



# LI-ION BATTERIES

Student: **Alberto Miró Peris**

ID number: **53382212V**

PhD: **Francisco Fabregat Santiago**

Subject: **Nanotechnology**

Faculty: **ESTCE**

University: **UJI**

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## 1. INTRODUCTION

The word “battery” comes from the Old French word “*baterie*”, meaning “action of beating,” relating to a group of cannons in battle. In the endeavor to find an energy storage device, scientists in the 1700’s adopted the term “battery” to represent multiple electrochemical cells connected together.



The battery consists of two electrodes that are isolated by a separator and soaked in electrolyte to promote the movement of ions. New active materials are being tried, each offering unique attributes but none delivering an ultimate solution.

Improvements have been slow. Whereas Moore’s Law\* doubled the number of transistors in an integrated circuit every two years, capacity gain of lithium-ion (Li-ion) has been about 8 percent per year in the last two decades. Theoretical battery models reveal specific energy levels that are ten times higher than the commercial equivalent. They remain theoretical, and these lofty goals may never be achieved in real life.

The battery is a feeble vessel that is slow to fill, holds limited energy, runs for a time like a wind-up toy, fades and eventually becomes a nuisance. It exhibits human qualities in that it needs recuperation from the daily travails by applying a long and restful charge. It then delivers for a time and quits on its own terms. Some batteries need as much charging time as they deliver, and there is a resemblance to growing teenagers.

The lithium-ion family receives the most attention and is gradually replacing the nickel-based predecessors that dominated the battery world until the 1990s. Lead acid with its many warts and blemishes holds a solid position for starter and standby batteries. No other system can meet its price and robustness for now.

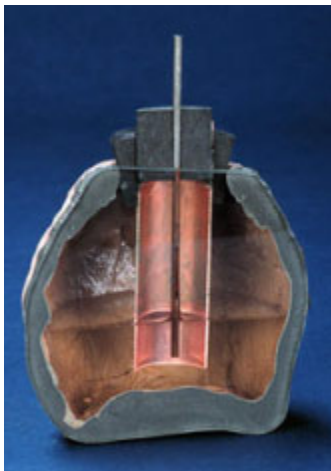
Li-ion is expensive but when calculating the price-per-cycle, it wins over lead acid when repeat cycling is required. Basing calculations on cost per kilowatt hour (kWh) no longer holds; operational costs must be considered. A battery expert said that the switch from lead acid to Li-ion will be faster than the advancement of the Internet.

\*In 1965, Gordon Moore said that the number of transistors in an integrated circuit would double every two years. The prediction became true and is being carried into the 21st century. Applied to a battery, Moore’s Law would shrink a starter battery in a car to the size of a coin.

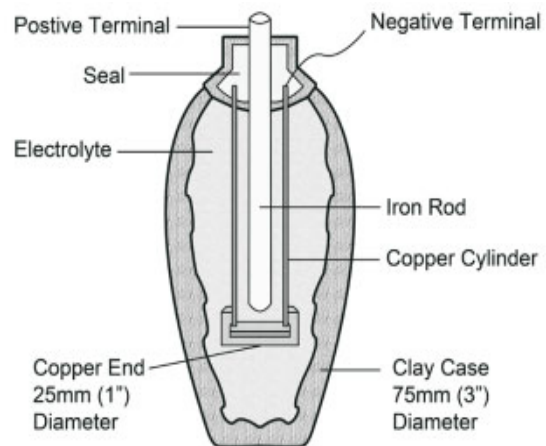
## 2. HISTORY

The use of electricity may go back far away. While constructing a railway in 1936 near Baghdad, workers uncovered what appeared to be a prehistoric battery, also known as the Parthian Battery.

The object dates back to the Parthian empire and is believed to be 2,000 years old. The battery consisted of a clay jar that was filled with a vinegar solution into which an iron rod surrounded by a copper cylinder was inserted. This device produced 1.1 to 2.0 volts of electricity. Following Figures illustrate the Parthian Battery.



Parthian battery



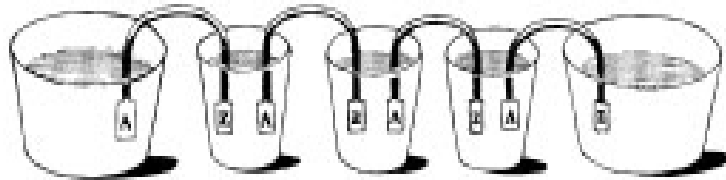
Parthian battery cross section

Not all scientists accept the Parthian Battery as a source of energy. It is possible that the device was used for electroplating, adding a layer of gold or other precious metals to a surface. The Egyptians are said to have electroplated antimony onto copper over 4,300 years ago. Archeological evidence suggests the Babylonians were the first to discover and employ a galvanic technique in the manufacturing of jewelry by using an electrolyte based on grape juice to gold-plate stoneware. The Parthians, who ruled Baghdad (ca. 250 BC), may have used batteries to electroplate silver.

Talking about electricity, the first practical use of static electricity was the “electric pistol” that Alessandro Volta (1745–1827) invented. He thought of providing long-distance communications, albeit only one Boolean bit. An iron wire supported by wooden poles was to be strung from Como to Milan, Italy. At the receiving end, the wire would terminate in a jar filled with methane gas. To signal a coded event, an electrical spark would be sent by wire to detonate the jar. This communications link was never built.

In 1791, while working at Bologna University, Luigi Galvani discovered that the muscle of a frog would contract when touched by a metallic object. This phenomenon became known as animal electricity. Prompted by these experiments, Volta initiated a series of experiments using zinc, lead, tin and iron as positive plates (cathode); and copper, silver, gold and graphite as negative plates (anode). Then was when galvanic electricity had born.

Volta discovered in 1800 that certain fluids would generate a continuous flow of electrical power when used as a conductor. This discovery led to the invention of the first voltaic cell, more commonly known as battery. Volta learned further that the voltage would increase when voltaic cells were stacked on top of each other. Next figure illustrates such a series connection.



Silver (A) and zinc (Z) metals are immersed in cups filled with electrolyte and connected in series

Until then, there was only the possibility of having a limited current during a limited time via material wasting.

### **Rechargeable batteries**

In 1836, John F. Daniell, an English chemist, developed an improved battery that produced a steadier current than earlier attempts to store electrical energy. In 1859, the French physician Gaston Planté invented the first rechargeable battery based on lead acid, a system that is still used today. Until then, all batteries were primary, meaning they could not be recharged.

In 1899, Waldmar Jungner from Sweden invented the nickel-cadmium (NiCd) battery that used nickel as the positive electrode (cathode) and cadmium as the negative (anode). High material costs compared to lead limited its use. Two years later, Thomas Edison replaced cadmium with iron, and this battery was called nickel-iron (NiFe). Low specific energy, poor performance at low temperature and high self-discharge limited the success of the nickel-iron battery. It was not until 1932 that Shlecht and Ackermann achieved higher load currents and improved the longevity of NiCd by inventing the sintered pole plate. In 1947, Georg Neumann succeeded in sealing the cell.

For many years, NiCd was the only rechargeable battery for portable applications. In the 1990s, environmentalists in Europe became concerned about the harm incurred when NiCd is carelessly disposed. The Battery Directive 2006/66/EC now restricts the sale of NiCd batteries in the European Union except for specialty industrial use for which no replacement is suitable. The alternative is nickel-metal-hydride (NiMH), a more environmentally friendly battery that is similar to NiCd.

Most research activities today revolve around improving lithium-based systems, first commercialized by Sony in 1991. Besides powering cellular phones, laptops, digital cameras, power tools and medical devices, Li-ion is also used for electric vehicles and satellites. The battery has a number of benefits, most notably its high specific energy, simple charging, low maintenance and being environmentally benign.

### 3. TYPES OF BATTERIES NOWADAYS

Batteries are classified into **primary** and **secondary** forms:

**Primary batteries** irreversibly transform chemical energy to electrical energy. When the supply of reactants is exhausted, energy cannot be readily restored to the battery.

**Secondary batteries** can be recharged; that is, they can have their chemical reactions reversed by supplying electrical energy to the cell, approximately restoring their original composition.

Some types of primary batteries used, for example, for telegraph circuits, were restored to operation by replacing the electrodes. Secondary batteries are not indefinitely rechargeable due to dissipation of the active materials, loss of electrolyte and internal corrosion.

**Primary batteries**, or primary cells, can produce current immediately on assembly. These are most commonly used in portable devices that have low current drain, are used only intermittently, or are used well away from an alternative power source, such as in alarm and communication circuits where other electric power is only intermittently available. Disposable primary cells cannot be reliably recharged, since the chemical reactions are not easily reversible and active materials may not return to their original forms. Battery manufacturers recommend against attempting to recharge primary cells.



In general, these have higher energy densities than rechargeable batteries, but disposable batteries do not fare well under high-drain applications with loads under 75 ohms (75  $\Omega$ ).

Common types of disposable batteries include zinc-carbon batteries and alkaline batteries.

**Secondary batteries**, also known as secondary cells, or rechargeable batteries, must be charged before first use; they are usually assembled with active materials in the discharged state. Rechargeable batteries are charged by applying electric current, which reverses the chemical reactions that occur during discharge/use. Devices to supply the appropriate current are called chargers.



The oldest form of rechargeable battery is the lead–acid battery. This technology contains liquid electrolyte in an unsealed container, requiring that the battery be kept upright and the area be well ventilated to ensure safe dispersal of the hydrogen gas it produces during overcharging. The lead–acid battery is relatively heavy for the amount of electrical energy it can supply. Its low manufacturing cost and its high surge current levels make it common where its capacity (over approximately 10 Ah) is more important than weight and handling issues. A common application is the modern car battery, which can, in general, deliver a peak current of 450 amperes.

The sealed valve regulated lead–acid battery (VRLA battery) is popular in the automotive industry as a replacement for the lead–acid wet cell. The VRLA battery uses an immobilized sulfuric acid electrolyte, reducing the chance of leakage and extending shelf life. VRLA batteries immobilize the electrolyte. The two types are:

Gel batteries (or "gel cell") use a semi-solid electrolyte.

Absorbed Glass Mat (AGM) batteries absorb the electrolyte in a special fiberglass matting.

Other portable rechargeable batteries include several sealed "dry cell" types, that are useful in applications such as mobile phones and laptop computers. Cells of this type (in order of increasing power density and cost) include nickel–cadmium (NiCd), nickel–zinc (NiZn), nickel metal hydride (NiMH), and lithium-ion (Li-ion) cells. Li-ion has by far the highest share of the dry cell rechargeable market. NiMH has replaced NiCd in most applications due to its higher capacity, but NiCd remains in use in power tools, two-way radios, and medical equipment.

Recent developments include batteries with embedded electronics such as USBCELL, which allows charging an AA battery through a USB connector, nanoball batteries that allow for a discharge rate about 100x greater than current batteries, and smart battery packs with state-of-charge monitors and battery protection circuits that prevent damage on over-discharge. Low self-discharge (LSD) allows secondary cells to be charged prior to shipping.

## Battery cell types

A **wet cell** battery has a liquid electrolyte. Other names are flooded cell, since the liquid covers all internal parts, or vented cell, since gases produced during operation can escape to the air. Wet cells were a precursor to dry cells and are commonly used as a learning tool for electrochemistry. They can be built with common laboratory supplies, such as beakers, for demonstrations of how electrochemical cells work. A particular type of wet cell known as a concentration cell is important in understanding corrosion.

Wet cells may be primary cells (non-rechargeable) or secondary cells (rechargeable). Originally, all practical primary batteries such as the Daniell cell were built as open-top glass jar wet cells. Other primary wet cells are the Leclanche cell, Grove cell, Bunsen cell, Chromic acid cell, Clark cell, and Weston cell. The Leclanche cell chemistry was adapted to the first dry cells. Wet cells are still used in automobile batteries and in industry for standby power for switchgear, telecommunication or large uninterruptible power supplies, but in many places batteries with gel cells have been used instead. These applications commonly use lead–acid or nickel–cadmium cells

Many types of electrochemical cells have been produced, with varying chemical processes and designs, including galvanic cells, electrolytic cells, fuel cells, flow cells and voltaic piles.

A **dry cell** uses a paste electrolyte, with only enough moisture to allow current to flow. Unlike a wet cell, a dry cell can operate in any orientation without spilling, as it contains no free liquid, making it suitable for portable equipment. By comparison, the first wet cells were typically fragile glass containers with lead rods hanging from the open top and needed careful handling to avoid spillage. Lead–acid batteries did not achieve the safety and portability of the dry cell until the development of the gel battery.

A common dry cell is the zinc–carbon battery, sometimes called the dry Leclanché cell, with a nominal voltage of 1.5 volts, the same as the alkaline battery (since both use the same zinc–manganese dioxide combination).

A standard dry cell comprises a zinc anode, usually in the form of a cylindrical pot, with a carbon cathode in the form of a central rod. The electrolyte is ammonium chloride in the form of a paste next to the zinc anode. The remaining space between the electrolyte and carbon cathode is taken up by a second paste consisting of ammonium chloride and manganese dioxide, the latter acting as a depolariser. In some designs, the ammonium chloride is replaced by zinc chloride.



## 4. BATTERIES LI-ION

### 4.1. Introducing to batteries Li-ion

Pioneering work of the lithium battery began in 1912 under G.N. Lewis, but it was not until the early 1970s that the first non-rechargeable lithium batteries became commercially available. Attempts to develop rechargeable lithium batteries followed in the 1980s but failed because of instabilities in the metallic lithium used as anode material.

Lithium is the lightest of all metals, has the greatest electrochemical potential and provides the largest specific energy per weight. Rechargeable batteries with lithium metal on the anode could provide extraordinarily high energy densities; however, it was discovered in the mid-1980s that cycling produced unwanted dendrites on the anode. These growth particles penetrate the separator and cause an electrical short. The cell temperature would rise quickly and approach the melting point of lithium, causing thermal runaway, also known as “venting with flame.” A large number of rechargeable metallic lithium batteries sent to Japan were recalled in 1991 after a battery in a mobile phone released flaming gases and inflicted burns to a man’s face.

The inherent instability of lithium metal, especially during charging, shifted research to a non-metallic solution using lithium ions. In 1991, Sony commercialized the first Li ion, and today this chemistry has become the most promising and fastest growing battery on the market. Although lower in specific energy than lithium-metal, Li ion is safe, provided the voltage and currents limits are being respected.

Credit for inventing the lithium-cobalt-oxide battery should go to John B. Goodenough (1922). It is said that during the developments, a graduate student employed by Nippon Telephone & Telegraph (NTT) worked with Goodenough in the USA. Shortly after the breakthrough, the student traveled back to Japan, taking the discovery with him. Then in 1991, Sony announced an international patent on a lithium-cobalt-oxide cathode. Years of litigation ensued, but Sony was able to keep the patent and Goodenough received nothing for his efforts. In recognition of the contributions made in Li-ion developments, the U.S. National Academy of Engineering awarded Goodenough and other contributors the Charles Stark Draper Prize in 2014. In 2015, Israel awarded Goodenough a \$1 million prize, which he will donate to the Texas Materials Institute to assist in materials research.

## 4.2. Mass production and Commercialization

The key to the superior specific energy is the high cell voltage of 3.60V. Improvements in the active materials and electrolytes have the potential to further boost the energy density. Load characteristics are good and the flat discharge curve offers effective utilization of the stored energy in a desirable and flat voltage spectrum of 3.70–2.80V/cell.

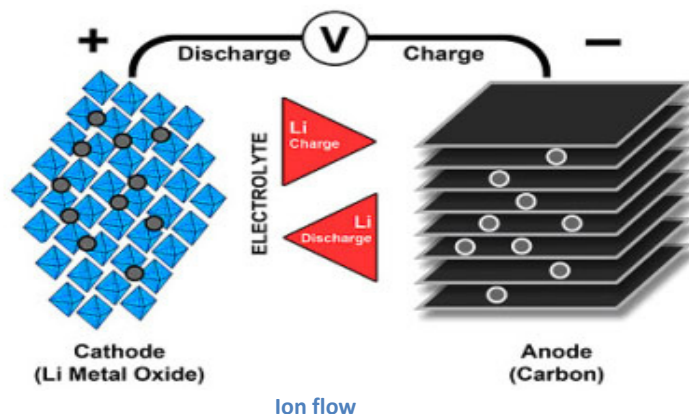
In 1994, the cost to manufacture Li-ion in the 18650 cylindrical cell was over US\$10 and the capacity was 1,100mAh. In 2001, the price dropped to below \$3 while the capacity rose to 1,900mAh. Today, high energy-dense 18650 cells deliver over 3,000mAh and the costs are dropping.

Cost reduction, increased specific energy and the absence of toxic material paved the road to make Li-ion the universally accepted battery for portable applications, heavy industries, electric powertrains and satellites. The 18650 measures 18mm in diameter and 65mm in length. Li-ion is a low-maintenance battery, an advantage that most other chemistries cannot claim. The battery has no memory and does not need exercising (deliberate full discharge) to keep it in good shape. Self-discharge is less than half that of nickel-based systems and this helps the fuel gauge applications. The nominal cell voltage of 3.60V can directly power mobile phones, tablets and digital cameras, offering simplifications and cost reductions over multi-cell designs. The drawbacks are the need for protection circuits to prevent abuse, as well as high price.



## 4.3. Way of working

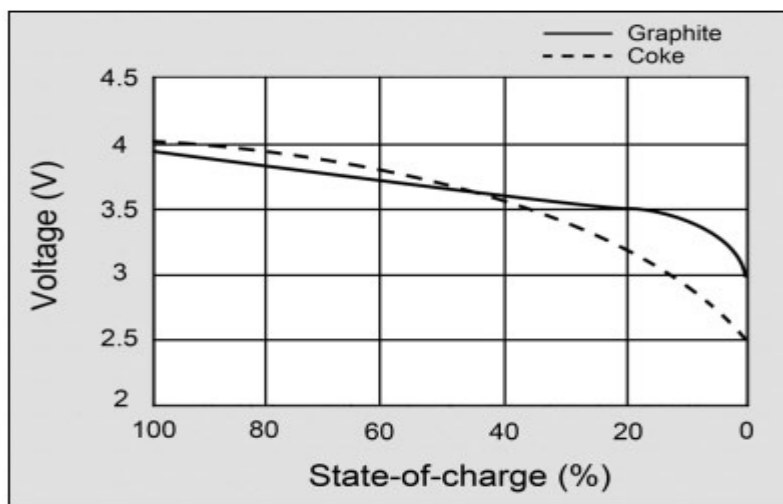
Lithium-ion uses a cathode (positive electrode), an anode (negative electrode) and electrolyte as conductor. The cathode is metal oxide and the anode consists of porous carbon. During discharge, the ions flow from the anode to the cathode through the electrolyte and separator; charge reverses the direction and the ions flow from the cathode to the anode. The following figure illustrates the process.



**Ion flow.** When the cell charges and discharges, ions shuttle between cathode (positive electrode) and anode (negative electrode). On discharge, the anode undergoes oxidation, or loss of electrons and the cathode sees a reduction, or a gain of electrons. Charge reverses the movement.

Sony's original lithium-ion battery used coke as the anode (coal product). Since 1997, most Li ion manufacturers, including Sony, shifted to graphite to attain a flatter discharge curve. Graphite is a form of carbon that has long-term cycle stability and is used in lead pencils. It is the most common carbon material, followed by hard and soft carbons. Nanotube carbons have not yet found commercial use in Li-ion as they tend to entangle and affect performance. A future material that promises to enhance the performance of Li-ion is graphene.

Next plot illustrates the voltage discharge curve of a modern Li-ion with graphite anode and the early coke version.



Voltage discharge curve of lithium-ion.

A battery should have a flat voltage curve in the usable discharge range. The modern graphite anode does this better than the early coke version.

Using **nano-structured** lithium-titanate as an anode additive shows promising cycle life, good load capabilities, excellent low-temperature performance and superior safety, but the specific energy is low and the cost is high.

Manufacturers can attain a high specific energy and low cost relatively easily by adding nickel in lieu of the more expensive cobalt, but this makes the cell less stable. While a start-up company may focus on high specific energy and low price to gain quick market acceptance, safety and durability cannot be compromised. Reputable manufacturers place high integrity on safety and longevity.

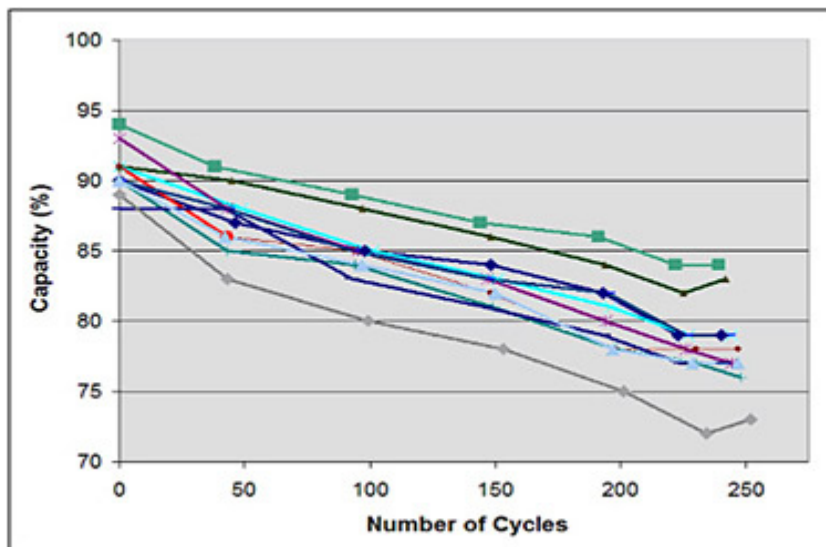
#### 4.4. Capacity, charge and discharge

A battery's capacity is the amount of electric charge it can deliver at the rated voltage. The more electrode material contained in the cell the greater its capacity. A small cell has less capacity than a larger cell with the same chemistry, although they develop the same open-circuit voltage. Capacity is measured in units such as amp-hour (A·h).

The rated capacity of a battery is usually expressed as the product of 20 hours multiplied by the current that a new battery can consistently supply for 20 hours at 20 °C, while remaining above a specified terminal voltage per cell. For example, a battery rated at 100 A·h can deliver 5 A over a 20-hour period at room temperature.

The fraction of the stored charge that a battery can deliver depends on multiple factors, including battery chemistry, the rate at which the charge is delivered (current), the required terminal voltage, the storage period, ambient temperature and other factors.

The expected capacity loss of Li-ion batteries was uniform over the delivered 250 cycles and the batteries performed as expected.



Capacity drop as part of cycling.

Eleven new Li-ion were tested on a Cadex C7400 battery analyzer. All packs started at a capacity of 88–94% and decreased to 73–84% after 250 full discharge cycles. The 1500mAh pouch packs are used in mobile phones.

The higher the discharge rate, the lower the capacity. The relationship between current, discharge time and capacity for a lead acid battery is approximated (over a typical range of current values) by Peukert's law:

$$t = \frac{Q_p}{I^k}$$

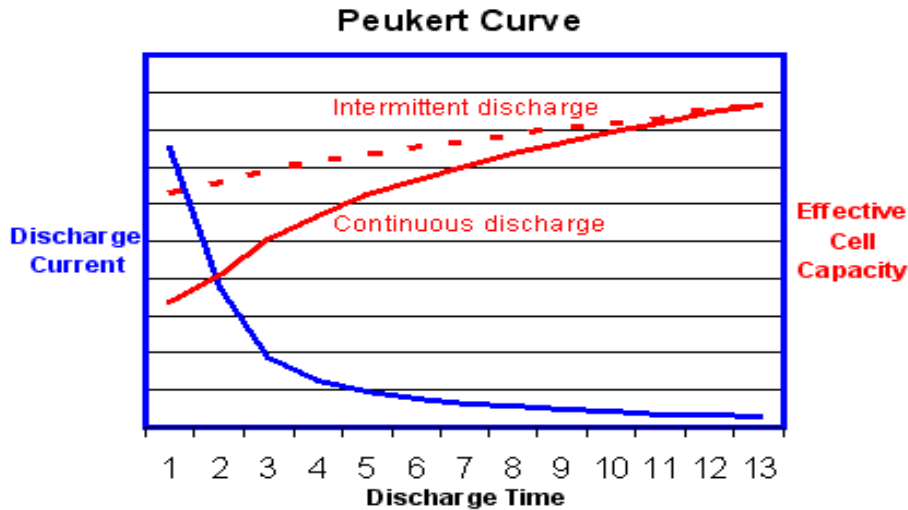
Where:

$Q_p$  is the capacity when discharged at a rate of 1 amp.

$I$  is the current drawn from battery (A).

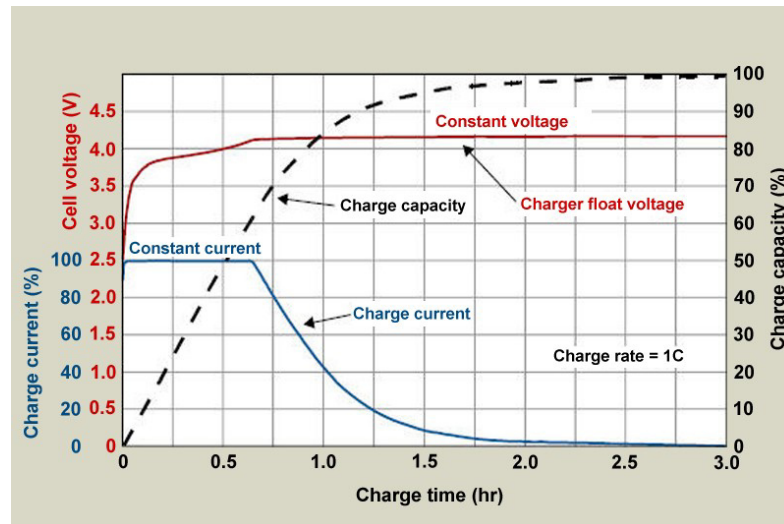
$t$  is the amount of time (in hours) that a battery can sustain.

$k$  is a constant around 1.3.



**The Li ion charger** is a voltage-limiting device that has similarities to the lead acid system. The differences with Li-ion lie in a higher voltage per cell, tighter voltage tolerances and the absence of trickle or float charge at full charge. While lead acid offers some flexibility in terms of voltage cut off, manufacturers of Li-ion cells are very strict on the correct setting because Li-ion cannot accept overcharge. The so-called miracle charger that promises to prolong battery life and gain extra capacity with pulses and other gimmicks does not exist. Li-ion is a “clean” system and only takes what it can absorb.

When the battery is first put on charge, the voltage shoots up quickly. This behavior can be compared to lifting a weight with a rubber band, causing a lag. The capacity will eventually catch up when the battery is almost fully charged. This charge characteristic is typical of all batteries. The higher the charge current is, the larger the rubber-band effect will be. Cold temperatures or charging a cell with high internal resistance amplifies the effect.



Volts/capacity vs. time when charging lithium-ion.

The capacity trails the charge voltage like lifting a heavy weight with a rubber band.

#### 4.5. Advantages and disadvantages of Li-ion batteries

The following lists summarize the advantages and limitations of Li-ion.

##### Advantages

- High specific energy and high load capabilities with Power Cells
- Long cycle and extend shelf-life; maintenance-free
- High capacity, low internal resistance, good coulombic efficiency
- Simple charge algorithm and reasonably short charge times
- Low self-discharge (less than half that of NiCd and NiMH)

##### Limitations

- Requires protection circuit to prevent thermal runaway if stressed
- Degrades at high temperature and when stored at high voltage
- No rapid charge possible at freezing temperatures (<0°C, <32°F)
- Transportation regulations required when shipping in larger quantities

## 4.6. Nanotechnology for Li-ion batteries

Nanotechnology has important contributions to make to the efficiency of energy storage. Note that the types of batteries where nano is making a difference are the ones in cars, laptops, and industrial power backups, rather than the batteries rolling around in your kitchen drawer.

A key factor in battery efficiency is the power density, or how much electrical power a battery can supply per weight. Of the various types of batteries in use, lithium-ion batteries have the greatest power density, which is why they are used in laptops and electric cars.

Lithium-ion batteries can store the same amount of power as a nickel-metal hydride battery in a lighter and smaller package. Lithium-ion manufacturers project that their batteries will last about ten years, about four years longer than nickel-metal hydride batteries.

However, lithium-ion batteries are slower to charge and have safety issues. (For example, in one publicized instance a few years ago, lithium-ion batteries in laptop computers caught fire.) Many companies are exploring the use of nanotechnology to change the material used in lithium-ion battery electrodes.

Each company has used its own proprietary material composition, both to reduce the risk of battery fires and to incorporate the capability of a nanostructured surface to increase the surface area on the electrodes. This increase in surface area provides more places for the lithium ions to make contact, allowing greater power density and faster battery discharging and recharging.

We expect the next few steps in nano-based battery improvements to increase power density over conventional lithium-ion batteries by five to ten times. These changes should make laptops lighter, allow them to go a longer time before recharging.

These improvements, however, depend on the manufacturers' choices. For example, electric cars may be capable of running a few hundred miles between recharges or may contain smaller, less expensive battery packs.

### **Future nanotechnology improvements to batteries**

Using nanotechnology in the manufacture of batteries could increase the power available from a battery through several methods being developed today. For example:

Coating the electrode's surface with nanoparticles, nanowires, or other nanostructures: Because the anode is where lithium ions are stored when the battery is charged, increasing the number of stored ions increases the stored electrical power.

Various researchers and companies working with lithium-ion batteries have used nanomaterials to develop anodes with a greater density of locations to which lithium ions can attach. This technique increases the surface area of the electrodes, allowing more lithium ions to be stored.

Changing the atoms to which the lithium bonds: Changing these atoms changes the electrochemical reaction, which could give off more energy, increasing the power produced by the battery for any given weight.

These techniques could increase the efficiency of hybrid or electric vehicles by significantly reducing the battery weight or increasing their range.

#### 4.7. Myths and advices about Li-ion batteries

Environmental conditions, not cycling alone, govern the longevity of lithium-ion batteries. The worst situation is keeping a fully charged battery at elevated temperatures. Battery packs do not die suddenly, but the runtime gradually shortens as the capacity fades.

Lower charge voltages prolong battery life and electric vehicles and satellites take advantage of this. Similar provisions could also be made for consumer devices, but these are seldom offered; planned obsolescence takes care of this.

A laptop battery could be prolonged by lowering the charge voltage when connected to the AC grid. To make this feature user-friendly, a device should feature a “Long Life” mode that keeps the battery at 4.05V/cell and offers a capacity of about 80 percent. One hour before traveling, the user requests the “Full Capacity” mode to bring the charge to 4.20V/cell.

The most typical question is: “Should I disconnect my laptop from the power grid when not in use?” Under normal circumstances this should not be necessary because charging stops when the Li-ion battery is full. A topping charge is only applied when the battery voltage drops to a certain level. Most users do not remove the AC power, and this practice is safe.

The best temperature range to charge Li-ion batteries is between 10°C and 30°C. But technically it is allowed to charge them between 0°C to 45°C.

The temperature range to discharge is wider, from –20°C to 60°C. Batteries perform better at higher temperatures rather than lower, but it may be dangerous and shorten its life.

It is still accepted the myth that charging your battery overnight kills the long-term battery life.

Leaving electronic device plugged in all the time can still lead to degradation, but it's not enough that you'll even notice. As we've pointed out before, if you want to extend the life of your battery, you want to keep it between 40%-80% all the time. That sounds great on paper, but it's pretty ludicrous for someone living in the modern world. The good news is leaving it plugged in overnight while you sleep, even if it's close to full, doesn't negatively affect it as much as it used to.



## **Heat and Cold Can Damage Batteries**

Heat can reduce a battery's capacity. This affects all types of devices — even smartphones heat up when performing demanding tasks — but laptops can become hottest of all when under load. The battery is in the laptop, near the electronics that become hot while working heavily — this contributes to battery wear.

If you have a laptop that you use plugged in all of the time and it gets quite hot, removing the battery can increase the battery's life by limiting the battery's exposure to the heat of your laptop. This won't make too much of a difference in normal use, but if you're using a laptop to play a lot of demanding games and it's heating up quite a bit, it may be helpful. Of course, this only applies to laptops with removable batteries.

Your climate is also a concern. If it gets very hot where you live or you store your device somewhere that gets very hot — say, a hot car left in the sun on a summer day — your battery will wear down faster. Keep your devices near room temperature and avoid storing them in very hot places, such as hot cars on summer days.

Extreme cold temperatures can decrease the lifespan of your battery, too. Don't put a spare battery in the freezer or expose any device with a battery to similarly cold temperatures if you're in a region with cold temperatures.

## **Don't Leave the Battery At 0%**

You shouldn't leave the battery in a fully discharged state for very long. Ideally, the battery wouldn't discharge all the way to zero very often — but if it does, you should recharge it as soon as possible. You don't have to race to a power outlet when your smartphone dies, but don't throw it in your drawer and leave it there for weeks without charging it. If you let the battery discharge completely and leave your device in a closet, the battery may become incapable of holding a charge at all, dying completely.

## 5. FUTURE BATTERIES

Experimental batteries live mostly in sheltered laboratories and communicate to the outside world with promising reports, often to entice investors. Some designs show unrealistic results with anticipated release dates that move with time. Most concepts disappear from the battery scene and die gracefully in the lab without anyone hearing of their passing.

Few other products have similar stringent requirements as the battery, and the complexity puzzles venture capitalists who did well during the dot-com era and expect similar generous returns of their investment in only 3 years; battery development typically takes 10 years. Most venture capitalists don't have the patience to wait and they pull back the money, leaving the developer in deep water. Raising capital is time consuming and many startups devote as much time and energy for this task as to doing research

Most experimental batteries in the lithium family have one thing in common; they use a metallic lithium anode to achieve a higher specific energy than what is possible with the oxidized cathode in lithium-ion, the battery that is in common use today.

Moli Energy was first to mass-produce a rechargeable Li-metal battery in the 1980s, but it posed a serious safety risk as the growth of lithium dendrites caused electric shorts leading to thermal runaway conditions. The local fire department knew exactly where to go on a fire alarm at the Moli plant; it was the battery warehouse. After a venting event injured a battery user, all lithium-metal packs were recalled in 1989. NEC and Tadiran tried to improve the design with limited success.

Very few companies make rechargeable lithium-metal batteries and most offer the primary versions only. Research continues and a possible solution with new materials as part of the solid-state lithium could be on hand. This design is described further in this section.

Researchers have also developed an anode structure for Li-ion batteries that is based on silicon-carbon nanocomposite materials. A silicon anode could theoretically store 10 times the energy of a graphite anode, but expansions and shrinkage during charge and discharge make the system unstable. Adding graphite to the anode is said to achieve a theoretical capacity that is five times that of regular Li-ion with stable performance, however, the cycle life would be limited due to structural problems when inserting and extracting lithium-ion at high volume.

Meeting the eight basic requirements of the octagon battery is a challenge. Commercialization appears to dwell on a moving target that is always a decade ahead, but scientists are not giving up. Here are some of the most promising experimental batteries.

### **Lithium-air (Li-air)**

Lithium-air provides an exciting new frontier because this battery promises to store far more energy than is possible with current lithium-ion technologies. Scientists borrow the idea from zinc-air and the fuel cell in making the battery “breathe” air. The battery uses a catalytic air cathode that supplies oxygen, an electrolyte and a lithium anode

The theoretical specific energy of lithium-air is 13kWh/kg. Aluminum-air is also being tried, and it is a bit lower at 8kWh/kg. If these energies could indeed be delivered, metal-air, as the battery is also known, would be on par with gasoline at roughly 13kWh/kg. But even if the end product were only one quarter of the theoretical energy density, the electric motor with its better than 90 percent efficiency would make up for its lower capacity against the ICE with a thermal efficiency of only 25–30 percent.

Li-air was proposed in the 1970s and gained renewed interest in the late 2000s, in part because of advancements in material science and the endeavor to find a better battery for the electric powertrain. Depending on the materials used, lithium-air produces voltages of between 1.7 and 3.2V/cell. IBM, MIT, the University of California and other research centers are developing the technology.

As with other air-breathing batteries, the specific power may be low, especially at cold temperatures. Air purity is also said to be a challenge as the air we breathe in our cities is not clean enough for lithium-air and would need to be filtered.

For all we know, the battery may end up with compressors, pumps and filters resembling a fuel cell, consuming 30 percent of its produced energy for auxiliary support to stay alive.

Another problem is the sudden death syndrome. Lithium and oxygen form lithium peroxide films that produce a barrier, which prevents electron movement and results in an abrupt reduction in the battery's storage capacity. Scientists are experimenting with additives to prevent the film formation. The cycle life will also need to improve; lab tests currently produce only 50 cycles.

### **Lithium-metal (Li-metal)**

After several failed attempts to commercialize rechargeable lithium-metal batteries, research and limited manufacturing of this battery continues. In 2010, a trial lithium-metal with a capacity of 300Wh/kg was installed in an experimental electric vehicle. DBM Energy, the German manufacturer of this battery, claims 2,500 cycles, short charge times and competitive pricing if the battery were mass-produced.

An Audi A2 with these batteries drove over 450km (284mi) from Munich to Berlin on a single charge. There is a rumor that the car was destroyed itself by a fire while on a laboratory test. Although the lithium-metal batteries passed the stringent approval tests, long-term safety remains an issue because metal filaments can form that might cause an electric short.

At 300Wh/kg, lithium-metal has one of the highest specific energies of lithium-based rechargeable batteries. NCA in the Tesla S 85 comes in at 250Wh/kg, LMO in the BMW i3 has 120Wh/kg and a similar chemistry in the Nissan Leaf has 80Wh/kg. The BMW i3 and Leaf batteries are made for high durability; Tesla achieves this by over-sizing.

### **Solid-state Lithium**

The current Li-ion uses a graphite anode and this reduces the specific energy. Solid-state technology replaces graphite with pure lithium and substitutes the liquid electrolyte soaked in a porous separator with a solid polymer or a ceramic separator. This resembles the 1970 lithium-polymer that was discontinued due to safety and performance reasons. (See BU-206: Li-polymer: Substance of Hype.)

The solid-state battery shares similarity with lithium-metal and scientists are trying to overcome the problem of metallic filament formation with the use of dry polymer and ceramic separators. Additional challenges are achieving sufficient conductivity at cool temperatures and the need to improve the cycle count. Solid-state prototypes are said to only reach 100 cycles.

Solid-state batteries promise to store twice the energy compared to regular Li-ion, but the loading capabilities might be low, making them less suited for electric powertrains and applications requiring high currents.

Targeted applications are load leveling for renewable energy source as well as EVs by cashing in on the short charge times that this battery allows. Research laboratories, including Bosch, predict that the solid-state battery might become commercially available by 2020 and be implemented in cars in 2025.

### **Lithium-sulfur (Li-S)**

By virtue of the low atomic weight of lithium and the moderate weight of sulfur, lithium-sulfur batteries offer a very high specific energy of 550Wh/kg, about three times that of Li-ion. Li-S also has a respectable specific power of 2,500W/kg. During discharge, lithium dissolves from the anode surface and reverses itself when charging by plating itself back onto the anode. Li-S has a cell voltage of 2.10V, offers good cold temperature discharge characteristics and can be recharged at  $-60^{\circ}\text{C}$  ( $-76^{\circ}\text{F}$ ). The battery is environmentally friendly; sulfur, the main ingredient, is abundantly available. A price of US\$250 per kWh is said to be possible.

A typical Li-ion has a graphite anode that hosts lithium-ions much like a hotel books guests. After charging, the battery releases the ions to the cathode on discharge, replicating guests checking out in the morning. In Li-S, graphite is replaced by lithium metal, a catalyst that provides double duty as electrode and supplier of lithium ions. The Li-S battery gets rid of “dead weight” by replacing the metal oxide cathode used in a Li-ion with cheaper and lighter sulfur. Sulfur has the added advantage of double-booking lithium atoms, something Li-ion cannot do.

A challenge with lithium-sulfur is the limited cycle life of only 40–50 charges/discharges as sulfur is lost during cycling by shuttling away from the cathode and reacting with the lithium anode. Other problems are poor conductivity, a degradation of the sulfur cathode with time and poor stability at higher temperatures. Since 2007, Stanford engineers have experimented with nanowire. Trials with graphene are also being done with promising results.

### **Sodium-ion (Na-ion)**

Sodium-ion represents a possible lower-cost alternative to Li-ion as sodium is inexpensive and readily available. Put aside in the late 1980s in favor of lithium, Na-ion has the advantage that it can be completely discharged without encountering stresses that are common with other battery systems. The battery can also be shipped without having to adhere to Dangerous Goods Regulations. Some cells have 3.6V, and the specific energy is about 90Wh/kg with a cost per kWh that is similar to the lead acid battery. Further development will be needed to improve the cycle count and solve the large volumetric expansion when the battery is fully charged.

## 6. CONCLUSION

The present essay was very instructional and useful for the student. This is because this technology field has been rising up in the real world and tech market. Almost everyone in the first world have any kind of portable electronic device which energy is supplied by Li-ion.

Going deeper into the knowledge of batteries, allowed the pupil to learn how to treat properly any battery in order to improve the long term performance of it and enlarge the life time of the device where the battery is placed in, postponing a little bit the dead of the device and trying to avoid, as much as possible, the obsolescence they have.

This essay also allowed the student to take into account many considerations for a possible future in research or in the working world.

There are many alternatives to Li-ion batteries that are being tested. It is for sure one of the best field to invest on, in the following years, as researcher, as financial investor or even as startup company.

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