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REVIEW

History of lithium batteries

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General introduction

The evolution of any device is obviously influenced by its general history and this applies also for lithium batteries. As well known, a battery or, more precisely, an electrochemical cell is a device that enables the energy liberated in a chemical reaction to be converted directly into electricity.

Although there is some belief that the electrochemical battery had its birth in the first century BC by the discovery of the so-called "Baghdad Battery", a vessel founded during archeological excavation in a zone near Bagdad and attributed to the Persian civilization [1, 2], it is now almost universally accepted to have been the works of Luigi Galvani at the University of Bologna, Italy and of Alessandro Volta at the University of Pavia, Italy that at the end of the eighteenth century made the electrochemical cell widely known to humanity. This important discovery actually resulted from a dispute between the two scientists. By his classic experiment where he observed that a frog's leg twitched when touched by a series of two different metals (Fig. 1), Galvani believed that animals could generate electricity. On the other hand, Volta claimed the opposite arguing his point by the demonstration of electricity production from his "voltaic pile" formed by an alternate sequence of two different metals (zinc and silver disks separated by a cloth soaked in a sodium chloride solution [3]; Fig. 2). Actually, the two discoveries are not in total contrast since Galvani's concept may be romantically associated with bio-energy and that of Volta to energy storage. It is impressing to read what Volta wrote in the late 1700s: "*…the electric current in the pile is not totally free since it is more or less hindered and retarded by the interruptions between metals, namely the interposed wet layers which are not good conductors…while in well-fabricated piles neither this nor other delaying causes occurring, the discharge proceeded more freely…*" [4], anticipating the critical role of the electrolyte and the electrode interface that rules the development of modern batteries and in particular of lithium batteries.

Indeed, Volta's work had a tremendous impact on the progress of the electrochemical science by catalyzing a rapid evolution of the battery history with the cumulative discoveries of many important electrochemical systems, most of them in the nineteenth century [5]. In 1866, the French engineer Georges-Lionel Leclanché disclosed his battery based on a zinc rod negative electrode (anode) and a manganese oxide–carbon mixture as positive electrode (cathode) immersed in an aqueous ammonium chloride solution [6] (see Fig. 3). It is interesting to notice that the Leclanché cell concept is still exploited in the consumer

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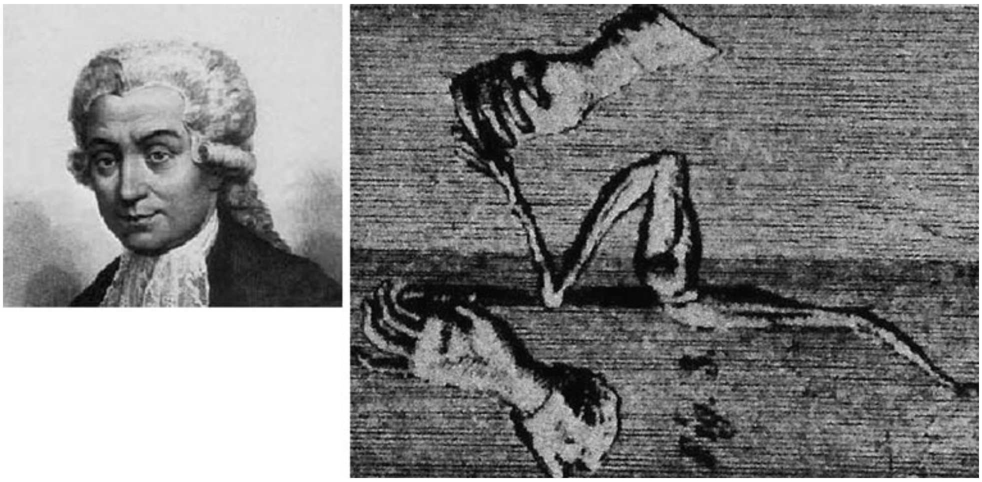


Fig. 1 Luigi Galvani and his experiment on frog legs

primary batteries commonly known as carbon–zinc and alkaline cells, respectively. In today's versions, the cells have been reengineered from the original Leclanché design by, in the zinc–carbon case, simply changing the electrolyte from liquid to paste (by mixing it with flour or starch) and the glass cell container and zinc anode rod by a zinc that can serve both functions. In the alkaline cell case, the design is inverted using a core of mixed powdered zinc and electrolyte paste, a fabric separator, and a mixed manganese dioxide–carbon electrolyte paste; all this being contained in a stainless steel case (Fig. 3).

Soon after the Leclanché discovery, another key step in the battery evolution was marked by the French Scientist Gaston Plantè who in 1859 invented the lead–acid rechargeable battery and by the Swedish engineer Waldmar Jungner with the discovery in 1901 of the rechargeable nickel–cadmium battery. Although modified by innovations in construction design and in materials packaging, these systems are also the bases of today's popular commercial batteries, addressed to important applications, such as power supply for car ignition and for portable tools.

Fig. 2 Alessandro Volta and his pile

Effectively not much innovation took place in the field for more than a century since the batteries based on the early concepts of Leclanché, Jungner, and Planté satisfactorily met the requirements of at the time technology. The situation changed dramatically in the late 1960s due to a series of innovations in the demand for portable energy. The most significant are listed below.

1. The progress of the implantable medical devices with the associated need of high-energy density, long-lasting reliable energy sources;
2. The request of high-energy and high-power sources for military purposes;
3. The explosion of the consumer electronic market.

It was soon realized that the conventional batteries could no longer cope with these fast-evolving events. The most crucial fault was in the lack of their energy density which is in turn associated with their electrode combination that could offer only a limited value of specific capacity (in terms of ampere-hours per gram) which reflects in a low energy density (i.e., watt-hours stored per weight or per volume). Figure 4 illustrates the relationship between gravimetric and volumetric energy density for, at that time, conventional batteries, i.e., alkaline–manganese, nickel–cadmium, or lead–acid; it is clear that they are offering very low energy density values, both in terms of Wh kg^{-1} and Wh cm^{-3}. Simply put, these batteries were too heavy and too big to satisfactorily serve the evolving technology.

The case of the implantable medical devices and, in particular, of the cardiac pacemaker is illustrative. This

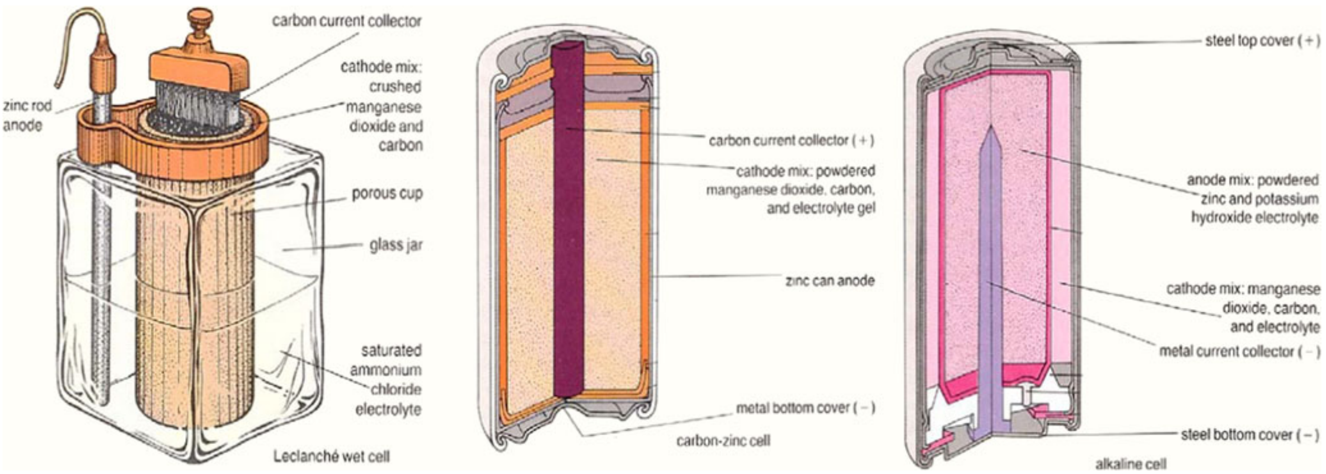


Fig. 3 The Leclanchè cell and its evolution to form commercial carbon zinc and alkaline cells

implanted device, essential to save the life of patients affected by serious arrhythmia, requires a battery to power the electronic micro-circuitry that on demand assists the heart beating. At the early stage, the pacemaker had to rely on at that time only battery available namely the primary zinc–mercury battery [7]. To fulfill the energy required for a correct operation, two Zn-HgO batteries in series were needed with the result that they occupied almost three quarters of the device's size. Accordingly, the early pacemakers were very heavy and bulky. In addition, the two zinc–mercury oxide batteries run down their charge in the 2-year round and their replacement required a new operation with serious stress for the patients. Clearly, new batteries, assuring higher energy-to-weight and energy-to-volume ratio, combined with a long operational life, were urgently needed. The breakthrough arrived with the development of new concept batteries exploiting lithium as one of the electrode material. Due to its electrochemical equivalent, the highest among all metals, lithium can in fact assure theoretical specific capacity much higher than zinc, i.e., 3,860 Ahkg^{-1} versus 820 Ahkg^{-1}. Obviously, lithium metal is not compatible with water and its use required moving from the common aqueous electrolytes to more electrochemically stable organic electrolytes, generally formed by a solution of lithium salt in a carbonate organic solvent (e.g., propylene carbonate, ethylene carbonate) or in a mixture of them.

It was easy to imagine that moving from 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 so called lithium–iodine battery [8], provided a practical energy density of about 250 Wh kg^{-1}, almost five times higher than that of the zinc–mercury oxide. The development of the lithium–iodine battery had a tremendous impact on the pacemaker efficiency and, consequently on the comfort of the patients, since its use in replacement of the zinc–mercury oxide resulted in a great reduction of weight and volume, as well as of operational life (extended to 6 or 7 years), see Fig. 5. Indeed, today,

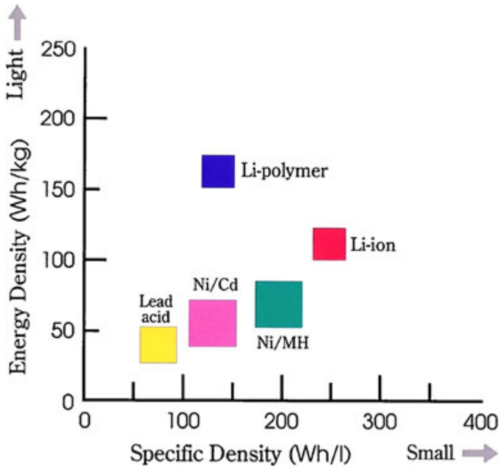


Fig. 4 Energy density versus specific density diagram for various types of batteries

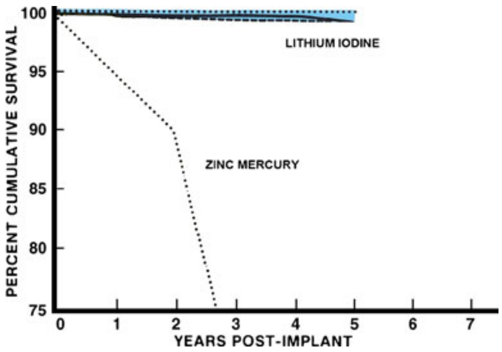


Fig. 5 Durability of batteries for cardiac pacemakers: comparison between early zinc–mercury oxide, and lithium–iodine batteries

almost all the implanted pacemakers are powered by the lithium–iodine battery.

The first era of lithium battery history

The success of the lithium–iodine battery highlighted the potentiality of lithium and in a way it opened the route for the development of a series of new batteries capable of meeting the requests of various, diversified applications. Considerable impulse to the lithium battery evolution was triggered by military demands for power sources characterized by high energy and, particularly high power. Special types of lithium batteries were developed using uncommon cathode materials, such as soluble (e.g., sulfur dioxide SO_2) and liquid (e.g., thionyl chloride, $SOCl_2$ or sulphuryl chloride SO_2Cl_2) reagents.

Another key driving force for lithium battery development in the 1970s was the diffusion of consumer electronics that brought into the market a series of popular devices such as electronic watches, toys, and cameras. These devices required batteries capable of providing a good powering operation with a small volume size and a contained price. This need was satisfied by the commercialization of lithium battery using a manganese dioxide cathode, fabricated in a coin-type cell version that well fitted into the device case [9].

All the batteries fabricated in the initial stage of the lithium battery technology were of the primary type. The success of these batteries stimulated an obvious interest for moving to secondary, rechargeable systems. In theory, there was no apparent difficulty at the anode side since lithium ions formed in discharge are expected to plate back into the lithium metal in charge. Although this is not totally true (see later), the attention was initially focused at the cathode side with the aim of identifying materials that could stand a long cycleability. The breakthrough was obtained in 1978 by the development of the so-called “insertion” or “intercalation” electrodes [10]. These are typically based on compounds that can reversibly accept and release lithium ions in and out their open structure. To allow the ongoing of the electrochemical reaction, as well as of the cycle life, the material must assure a reversible evolution of both the electronic structure (to balance the positive charge of the inserted lithium ions) and of the crystal structure (to prevent the lattice to collapse). These requirements can be met by transition metal compounds such as titanium sulfide that can exchange lithium ions across its layered structure accompanied by a change from IV to III in the valence state. By exploiting this type of cathode materials, the first commercial rechargeable lithium batteries appeared in the late 1970s to early 1980s, one manufactured by the Exxon Company in the USA with a TiS_2 cathode and one by at that time Moli Energy in Canada with a MoS_2 cathode, both using liquid organic electrolytes.

However, some operational faults, including fire incidents, led to the rapid conclusion that there were some problems that prevented the safe and long operation of these lithium batteries. These were clearly associated with the anode; due to its very high reactivity, lithium metal easily reacts with the electrolyte with the formation of a passivation layer on its surface. The layer, usually called solid electrolyte interface (SEI) [11] is permeable to lithium ions, thus allowing the ongoing of the discharge process; however, irregularities on the SEI surface may lead to uneven lithium deposition upon charge with dendrite formation that eventually grew to short the cell. In extreme cases, these uncontrolled events gave rise to overheating effects with thermal runaway and explosions.

Clearly, to assure cycle life and safety, two options were possible: (1) a careful choice of the electrolyte system in order to assure optimized, smooth lithium deposition or (2) the replacement of the lithium metal with a less aggressive anode material. The feasibility of the first choice was demonstrated by Armand in 1978 who originally proposed the use of a solvent-free polymer electrolyte, formed by a complex between a lithium salt and a coordinating polymer (e.g., lithium triflate and poly (ethylene oxide) PEO) complex and demonstrated its efficient use in a rechargeable lithium polymer battery [12, 13]. Later on, the concept was exploited for the fabrication of a large size, laminated battery module based on a lithium foil anode, a PEO-based electrolyte and a vanadium oxide cathode, developed jointly by Hydro Québec in Canada and 3 M Company in the USA.

However, despite of this and other successful demonstration projects, the lithium polymer battery never reached the stage of large-scale commercial production, mainly for the concern on the lithium metal electrode since the risks associated with its operation were never fully overcome. Clearly, the route for the development of the rechargeable lithium battery had to pass through the replacement of the lithium metal with another more reliable electrode. The winning approach was that of relying on a totally new concept that considered the 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 one as “lithium source” and the total electrochemical process of the cell involved the transfer of x equivalents of lithium ions between the two intercalation electrodes; the process is then reversed upon discharge and cyclically repeated. These systems are actually concentration cells in which lithium ions “rock” across the electrodes, giving

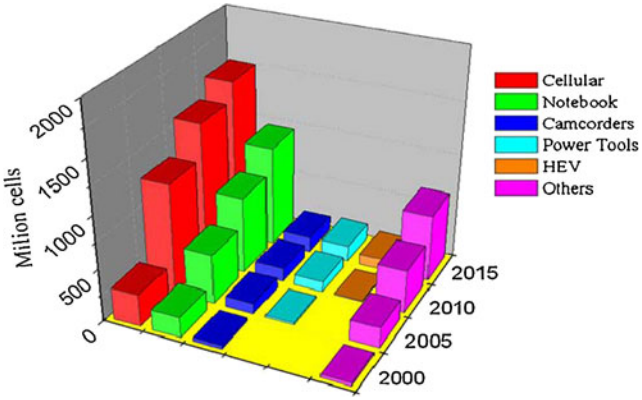


Fig. 6 Time evolution of the lithium ion battery consumers' electronic market

birth to a new type of system, called *lithium rocking chair battery.*

Actually, the concept of a rocking chair battery dates back to the late 1970s [14, 15] and practically demonstrated in the early 1980s [16–19]. However, more than 10 years had to pass before the concept could reach a practical application as demonstrated by a battery introduced by the Japanese Sony manufacturer in 1991 [20]. The winning feature of the Sony 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. Particularly important is the role of the cathode that must be capable of providing the 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 provided by $LiCoO_2$, a material disclosed by Goodenough in 1980 [21]. Without this fundamental discovery, the success of the rocking chair battery could

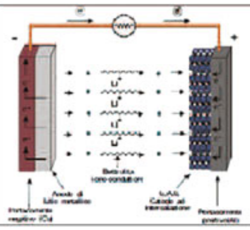
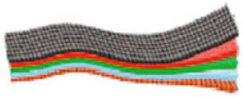
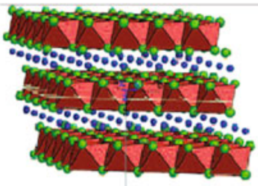
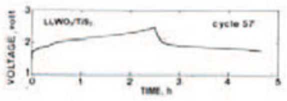
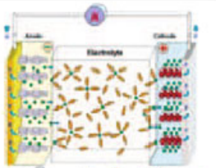
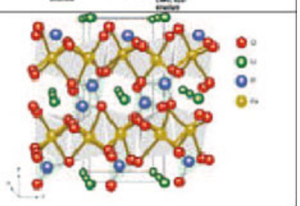
Table 1 A bird's eyeview of the history of lithium batteries at a glance

Early stage			
Year	Cell	author	
1800	Galvanic cell: M/electrolyte/M'	Volta	
1859	Rechargeable lead acid: $Pb/H_2SO_4/PbO_2$	Planté	
1864	$Zn/NH_4Cl/MnO_2$	Leclanché	
1899	Rechargeable nickel-cadmium Ni/KOH/NiOOH	Jungner	

never be achieved. Although other cathode materials have been developed, most of the commercial production of lithium rocking chair batteries in fact still relies on lithium cobalt oxide as cathode.

The work of Sony triggered interest worldwide and, presently, many battery manufacturers, mainly located in Asia, are producing lithium rocking chair batteries that are renamed *lithium ion batteries*. The success of these

Table 2 A bird's eyeview of the history of lithium batteries at glance

First age			
1972	Lithium primary battery Li/org elect/CFx	Matsushita	
1972	Solid lithium iodine battery Li/LiI/I-PVP	Moser	
1977	Rechargeable lithium battery Li/ org elect/ TiS_2	Whittingham	
1978	Polymer electrolyte battery Li/PEO electr/V2O5	Armand	
1980	First lithium ion cathode LiCoO2	Goodenough	
1980	Rocking chair battery Li_xWO_2/org electr/TiS_2	Scrosati	
1991	Lithium ion battery C/org electr/$LiCoO_2$	Sony	
1997	Olivine type cathode, $LiFePO_4$	Goodenough	

batteries was, and still is, outstanding. Due to their specific properties, mainly in terms of energy densities that are largely outcomes of conventional nickel–cadmium and also of younger systems such as the nickel–metal hydride battery [25] (see Fig. 6), lithium ion batteries are today the power sources of choice for a series of very popular portable devices, such as cellular phones, notebooks, camcorders, Mp3, and others. Accordingly, the production of these batteries amounts to several billions of units per year (Fig. 6).

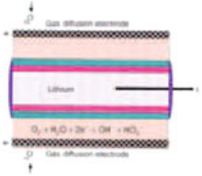
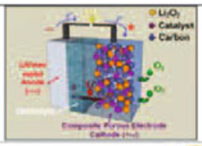
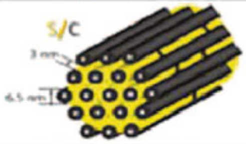
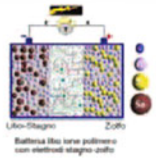
The new era

This outstanding success, however, did not mark the end of the story of these unique electrochemical energy storage devices. Once the market of consumer electronics is gained, a new challenge is now opened for the lithium ion batteries. The continuous decrease of the oil resources and the growing concern on the climate changes call with constantly increasing urgency for a larger use of green, alternative energy sources, such as solar and wind. The replacement of polluting, internal combustion cars with more efficient, controlled emissions vehicles, such as hybrid vehicles (HEVs) or, ideally, electric vehicles (EVs) is another urgent request of our present society.

On the other hand, wind does not blow on command and the sun does not always shine: this discontinuity in operation requires suitable storage systems to efficiently run renewable energy plants (REPs); similarly, a power source is needed to drive the electric engine in HEVs and EVs. Lithium ion batteries, due to their high-energy efficiency, appear as ideal candidates for this purpose. However, although these batteries are established commercial products, further research and development is required to improve their performance to meet the REP and HEV–EV requirements. In particular, enhancement in safety, cost, and energy density are needed. Some fire incidents have occurred (likely associated to thermal runaway phenomena in the electrolyte), the cost of the battery is highly influenced by market price of its components (especially cobalt) and the energy density is still too low to limit the weight of the battery pack in the vehicle.

The challenge is then to move a step forward passing from the intercalation chemistry to novel concepts that may increase safety, assure a drastic reduction in cost, and particularly a jump in energy density. These are not easy tasks; however, the importance of the final goal, i.e., the renewal of the energy policy and of the automobile market, has promptly led most of the developed countries in North America, Europe, and Asia to budget very large financial investments to achieve them. Accordingly, the recent history

Table 3 A bird's eyeview of the history of lithium batteries at glance

New era			
1996	Lithium-air battery Li/org elect / O_2,C	Abraham	
2006	Lithium-air battery Li/film/acq elect / O_2,C	Visco	
2006	Lithium-air battery Li/org elect / O_2,C, catalyst	Bruce	
2009	Lithium-sulfur battery Li/org elect / S,C	Nazar	
2010	Lithium ion sulphur battery Sn-C/ org electr /Li2S,C	Hassoun-Scrosati	

of the lithium batteries sees a fizzy impulse worldwide directed to the development of new materials to: (1) improve safety by looking to electrolytes more thermally stable and/or more inert than the present solutions of $LiPF_6$ in the organic carbonate solvent mixtures, e.g., ionic liquids [22] or even to a revival of the solvent-free polymer electrolytes [23]; (2) reduce cost, by replacing $LiCoO_2$ with materials using less-expensive elements, such as $LiMn_2O_4$ lithium spinel [24] and more recently, $LiFePO_4$ [25].

More challenging is the energy density task. It may be roughly said that a middle-sized urban electric car, using presently available lithium batteries (~150 Wh kg^{-1}) requires about 200 kg of them to assure a driving range of 250 km with a single charge. This is too-high weight penalty; hence, enhancement of about two to three times in energy density is needed. The achievement of this ambitious task is the challenge of the present (and future?) history of lithium batteries. Attention is focused on batteries based on electrode combinations that in theory assure a quantum jump in energy density. They are mainly the lithium–sulfur, Li–S and the lithium–air, Li-O_2 batteries having theoretical energy density of the order of 2,600 Wh kg^{-1} and 11,400 Wh kg^{-1}, respectively [26, 27].

The road of these *superbatteries*, however, is still long since many are the issues that have to be overcome before they can reach a viable status. We may then state that the history of lithium battery is presently facing a second, new age: as the first one led to the revolution in the consumer electronic market and the new one is expected to favor an epoch-making change in energy renewal and in vehicle transportation. If this will eventual verify, once again, lithium batteries will play a key role for the improvement of our society and of the condition of our planet. To conclude, Table 1 summarizes the history of lithium batteries from their birth to our present time (Tables 2, 3).

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