

LITHIUM BATTERIES: FROM EARLY STAGES TO THE FUTURE

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1 INTRODUCTION

The evolution of any device is influenced by its past history, and this also applies to lithium batteries. In 1800, when Alessandro Volta, professor at the University of Pavia in Italy, went to the court of Napoleon in France to disclose his “electric pile,” he certainly could not have imagined that his invention, simply a result of a dispute with his colleague and competitor Luigi Galvani at the University of Bologna (Fig. 1), would, via various progressive steps in technological evolution, open up a route that lead eventually to the development of the electrochemical power source that today dominates the consumer electronics market and that is about to revolutionize our common concept of road transportation. This is the lithium battery. Without its advent we could not rely on multifunctional, year-by-year more sophisticated cellular phones and long-lasting laptops, or enjoy Mp3 music to enliven our exercise routines.

Indeed, Volta’s work had a tremendous impact on the progress of electrochemical science by catalyzing the rapid evolution of battery history through the cumulative discoveries of many important electrochemical systems, most of them in the nineteenth century. These include the zinc–manganese oxide cell, invented in 1866 by the French engineer Georges-Lionel Leclanché; the lead–acid rechargeable battery, invented in 1859 by the French scientist Gaston Planté; and the rechargeable nickel–cadmium battery, invented in 1901 by the Swedish engineer Waldmar Jungner [1]. It is interesting to notice that although improved by innovations in construction design,



Luigi Galvani



Alessandro Volta

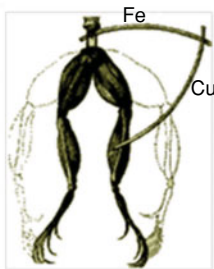


FIGURE 1 In 1781 at the University of Bologna, Italy, Luigi Galvani carried out his classical experiment in which he observed that because a frog's leg twitched when touched by a series of two different metals, the animal's muscle could generate electricity. In 1800, Alessandro Volta at the University of Pavia in Italy claimed the opposite: namely, that the muscle responded by stimulus of the two metals, arguing his point by the demonstration of electricity production from his "voltaic pile," formed by an alternating sequence of two different metals (zinc and silver disks) separated by a cloth soaked in a sodium chloride solution. Actually, the two discoveries are not in total contrast since Galvani's concept may imaginatively be associated with bioenergy and that of Volta with energy storage.

all of the electrochemical power systems cited above are still used for the development of commercial batteries designed for important applications, such as powering electronic devices, portable tools, and car engine ignition. In today's versions, the early batteries have been reengineered from the original concept: for example, in the case of the Leclanche cell, by changing the electrolyte from a liquid to a mixed manganese dioxide–carbon paste, the zinc rod to a core of mixed powdered zinc and electrolyte paste, and the container to a stainless-steel case to form the common alkaline battery. Similar to the improved electrode structure and case design of Planté cells are the lead–acid batteries used widely for car lighting and ignition. Both alkaline and lead–acid batteries are currently produced and commercialized at yearly rates of several billion units and, accordingly, one may wonder whether other batteries are really needed to fulfill the needs of the portable electronic and transportation markets. Effectively, not much innovation took place in the battery market for more than a century after the discovery of alkaline, nickel–cadmium, and lead–acid batteries, since, with minor changes in their chemistry and configuration, these early systems met the requirements of the technology at that time. It was not until the late 1960s that a change in battery technology took place, triggered by a series of innovations in the demand for portable energy, including progress in implantable medical devices, the first oil crisis, and the outbreak of the consumer electronics market.

In this respect, it soon became clear that the most crucial deficiency of conventional batteries was their low energy density, which is associated with their electrode

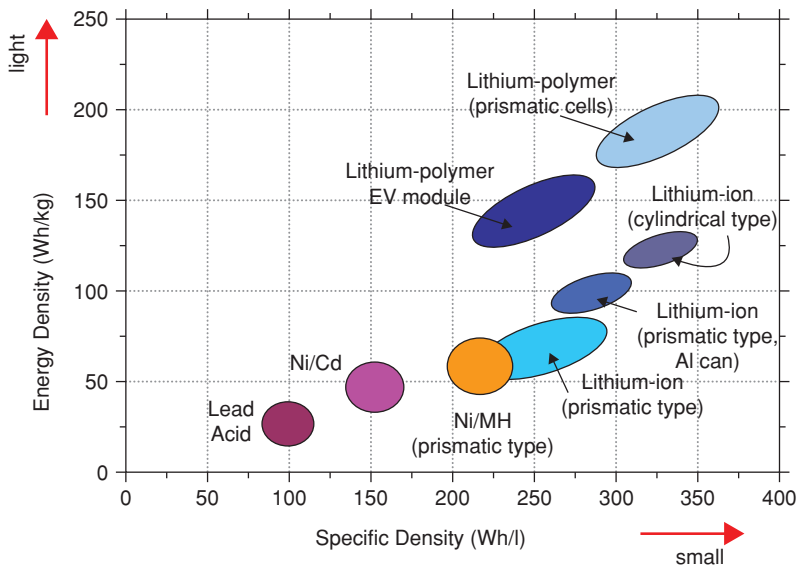


FIGURE 2 Energy density (Wh/kg) vs. specific density (Wh/L) for a series of batteries. A battery directed to the consumer electronics market, especially to the electric vehicle market, should be as light (high energy density) and as small (high specific density) as possible, that is, the ideal battery should lay in the upper right corner of the diagram. Conventional batteries such as lead–acid, Ni/Cd, and Ni/MH are in the opposite corner, being heavy and bulky. Different is the case for lithium batteries, which approach the ideal target. Due to their unique energy content, today lithium batteries are the power source of choice for the portable electronic market and are considered to be the most promising powering system for sustainable electric road transport. (From [2].)

combinations, which could offer only a limited specific capacity value (in terms of ampere-hours per gram, Ah/g), which reflects in a low energy density (i.e., watthours stored by weight, Wh/kg, or by volume, Wh/L). As shown in Figure 2, which illustrates the relationship between gravimetric and volumetric energy density for a series of batteries, it is clear that alkaline–manganese, nickel–cadmium, and lead–acid batteries offer very low energy density. Simply put, these batteries were too heavy and too large to serve the evolving technologies satisfactorily.

Illustrative is the case of implantable medical devices, in particular the cardiac pacemaker. This device, essential to save the lives of patients affected by serious arrhythmia, requires a battery to power the electronic microcircuitry that, on demand, assists the heart to beat. In its early stages, pacemakers had to rely on the only battery available at the time, the primary zinc–mercury battery (Fig. 3). To provide the energy required for proper operation, four Zn–HgO batteries were needed, occupying almost three-fourths of the device’s size, so early pacemakers were very heavy and bulky (Fig. 4). In addition, zinc–mercury oxide batteries lost their charge within two years, and their replacement required a new placement operation, with serious stress on patients. Clearly, new batteries, assuring higher energy from the weight/volume ratio, combined with a long operational life, were urgently needed.

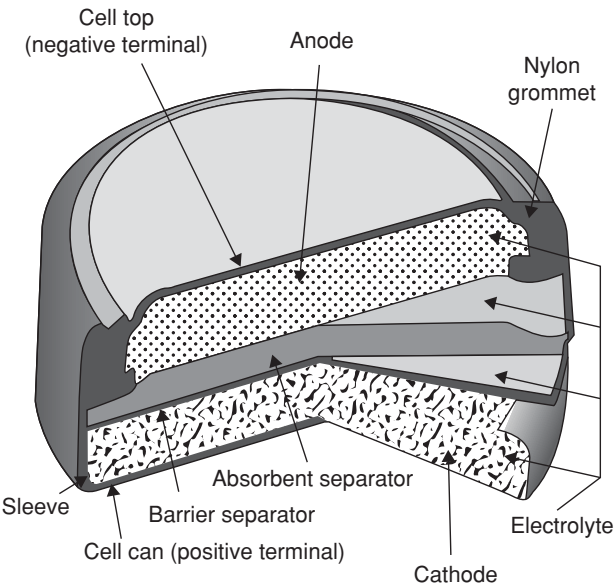


FIGURE 3 Zinc–mercuric oxide battery, button configuration. This battery was used to power cardiac pacemakers in their very earliest stage. To provide the energy required for correct pacemaker operation, four Zn/HgO batteries were needed, which resulted in high weight and volume encumbrance.

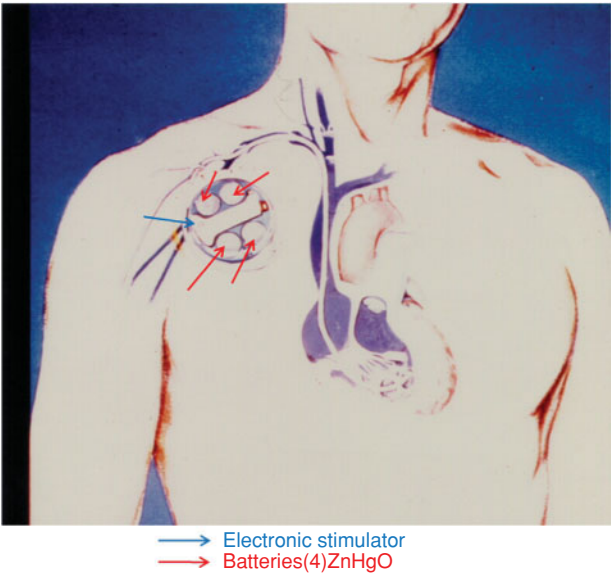


FIGURE 4 At their early implant stage, cardiac pacemakers used four Zn–HgO batteries to power the electronic stimulator. The batteries alone occupied almost three-fourths of the device’s size, so the device was very heavy and bulky. In addition, the zinc–mercury oxide batteries lost their charge within two years, and their replacement required a new operation, with serious stress on patients.

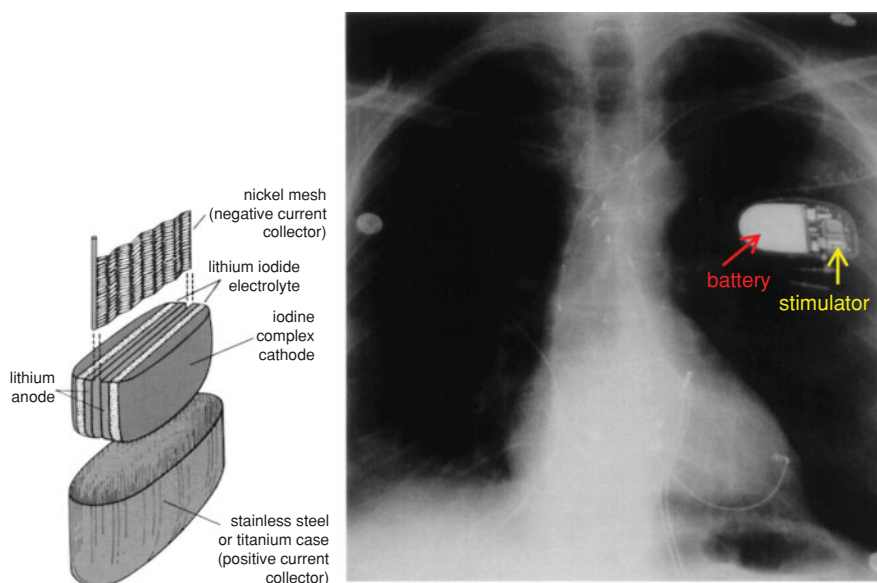


FIGURE 5 The lithium–iodine battery is fabricated with a special shape (on the left) designed to fit the pacemaker case.

A breakthrough arrived with the development of new-concept batteries exploiting lithium as one of the electrode materials. Due to its electrochemical equivalent, the highest among all metals, lithium can provide a much higher specific capacity than that of zinc: 3860 Ah/g vs. 820 Ah/g. Obviously, lithium metal is not compatible with water, and its use required moving from common aqueous electrolytes to more electrochemically stable organic media, generally formed by a solution of a lithium salt in a carbonate organic solvent (e.g., propylene carbonate, ethylene carbonate) or in a mixture of them.

It is easy to imagine that in moving from a zinc-based to a lithium-based battery, a considerable increase in energy density could be obtained. Indeed, a battery combining a lithium metal anode with an iodine-based cathode, the lithium–iodine battery [3], provided a practical energy density of about 250 Wh/kg, almost five times higher than that of a zinc–mercury oxide battery, which is limited to 50 Wh/kg.

The lithium–iodine battery was fabricated with a special shape designed to fit the pacemaker case (Fig. 5). The development of this battery had a tremendous impact on pacemaker efficiency and, consequently, on patient comfort, since its use to replace the zinc–mercury oxide battery resulted in a great reduction in weight and volume (compare Fig. 5 with Fig. 4) as well as an increase in the operational life of the cardiac device, extending it from two years to six or seven years [4]. Indeed today, almost all implanted pacemakers are powered by a lithium–iodine battery.

The success of the lithium–iodine battery highlighted the validity of lithium as a high-energy electrode material, and it opened a route for the development of a series of new batteries addressed to meet various diversified applications. The lithium

battery evolution was accelerated by the explosion in the 1970s of consumer electronics, which brought onto the market a series of popular devices such as electronic watches, toys, and cameras. These devices required batteries capable of combining good powering operation with a small volume size and a contained price. This need promoted extended research and development and a series of batteries exploiting new cathode materials (e.g., manganese dioxide cathode, MnO_2 [5]; carbon fluoride, CF_x [6]; iron sulfide, FeS_2 [7]; copper oxide, CuO [8]) most fabricated in a coin-type shape that could fit easily into a device case, were soon commercialized.

2 ADVENT OF THE RECHARGEABLE LITHIUM BATTERY

All the batteries fabricated in the initial stage of the lithium technology were of the primary type. The success of these batteries stimulated an obvious interest in moving to secondary, rechargeable systems. In theory, there was no apparent difficulty on the anode side since lithium ions formed in discharge were expected to plate back reversibly onto the lithium metal in charge. Indeed, lithium deposition from propylene carbonate-based solutions was demonstrated as early as 1958 [9]. Although the assumption of a facile lithium electrodeposition process involving many lithium plating and stripping (charge–discharge) cycles was not totally true (see below), initially the attention was directed toward the cathode side, with the aim of identifying materials that could withstand a long cycle life. The breakthrough arrived in 1978 with the development of insertion or intercalation electrodes [10]: namely, compounds that can reversibly accept and release lithium ions from their open structure and at the same time can assume various valence states. These conditions are met by transition metal compounds, of which titanium sulfide is a classic example.

The basic structure of a Li-TiS_2 cell is schematized in Figure 6. The overall process involves lithium oxidation at the anode, with the formation of lithium ions that travel through the nonaqueous electrolyte to reach the cathode to finally insert into its layer structure. Because the guest lithium ions keep their charge when intercalated in the TiS_2 , to maintain electroneutrality, a modification of the electronic structure of the TiS_2 host also occurs by a variation in the oxidation state of the transition metal, which passes from Ti(IV) to Ti(III) . In addition, to allow the electrochemical reaction to go on to multiple cycles, hence to assure the cycle life of the battery, a highly reversible evolution of both the electronic structure (to balance the positive charge of the inserted lithium ions) and the crystal structure (to prevent the lattice to collapse) is required.

Basically, batteries using intercalation electrodes (e.g., TiS_2) can be regarded as concentration cells where the activity of lithium varies from zero (at the TiS_2 pristine state) to 1 (at the fully intercalated LiTiS_2 state). The total electrochemical process may in fact be written as



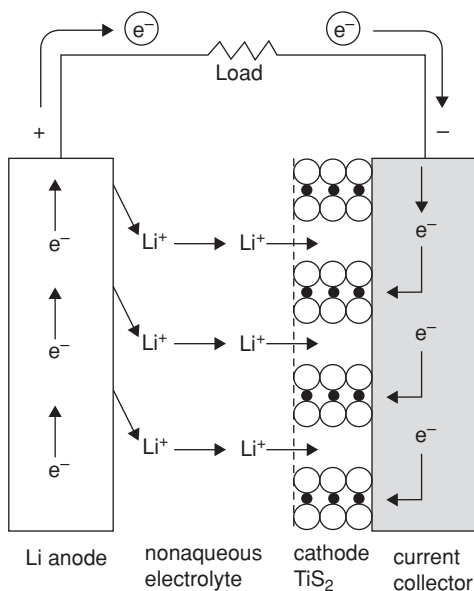


FIGURE 6 Basic structure of a Li-TiS₂ cell.

where x , the intercalation degree, may vary from 0 to 1. Accordingly, the potential of the cell is given by the Nernst equation:

$$E = E^0 - \frac{RT}{xe} \ln \frac{a_{\text{Li}^+}(\text{inLi}_x\text{TiS}_2)}{a_{\text{Li}^+}a_{\text{TiS}_2}} = E^0 - \frac{RT}{xe} \ln [a_{\text{Li}^+}(\text{inLi}_x\text{TiS}_2)] \quad (2)$$

As the intercalation proceeds, the activity of Li⁺ in Li_{*x*}TiS₂ increases and thus the cell potential E decreases. A voltage decay upon operation is the typical behavior of lithium intercalation batteries. If the intercalation degree is maintained within limited levels (generally, ≤ 1), the electrochemical process is highly reversible and the cell can be cycled many times, provided that the same reversibility conditions are matched at the anode side.

The success of intercalation electrodes stimulated large academic and industrial interest, and accordingly, many announcements of the development of new types of rechargeable lithium batteries appeared in the 1980s. One that stimulated considerable debate was the proposal to use conducting polymers such as poly(acetylene) or poly(pyrrole) as positive electrodes [11]. However, the initial enthusiasm cooled down rapidly when it became clear that these polymer materials had a very poor electrochemical behavior [12].

Nevertheless, despite the limitations, the interest in lithium batteries remained high and the number of laboratories involved in lithium battery R&D grew rapidly, making the time ripe for worldwide discussion and confrontation; in fact, a first international meeting on lithium batteries (IMLB 1) was held in 1992 in Rome, Italy. Although only 80 participants attended, the scientific value and concrete prospects of a fast evolution of lithium batteries were already evident. Indeed, the IMLBs grew into valuable series that now experience the participation of over 1000 delegates.

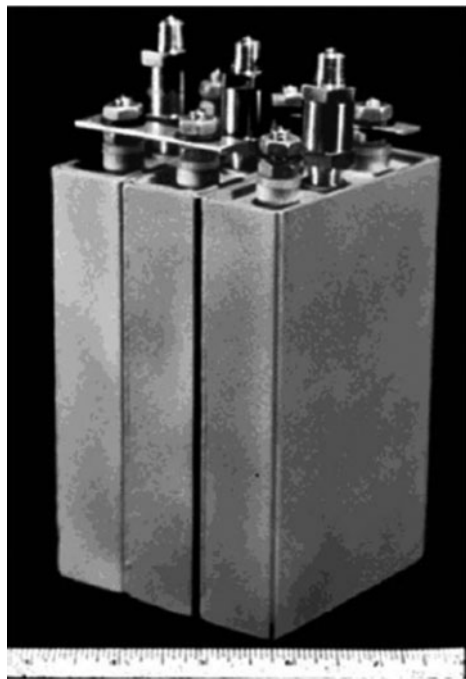


FIGURE 7 Large Li-TiS₂ battery fabricated in 1977. Lithium metal was used as the anode, and a solution of LiB(CH₃)₄ salt in dioxolane was used as the electrolyte. The operation of this early rechargeable lithium battery was affected by unsafe events associated primarily with the highly reactive anode material.

All these important events focused notable attention on rechargeable lithium batteries. The first commercial prototypes appeared in the late 1970s, one produced by the Exxon Company in the United States using a TiS₂ cathode [13] (Fig. 7) and another by the Moli Energy Battery group in Canada using a MoS₂ cathode [14], both with liquid organic electrolytes. However, some operational faults, including fire incidents, led to the rapid conclusion that there were some problems that prevented safe, extended operation of these first lithium batteries. It was soon realized that the problems were associated with the anode; due to its very high reactivity, lithium metal reacts readily with the electrolyte, with the formation of a passivation layer on its surface. The layer, usually called the solid electrolyte interphase (SEI) [15], is permeable to lithium ions, thus allowing continuation of the discharge process; however, irregularities at the SEI may lead to uneven lithium deposition upon charge, with consequent dendrite formation that eventually grows to short the cell. In extreme cases, these uncontrolled events give rise to overheating effects with associated thermal runaway and explosions. Clearly, to assure cycle life and safety, two options were possible: (1) a careful choice of the electrolyte system to assure optimized, smooth lithium deposition, or (2) replacement of the lithium metal with a less aggressive anode material.

The feasibility of the first choice was demonstrated as early as the early 1980s by Abraham and co-workers, who showed that by selecting proper organic electrolytes, for example, those based on solutions of lithium hexafluoroarsenate, LiAsF₆, in aliphatic ethers such as 2-methyltetrahydrofuran, 2MeTHF, with an additive of 2-methylfuran, lithium batteries using a range of positive electrodes, including TiS₂,

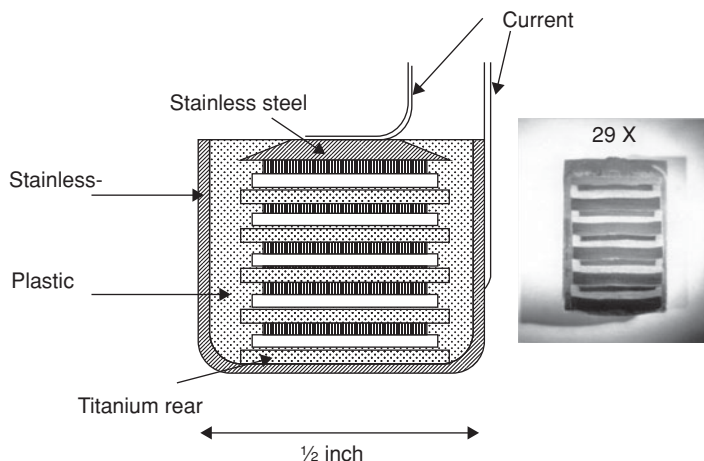


FIGURE 8 Solid-state battery using a solid RbAg_4I_5 electrolyte. To obtain an useful voltage of 3 V, five cells in series were used.

MoS_3 , and V_6O_{13} , could be developed with operational lives extending several hundred cycles [16,17].

Another popular route for assuring safe lithium cycling was to switch from liquid, reacting solutions to solid, inert electrolytes. Obviously, to prevent serious ohmic polarization, only solid media having a high level of lithium ion conductivity over a wide temperature range could be used. Not many materials fulfill this condition. A known solid having a conductivity comparable to that of liquid solutions is silver rubidium iodide, RbAg_4I_5 [18,19]. Ceramic-type materials such as RbAg_4I_5 are ideal electrolytes since they allow the construction of very reliable solid-state batteries. This is, in fact, the case with RbAg_4I_5 -based batteries. In a recent study it was reported that these batteries maintained their charge unchanged even after 33 years of storage [20]. To obtain a useful voltage of 3 V, a battery formed by five cells connected in series was produced (Fig. 8). Unfortunately, this RbAg_4I_5 battery operates by transport of silver ions and thus is of no use in lithium batteries.

Much effort has been devoted to developing lithium ion-conducting solids. One example is, of course, the lithium iodide used in the above discussed pacemaker batteries. This material, however, has, in its pure state, a too low an ionic conductivity level to be used for applications which are more energy demanding than a cardiac pacemaker. Upgrading the material by adding aluminum oxide particles was attempted in 1980 by Liang [21]. The idea was to promote preferential conductive paths along the surface of the filler particles to favor lithium transport. Effectively, an increase in conductivity of two orders of magnitude (i.e., 10^{-4} S/cm) was obtained when passing from pure LiI to Al_2O_3 -added LiI ; however, still a too low level to be of practical interest. Other potential lithium solid conductors were sought in the LISICON family [22] and β -aluminas [23], but generally their input was marginal. This situation may change by virtue of a recently disclosed new solid electrolyte, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, which has a conductivity on the order of 10^{-3} S/cm [24],

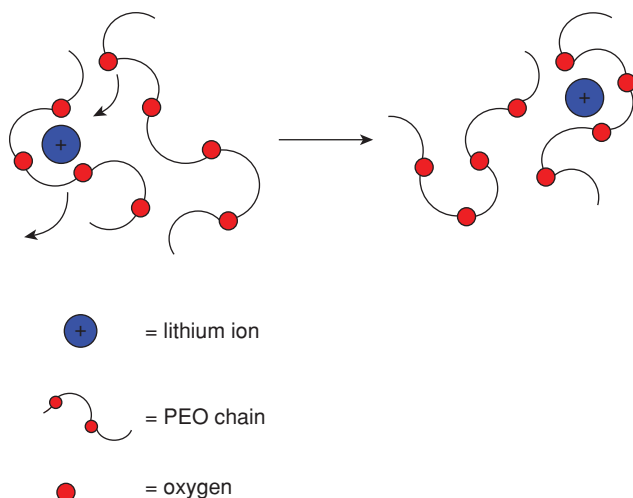


FIGURE 9 Lithium-ion transport mechanism in a polymer electrolyte formed by a complex between a lithium salt and a coordinating poly(ethylene oxide) (PEO) polymer. By coulombic attraction the excess of negative charge on the oxygen in PEO chains coordinates the Li^+ ions, thus separating them from the anions. Because of the large size and encumbrance of the chains, Li^+ ion transport requires sufficient chain flexibility so that they can unfold to free the Li^+ ions to move from one chain loop to the other.

although its practical application in an effective lithium solid battery is yet to be fully demonstrated.

A breakthrough arrived in the late 1970s with the discovery by Michel Armand of a solid-state polymer electrolyte formed by an aggregate between a lithium salt and a coordinating polymer [e.g., lithium triflate and poly(ethylene oxide) (PEO)] [25]. The excess of negative charge on the oxygen in the PEO chains coordinates the Li^+ ions through coulombic attraction, thus separating them from the anions. By this process, the lithium salt is “dissolved” in the PEO matrix, in analogy with the process of salt dissolution in liquid solvents. The main difference is that whereas in liquids the ions can move within their solvation shell, this is not possible in PEO complexes, due to the large size and encumbrance of the polymer chains. Therefore, ion transport in the polymer electrolytes requires flexibility in the PEO chains so that they can unfold to free the Li^+ ions to move from one chain loop to the other (Fig. 9) [26].

Figure 10, which illustrates the general configuration of a PEO–lithium salt (here LiBr) polymer electrolyte, demonstrates the complex structure of the system, where in addition to Li^+ ions trapped in the PEO chain cages and the separated Br^- anions, various cation–anion ion-pair interactions and elaborate chain entangling occur. Due to this configuration, fast ion transport may occur only when the polymer is in the amorphous state, which is reached above 70°C [26], a condition that obviously limits the range of application of PEO-based polymer batteries. However, the unique advantages of polymer electrolytes, which include chemical stability, compatibility with the lithium metal electrode, and moderate cost, still make these

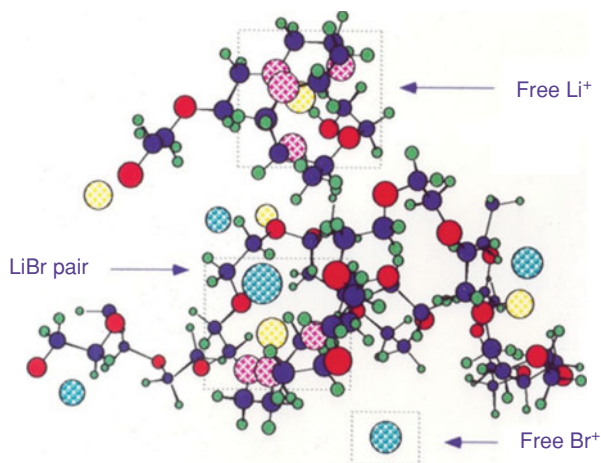


FIGURE 10 General configuration of a PEO-lithium salt (here, LiBr) polymer electrolyte.

media quite suitable and interesting for the development of lithium batteries designed for applications where temperature is not a limiting factor (e.g., uses associated with electric vehicles). The polymer version of the lithium battery is the one that assures the highest energy content (Fig. 2).

PEO-based polymer electrolytes were exploited in the late 1990s for the fabrication of large laminated battery modules based on cells formed by a lithium foil anode, a PEO-based electrolyte layer, and a vanadium oxide cathode (Fig. 11),

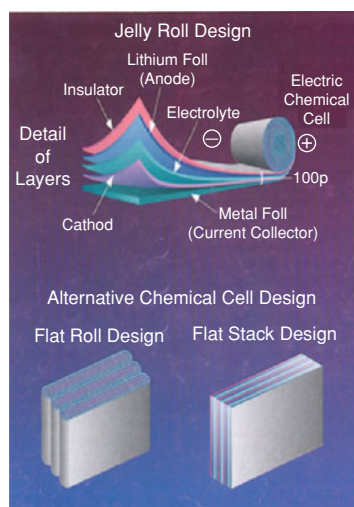


FIGURE 11 Concept and module of the all-solid advanced electric vehicle battery using a dry polymer electrolyte and a metallic lithium anode developed jointly in 1993 by 3M and Hydro Québec under U.S. Advanced Battery Consortium contracts. The goal was to produce a series of full-sized lithium polymer battery packs for extensive platform and road testing. Unfortunately, despite initial success, the project was abandoned.

developed jointly by Hydro Québec in Canada and 3M in the United States. The battery module had very good performance in terms of energy density (155 Wh/kg) and cycle life (600 cycles at 80% depth of discharge), and it was proposed as a power source for electric vehicles [27], a very futuristic application in 1996. However, despite this and other successful demonstration projects, the lithium polymer battery project was abandoned and only very recently reconsidered by a French battery manufacturer for use in an electric vehicle, the Bolloré blue car.

The recognition of the low conductivity of PEO-based solid polymer electrolytes led to the development of gel polymer electrolytes, in which a liquid electrolyte is introduced to plasticize the polymer, which in turn produces highly conductive solid polymer electrolytes with conductivity approaching that of liquid electrolyte [28]. These gel-type electrolytes, with modifications, form the engineering basis of today's lithium batteries used in cell phones, iPads, and other high-tech consumer products. Clearly, the route for the development of a successful rechargeable lithium battery had to pass through the second option: replacement of the lithium metal with another, more reliable anode. The winning approach relied on a totally new concept, based on a combination of two insertion electrodes, one capable of accepting lithium ions, operating as the anode, and the other, capable of releasing lithium ions, operating as the cathode. During charge the negative intercalation electrode acts as a "lithium sink" and the positive electrode as a "lithium source," and the total electrochemical process of the cell involves the transfer of x equivalents of lithium ions between the two intercalation electrodes; the process is then reversed upon discharge and repeated cyclically. These systems are actually concentration cells in which lithium ions "rock" across the electrodes, giving birth to a new type of system, the *lithium rocking chair battery* (Fig. 12).

It is interesting to note that the concept of a rocking chair battery dates back to the late 1970s [29–31] and was demonstrated practically as early as the 1980s [32–34]. However, more than 10 years had to pass before the concept could reach a practical application with a battery introduced by the Japanese manufacturer Sony in 1991 [35]. The key feature of the Sony battery, which was called "lithium-ion battery", was in the definition of proper electrode materials, identified in graphite as the lithium sink anode and in lithium cobalt oxide as the lithium source cathode (Fig. 12).

The use of a reversible graphite electrode for the anode can be considered the key advance that enabled commercial lithium-ion batteries [36, 37]. Effectively, the choice of graphite as anode is rather surprising, since its electrochemical process evolves outside the stability window of most common electrolytes. The electrolyte, in fact, decomposes at the graphite surface; however, the formation of an electronically blocking but ionically conducting layer that stops the decomposition, still allows the electrochemical process to continue. Therefore, graphite is thermodynamically unstable but kinetically protected. The investigation and clarification of the electrode interface, promoted particularly by the pioneering work of Peled, who named the passivating layer the (solid electrolyte interphase), SEI [15], and later by Jeong et al., who demonstrated its formation [38], have been of fundamental importance to an understanding of the lithium-ion battery process and for correct use of the graphite anode.

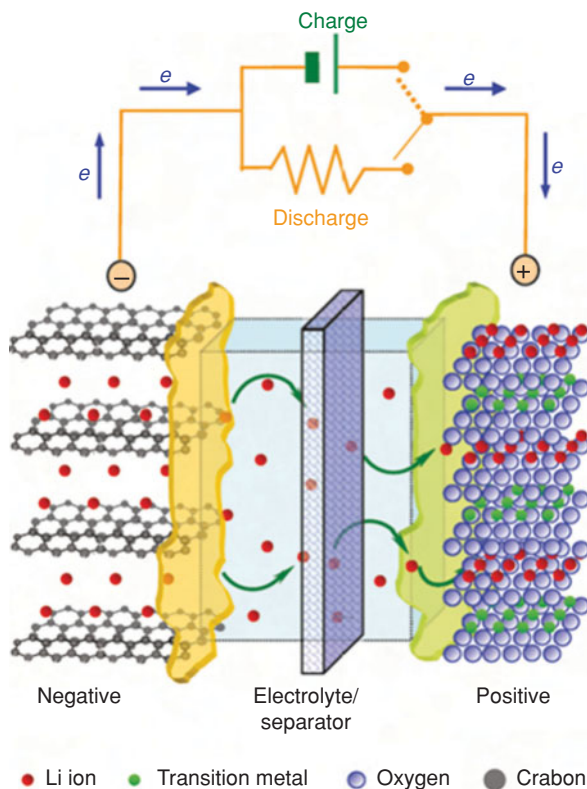


FIGURE 12 The lithium-ion battery. In its most conventional configuration the battery uses a graphite lithium-sink negative electrode, a transition metal oxide (e.g., lithium cobalt oxide) lithium-source positive electrode, and a liquid organic solution (e.g., LiPF_6) in carbonate solvent (e.g., ethylene carbonate–dimethyl carbonate electrolyte). During charge, lithium ions, removed from the LiCoO_2 positive electrode travel through the electrolyte and reach the negative electrode, where they are intercalated into the graphite structure. To compensate for the transfer of the ionic charges, electrons are also exchanged between the two electrodes.

The work of Sony triggered interest worldwide, and many battery manufacturers, located mainly in Asia, are now producing lithium ion batteries. The success of these batteries has been outstanding. Due to their specific properties, primarily in terms of their energy density, which generally exceeds that of conventional nickel–cadmium and younger systems, such as the nickel–metal hydride battery (Fig. 2), lithium-ion batteries are today the power sources of choice for very popular portable devices, such as cellular phones, notebooks, camcorders, and Mp3 players. Accordingly, the production of these batteries amounts to several billions of units per year.

3 A LOOK INTO THE FUTURE

Although graphite is generally the anode of choice in lithium-ion batteries, other materials are under consideration as valid alternatives. One example is lithium titanium oxide, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO). This material, disclosed in the middle 1990s by Ohzuku [39], has a defective spinel-framework structure and is characterized by a two-phase electrochemical process evolving with a flat voltage profile. The theoretical specific capacity is lower, and the voltage level higher, than those of conventional graphite.

Both differences may result in a lower specific energy for the battery; however, the interest in LTO remains high because of its specific properties, including negligible changes in the lattice structure upon accepting and releasing lithium ions and an operation process evolving within the stability domain of the electrolyte. Indeed, batteries using LTO have demonstrated long cycling life and high reliability [40–42]. Thus, it is very likely that LTO may soon also be exploited in large-scale commercial prototypes because the material is now available commercially.

Another appealing class of anode materials is that of the lithium metal alloys (e.g., lithium–silicon and lithium–tin alloys), which, in principle having a specific capacity which largely exceeds that of lithium–graphite, are among the most promising negative electrodes for advanced lithium-ion batteries. As shown by the pioneering work of Winter and Besenhard [43], lithium alloys cannot be used as such in lithium cells, the main issue being the large volume expansion–contraction that occurs during the charge–discharge processes, which in turn induces mechanical disintegration, and thus electrode failure, in the round of a few cycles. This issue has been addressed successfully by moving from bulk to nanostructures and, in particular, to nanocomposites [44,45]. Effectively, the practical validity of the nano concept has been demonstrated in a commercial battery, under the trade name of Nexelium [46]. Table 1 compares the pro and cons of the various anode materials presently under consideration for future development of lithium-ion batteries.

Particularly important also is the role of the cathode, which must be capable of providing lithium ions to assure the electrochemical process, as well as to accept them back in a reversible matter to assure the life of the battery. These characteristics were

TABLE 1 Summary of Characteristics and Properties of Anode Materials Designed for Lithium-Ion Batteries

Material	Theoretical capacity (mAh/g)	Advantages	Issues
Li ₄ Ti ₅ O ₁₂	170	Negligible volume expansion, low cost, stable electrochemical operation, high thermal stability in the charged–discharged state; already in large-scale production	Low specific capacity, high voltage
Li _x Sn _y	990	High capacity, low cost	Large volume changes, nanostructures required
Li _x Si _y	2000	Very high capacity, low cost	Large volume changes; nanostructures required; production announced for 2012 (Panasonic)
Sn _x Co _y C _z	500	High capacity, tested commercially	Cycle life to be demonstrated
C, MCMB	370	Field-tested operation	Operation outside electrolyte stability

TABLE 2 Summary of Characteristics and Properties of Cathode Materials Designed for Lithium-Ion Batteries

Material	Theoretical capacity (mAh/g)	Advantages	Issues
$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	145	High voltage, good specific capacity	Operation within the limits of the electrolyte stability domain
LiFePO_4	170	Basic low cost, intrinsic safety, environmental compatibility	Low electronic conductivity, low tap density, needs carbon coating
LiCoO_2	140	Field-tested operation	High cost

fulfilled by LiCoO_2 , a material disclosed by Goodenough and co-workers in 1981 [47]; without this fundamental discovery, the success of the lithium-ion battery could not be achieved. However, although still the most used cathode for the commercial production of lithium-ion batteries, lithium cobalt oxide has some drawbacks, such as high cost and a certain degree of toxicity; hence, other cathode materials are currently under study.

The most qualified alternative to lithium cobalt oxide is lithium iron phosphate, LiFePO_4 , another important success of Goodenough's group [48]. The wide interest in this material is motivated by its many appealing features, which include good capacity, a two-phase electrochemical process that evolves with a flat, 3.5 V vs. Li voltage, and, most significantly, a cost which in principle is much lower than that of LiCoO_2 . On the other hand, LiFePO_4 suffers from a very high intrinsic resistance which requires special electrode preparations involving sophisticated coating processes to lead to enhancement of the electronic conductivity and, finally, allowing full capacity delivery. Also, commercial LiFePO_4 lithium-ion cells have a lower energy density.

Attention has also been directed toward lithium nickel manganese oxide, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [49]. This material, which adopts a spinel structure, is characterized by a two-phase electrochemical process reflecting in a flat voltage profile evolving around 4.5 V vs. Li. The theoretical specific capacity is on the same order as that of the conventional lithium cobalt oxide, LiCoO_2 . However, the key difference is in the high operational voltage, which makes $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ a very competitive cathode for the progress of lithium-ion battery technology. Table 2 compares the pro and cons of the cathode materials presently under evaluation.

4 BEYOND THE HORIZON

The triumphal march of lithium-ion batteries did not stop with the success gained in the consumer electronic market. A new challenge is now opening for these unique

power sources. The continuous decrease in the oil resources and the growing, alarming concern for the deterioration of the climatic conditions of our planet call with constantly increasing urgency for a larger use of green, alternative energy sources such as solar and wind. In addition, the replacement of polluting, internal combustion cars with more efficient, controlled-emission vehicles, such as hybrid vehicles, plug-in hybrid vehicles, and ultimately, full electric vehicles, is another urgent need in our society. Since sun and wind are discontinuous energy sources and electric engines need to be powered, the success of these ecological renewals depends on efficient storage systems. In this respect, among the various possible alternatives, electrochemical batteries, and lithium batteries in particular, are the best choices, since they are able to convert stored chemical energy into electrical energy with high conversion efficiency and without toxic emission.

However, the lithium-ion batteries presently available, although commercial realities, are not yet at a high enough technological level to meet the powering requirements of hybrid or electric vehicles. The major concerns are the lack of safety, the high cost, and, the still too low energy density. The challenge is to move a step forward passing from the present intercalation chemistry to novel concepts that may lead to advanced batteries. This is not an easy goal to achieve. On the other hand, its implications, not only ecological, but also economical and political, are so important that many countries worldwide are budgeting tremendous amounts of funding to stimulate research and development in the lithium battery technology. Catalyzed by this large money flow progress has been rapid, and many new battery systems have been proposed in recent years. Using the colorful but forceful words of Fletcher [50,51]: “Advanced-battery start-ups started to pop up as mushrooms after a spring rain.” Regretfully, this intense activity also gave rise to a series of patent conflicts and endless legal battles. No doubt Alessandro Volta is turning in his grave: His dispute with Luigi Galvani that affected him so much is nothing compared to the fierce litigation among lithium battery manufacturers.

Fortunately, this violent atmosphere has not influenced too badly the lithium battery science community, which has continued to report progress in the field. As result, many innovative materials, concerning all three battery components—anode, cathode, and electrolyte—are now being investigated intensively with the goal of upgrading battery performance to automotive levels. However, although notable successes have been achieved, the turning point has not yet been attained. One may estimate that to assure a valid, single-charge driving range for a common subcompact passenger electric car, based on presently available lithium-ion technology, the weight of the battery would largely exceed any acceptable practical limit. Clearly, revolutionary batteries, having levels of energy density two or three times higher than those offered by conventional systems, are urgently needed. The achievement of this ambitious task is the challenge of the present (and future?) history of lithium batteries. Attention is focused on systems based on electrode combinations that in theory assure a quantum jump in energy density. These are primarily the lithium–sulfur [52,53] and lithium–air [54,55] batteries, pioneered by Abraham and others [52–55], having a theoretical energy density on the order of 2600 and 5000 Wh/kg, respectively [52–58].

The road to practical applications of these *superbatteries*, however, is still long, since many issues have to be overcome before they can be considered practically feasible. These aspects are treated competently and exhaustively in other chapters of this book, hence are not discussed here. We may then conclude by stating that the history of the lithium battery is presently facing a second, new age. As the first one led to a revolution in the consumer electronic market, the second is expected to favor an epoch-making change in energy renewal and vehicle transportation. If this will eventually be verified, lithium batteries will once again play a key role in the improvement of our society and the condition of our planet.

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