sometimes called the 'intercalation level', determines the capacity of a given LPB.

There are several specific advantages that a LPB may offer over a conventional electrochemical storage system. The most representative is its thin-film, all-solid-state construction which gives rugged (i.e. tolerant to shock, vibration and mechanical deformation), leak-proof (i.e. absence of corrosion of case or seals), gassing-free (i.e. absence of electrolyte pressure build-up) and variable geometry (i.e. modular design) configurations.

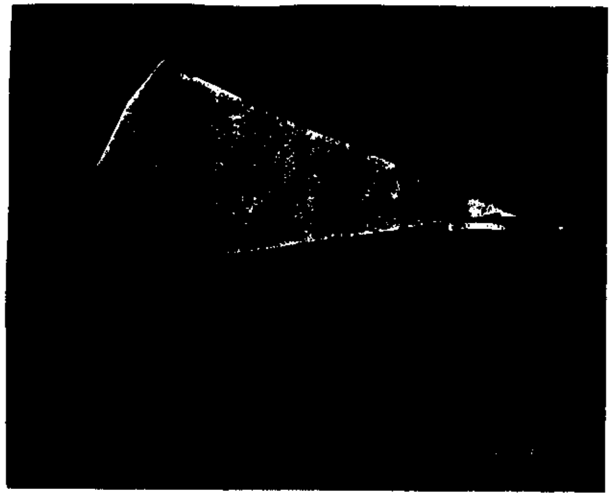


Figure 25. Photograph of the LPB components. From the rear: the lithium foil anode, the PEO-LiX electrolyte membrane and the IC, PEO-LiX, C composite catode.

(*From : 'Applications of Electroactive Polymers', B.Scrosati Ed., Chapman & Hall, London, 1993*)

Furthermore, and of great importance when considering battery cost, the cell components can be easily manufactured by authomatic processes. In fact the most efficient form of LPBs is a laminate constituted by the three main components, i.e. the lithium foil, the electrolytic membrane and the composite cathode (Fig. 25). Lithium foils are commercially available in large range of thickness down to 50 µm. The electrolytic and the composite cathode membranes can both be obtained using a number of coating techniques, such as the Doctor Blade solvent casting. Figure 26 shows the general principle: the electrolyte membrane may be cast from solution onto a paper coated with a releasing agent in order to aid subsequent fim removal, while the composite cathode is cast from a slurry directly onto the metal foil current collector.

The construction of the overall cell is realized by a laminaton (combining heat and pressure) of the three components in the

correct order. Due to the sensity to moisture of lithium and of lithium compounds, the entire operation is run in controlled-atmosphere dry boxes or, for larger production, in dry rooms where the moisture content is maintained within >1% relative humidity.

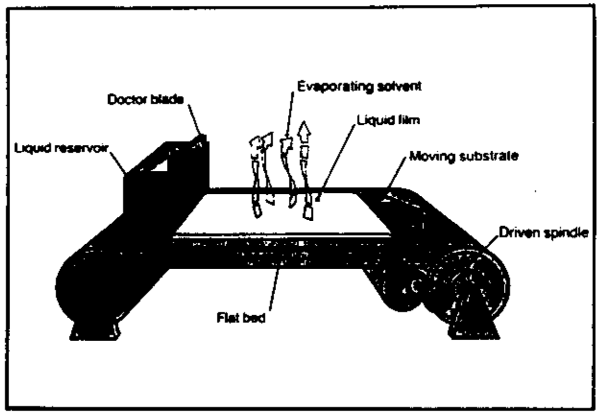


Figure 26- The Doctor Blade coating method for laminating of electrolyte and cathode membranes for LPBs.

(*From : 'Applications of Electroactive Polymers', B.Scrosati Ed., Chapman & Hall, London, 1993*).

A convenient way of preparing laboratory prototypes is to house the cell in aluminum 'coffee bag' envelopes, which are sealed under vacuum so to be safely removed from the dry room for the characterization tests (Figure 27).This fabrication procedure, which allows freat flexibility in the cell construction, is indeed one of the major and unique feature of the LPB technology. The cells can be constructed in any desired shape so that, for example, they can be placed in any available empty space of the addressed portable electronic device or automobile body. For uses of more direct technological impact, LPBs can be readily prepared in a flat, thin design for powering 'smart' credit cards, in a prismatic packaging for powering portable computers, in C -cell cnfigurations for powering consumer electronic devices and in high-capacity, cylindrical, spiral assembly or prismatic stack modules for electric vehicle applications. For all these uses, which imply large scale production, various authomated methods can be envisaged, possibly taking advantage of the existing laminating machinaries routinely used in the capacitor industry.

Figure 27-LPB prototype housed in aluminum envelope for handling and manipulation.

(*From : 'Applications of Electroactive Polymers', B.Scrosati Ed., Chapman & Hall, London, 1993).*

Another major advantage of LPBs is the high energy content associated with the intercalation reactions. Figure 28 compares the specific energy of some LPB couples with those used in conventional batteries. One can clearly see that all the LPB couples have much higher energies than those associated with conventional electrodes. Admittedly, the theoeretical energy only provides a relative assesment of the energy content since the really significant figure is the practical specific energy, namely the value which includes the weight of the electrolyte, separators, excess of electrode materials and all the packaging hardware. However, the particular design of LPBs gives expectations of excellent packing efficients and thus outstanding practical specific energies are anticipated. indeed, these expectations have been confirmed by the direct evaluation of various LPB prototypes assembled and tested by different industrial and academic laboratories.

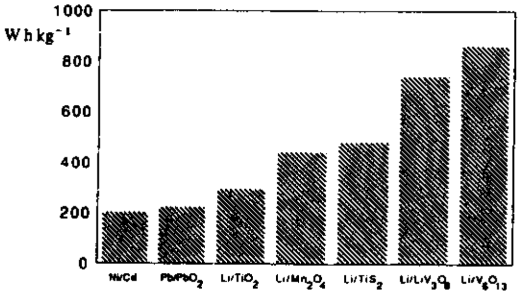


Figure 28- Theoretical specific energy of various Li-intercalation couples in comparison with the lead-acid and the nicad system.

(*From : 'Applications of Electroactive Polymers', B.Scrosati Ed., Chapman & Hall, London, 1993).*

Since the electrolyte membranes based on the combination of PEO and lithium salts reach useful conductivity values only above their crystalline to amorphous transition, LPBs must operate at temperatures higher than ambient, typically around 100°C. This is not a serious drawback if the battery is designed for electric vehicle applications, where operational temperature higher than ambient can be easily controlled by relatively simple thermal managements. Indeed, other advanced battery systems, such as the discussed sodium-sulfur and lithium-iron disulfide, which are currently proposed as leading batteries for powering road vehicles, operate at temperatures much higher than 100°C.

The problem arises for those LPB versions which are proposed for the electronic consumer market, where a high temperature of operation is clearly not acceptable. Since this is considered a market sector where LPBs may play an exclusive and important role in replacing the present, low-energy, enviromentally unfriendly nicad batteries, research has been devoted over recent years to the development of polymer ionic membranes with enhanced transport properties and today LPBs operating at ambient and subambient temperatures are currently under production.

6- CONCLUSIONS.

The main objective of this certainly not-exhaustive review was hopefully that to illustrate the major developments and achevements of the present battery technology, as well as to outline the problems which stll affect this important field. In the primary cell range, the common dry batteries and the emerging lithium batteries provide a satisfactory powering action for the majority of the portable consumer electronic devices. A major concern, however, is placed in the polluting fallout of the exhausted batteries which are daily inserted by tons into the urban solid waste stream. Attention and research should then be devoted with urgency to the definition of the most effective inertization processes and to the construction of large-capacity recycling plants.

In the secondary area the 'classic' nicad and lead-acid batteries still cover almost the 100% of the market without having, however, sufficient energy content and enviroment compatibility to be used and accepted for the today imperative needs of energy renewal and of life improvements. A major research task is therefore the development of advanced batteries and, indeed, massive financial and human resources are currently devoted to reach this important goal. Hopefully, the turn of this century will finally mark the passage from a dark era of poor energy policy and a devastating enviromentally uncare to one where the equilibrium of the planet and the quality of the life will finally be priority tasks.

The realization of this envised prospective is obviously dependent on various and diversified technological achievements among which an important and crucial one is the availibility of reliable and powerful advanced batteries.