

Battery Technology: A review

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Abstract

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Abstract

The aim of this thesis is to theoretically design an automatic 'in house' battery testing facility for further construction and implementation in the Technobotnia laboratory (Vaasa).

Theoretical information about the battery world is provided and explained, including the definition of battery, the battery operation, the main parameters and characteristics, and the different types of batteries that are available in the market and the ones that will be in the future. The theoretical introduction and explanation of battery principles lead to the project development which contains basic information to consider for the design of the hardware, and the design itself. A constant voltage battery charger system is proposed, which is designed to charge all types of batteries with its respective scheme and calculations. The concept will automatically disconnect when the battery is full.

In addition, the project development analyzes the different methods for calculating the state of charge of a battery which is essential to inform the user, to increase the life of batteries or to be able to perform a controlled shutdown of the device and to avoid possible loss of information or damage to the batteries. A special attention is placed on the Peukert's law since its implication in the State of Charge of batteries is crucial to compare the theoretical and practical development and calculation of the battery charger intended to be built.

Language: English

Key words: Battery, Charge, Discharge, Peukert's Law

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1 Introduction

In recent years portable technology has evolved more than ever, creating a need for portable power sources that can supply all electronic devices that are and will be on the market in the near future. Meeting this demand has become a priority for technology companies that seek to innovate with different options in the hope of revolutionizing the technological world. Even so, batteries have been and still are the protagonists in this field. Due to the great variety that exists, they can be adapted to the requirements that are asked for and their reliability as a source of portable energy for more than 100 years that this proven and with much travel ahead.

For years, the technologies have been invested heavily in research and development to make batteries lighter, smaller, cheaper and having more energy capacity. At the same time, intelligent chargers that recharge batteries faster, are lighter and protect batteries from overcharging, are being developed. From cameras to electric cars to mobile phones, tools or robots, among many other applications, batteries surround us in a world increasingly dependent on these devices.

Our work focuses on creating an automatic 'in-house' battery testing facility that can adapt to different batteries and allows analyzing the evolution of the discharge and testing them in different conditions. Because of pandemic situation, our work had to be done theoretically with calculated results that would like to be proved, but the design of the project can be projected to be practical in the future so our goal can be completed.

The batteries, that we based the calculations on, are lithium-ion and lead acid since they are two of the most common ones, due to its clear preference by the consumers in different sectors. The basics of the batteries are also reviewed as an introduction to this world, going through the evolution of this technology from its creation to future innovations and its applications in our world.

2 Aims and Objectives

The aim of this thesis is to design an automatic 'in-house' battery testing facility. This facility should be capable to analyze and compare a range of battery types in order to determine and optimize the efficiency of the load.

One of the factors determining battery life is the charge-cycle. It has been noted (Colby, 2020) and (Wasson, 2017) that some commercial chargers can be detrimental to battery health, whereas smart charging will extend battery life. For that reason, it would be necessary to have greater understanding concerning theoretical aspects of the battery charging and discharging.

The facility must be designed to work with a wide variety of batteries which is not usual in the current market and would represent a useful facility for the Technobotnia Laboratory. Then, the theoretical work undertaken in this thesis can be useful for future students who would be able to implement it.

Objectives to meet this aim:

- Investigate the principles and evolution of the battery types and determine the most potential future batteries.
- Analyze the different kinds of estimation at the discharge process.
- Design a schematic prototype of a battery charger.

3 Theoretical Background

Our society's dependence on batteries is evident. The global market value of this sector reached 108.4 billion USD in 2019. The continuous and growing demand for portable technologies as well as the emergence of the electric car forecasts that this demand will continue to rise with an estimated substantial annual growth of 14.1% between 2020 and 2027 (Anon., 2020a).

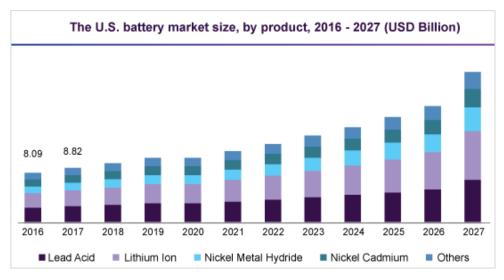


Figure 1- U.S. battery market size expectation by type of battery (Anon., 2020b)

This growth is majorly attributed to the growth in demand of secondary batteries used in portables devices such as laptops, mobile phones, tablets, wearable devices and powered tools. The use of this kind of technologies evolves quickly and the need of the population to be keep up to date puts the pressure on the manufacturers to keep up with the demand. On the other hand, the evolution and popularization of the electric vehicles (EV) is another main reason for the growth on demand of secondary batteries. technological advances in the sector have led to a drop in manufacturing costs and improved efficiency in both charge and discharge process, making the EV a reliable option as the substitute of the internal combustion engine car. In addition, policies in favor of an energy transition to a more sustainable one has benefited this change (Anon., 2020).

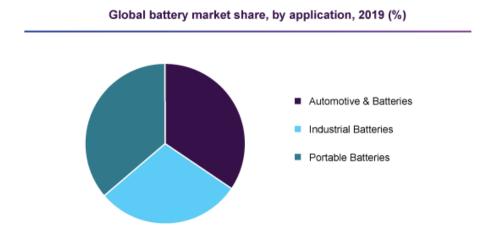


Figure 2 – Global battery market share (Anon., 2020c)

Similarly, energy storage for industrial purposes such as grid energy storage or emergency energy storage, in a major scale, could contribute to substitute other energy sources that produce pollutants and are used to keep up with the demand on the grid when it grows or in case other energy sources are cut off.

This growth in batteries demand is also expected to affect developing markets such as Asia Pacific and African were the introduction of new technology can boost their industry making them more competitive and opening new opportunities in sectors such as automotive or aircraft manufacturing (Anon., 2020a).

The following decade batteries will lead the change to a more sustainable society in line with the ecological policies promoted by governments around the world and international agreements to stop climate change such the European 2030 climate and energy framework that targets several objectives in greenhouse gasses emissions reduction and investment in renewable energies (Anon., 2014).

3.1 What is a battery?

A battery is a device that contains limited energy in chemical form, which can be converted into electrical energy by means of an electrochemical oxidation-reduction reaction. When connected to an external circuit, the chemical reaction starts, creating an electron flow through the circuit and back to the opposite pole of the battery, and thus generating useful electricity. In rechargeable batteries this process can be reversed, the electrochemical process is reverted when recharged and the active materials in the battery return to its original state to be used again (Linden, 2011).

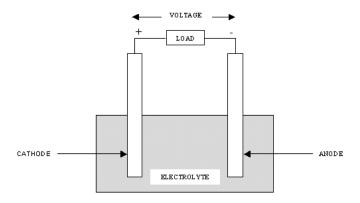


Figure 3 – Battery scheme (Anon., 2020)

Batteries are made up of one or more electrochemical cells arranged in series or parallel to provide the desired current levels or operating voltage. Cells contain the active materials, specifically three main components that are the responsible for this oxidationreduction reaction, also known as redox reaction:

- Anode or negative electrode which is oxidized during the electrochemical reaction and gives up the electrons to the external circuit creating the electron flow. The material that works as anode needs to be efficient as reducing agent, good conductivity, stability, high coulombic output, ease of fabrication and low cost. Because of their properties and because they meet the requirements with cost and fabrication, metals are the commonly used materials. Zinc was the most common one in the 20th century and since the 2000's, lithium is now taking over zinc as the most common, due to methods of control over this metal have been found in recent years (Linden, 2011).
- Cathode or positive electrode which is reduced during the electrochemical reaction and receives the electrons from the external circuit. Required properties for the materials for this task are efficiency as oxidizing component, stability in contact with the electrolyte and having a useful voltage. Like in the anode, materials used as cathodes are mostly metallic oxides, with some exceptions such oxyhalides, halogens and air in some cases or for special functions.
- The electrolyte is situated between the electrodes and provides a medium for transfer of charge so ions released from the cathode can move to the anode. The electrolyte has to have good ionic conductivity but not electrical conductivity because that would suppose an internal short-circuiting in the battery. Moreover, it needs to be stable in a certain range of temperature and not to react with the electrodes chemically, in addition of being inexpensive and safety for its use. Usually, electrolytes consist of aqueous solution but in some cases solid electrolytes and molten salt is used to avoid undesired chemical reactions.

In addition to those main components, there is a separator material that physically separates the anode and cathode to avoid any internal short-circuiting, but it is permeable

to the electrolyte so it can be all around in between the electrodes and assure the ionic conductivity through it.

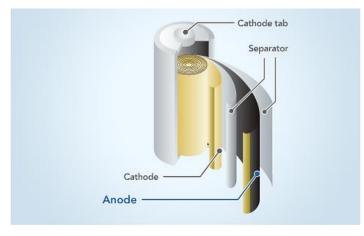


Figure 4 – Dry cell parts (Anon., 2020)

As seen in figure 4, for a simple dry cell, the inside and outside parts of the cell are the anode and cathode, respectively, separated by the electrolyte and everything kept inside the outside shell. But this is just one of many designs for batteries or cells that are available. Different shapes and configurations assure that there are available options for the different necessities on today's products that requires batteries. In addition, the designs have been improved over time to prevent leakage or dry outs (Linden, 2011).

4 Battery analysis

To comprehend better the concept of a battery we must understand what it is going on inside the external shell and understand the chemical reactions that happen between the materials that compose each cell and the battery itself. The materials responsible for these reactions and the circumstances in which the process happen results in different outputs, and the relation between this events is explained in the following chapter, in addition to the related concepts that are required to understand the life cycle of a battery.

4.1 Redox reaction

Even though a wide range of types of batteries exist with different combinations of materials, all of them use the same principal of the oxidation-reduction reaction. The redox reaction is a chemical reaction that produces a change in the oxidation states of the atoms involved. Electrons are transferred from one element to another. As a result, the donor element, which is the anode, is oxidized (loses electrons) and the receiver element, the cathode, is reduced (gains electrons) (Anon., 2002).

 Reduction

 Oxidant + e⁻ → Product

 (Gain of Electrons) (Oxidation Number Decreases)

 Oxidation

 Reductant → Product + e⁻

 (Loss of Electrons) (Oxidation Number Increases)

Figure 5 – Redox reaction equations (Anon., 2020)

Each of these reactions (oxidation and reduction) has a particular standard potential. Depending on the materials used the capacity or efficiency of absorbing and giving up electrons will change. To measure it, oxidation and reduction are studied separately as half-reactions. Both happening at same time and each one requiring the other to happen. The value that compares the strength of the electrochemical potential of the reaction to the willingness of the hydrogen electrons to be given up is known as E^o [V]. This information tells us how prone a material is to give up electrons or receiving them. With this is mind, it is understandable which combinations are more favorable for a battery purpose. As the value is compared to the willingness of the hydrogen electrons to be given up, the value E° for hydrogen is 0, and it is the reference number. The value of E° can be positive or negative, being the elements with positive value willing to receive electrons and elements with negative values willing to give up electrons. As the atomic structure for different materials are different, the electron affinity of different materials will differ. That way the combinations of elements to work as anode and cathode in a battery can be easily made, where a greater valued E° material will act as cathode and a lower valued E^o material will act as anode, within the combination of both. The difference between the standard potential of each material provides the terminal voltage of the cell (Anon., 2016).

Half-Reaction $E^{\circ}(V)$ $Li^+(aq) + e^- \rightleftharpoons Li(s)$ -3.040 $Al^{3+}(aq) + 3e^{-} \rightleftharpoons Al(s)$ -1.676 $Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$ -0.7618 $Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}(aq)$ -0.71 $Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$ -0.44 $Cd^{2+}(aq) + 2e^{-} \rightleftharpoons Cd(s)$ -0.4030 $Ni^{2+}(aq) + 2e^{-} \rightleftharpoons Ni(s)$ -0.257 $\operatorname{Sn}^{2+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Sn}(s)$ -0.14 $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ 0.00 $Cu^{2+}(aq) + e^{-} \rightleftharpoons Cu^{+}(aq)$ 0.159 $MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$ 0.60 $O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$ 0.695 $Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$ 0.771 $Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$ 0.7996 $MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$ 1.23 $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ 1.396 $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$ 1.763 $F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$ 2.87

 Table 1 – Half-reactions equations (Anon., 2020)

As can be seen in Table 1, lithium is the material with the biggest negative value (-3.040 V) which means is the ideal one to work as the anode and fluoride is the one with the biggest positive value (2.87 V) so it would be the ideal one to work as the cathode. If a possible combination of these two materials could be found for a battery purpose, the resulting cell voltage of the battery would result in 2.87 - (-3.040) = 5.91 V. Following this rule, a ranking of combinations can be made depending on how much standard voltage would the materials combination create and analyze if that can be put into practice for battery production.

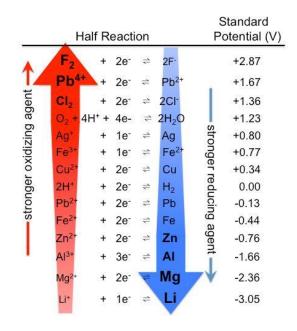


Figure 6 – Standard potential of half-reactions (Anon., 2020)

As said, combinations of anode and cathode (figure 6) that gives high cell voltage and capacity, being light weight are the most favorable but such combinations may not always be practical, some other characteristics will influence, like mentioned above, reactivity with other components, polarization, cost, manufacturing...

4.2 Battery operation

In this section, the operational concepts of a battery are explained one by one to understand the functionality of a battery. All these concepts depend on the material combination explained on the section above, that govern the capabilities of the battery and determine how the battery react when outputting their power.

4.3 Battery discharge

When battery is connected to an external load the electrons start flowing through the external circuit from the anode to the cathode, being the first one oxidized and the second one reduced. To close the electric circuit, the ions flow internally in the battery through the electrolyte, where anions (negative charge) are transferred from the cathode to the anode and cations (positive charge) are transferred from the anode to the cathode (figure 7) (Linden, 2011).

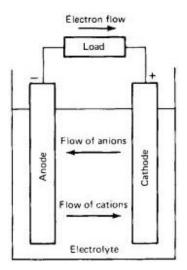


Figure 7 – Discharge scheme (Linden, 2011)

The load is representative of the device that is connected to the battery and uses the electron flow, which is electricity, to be turned up and work. The discharge must be able to satisfy the loads demand and to do it without leaving energy stored behind when the equipment cuts off.

The electrochemical battery discharge follows a pattern of an exponential curve where the energy stays high for most of the discharge time and drops when the discharge is nearly completed. This process depends on different factors such as temperature or Crate of discharge, which is the amount of energy given per unit of time, and will affect to the output of the battery.

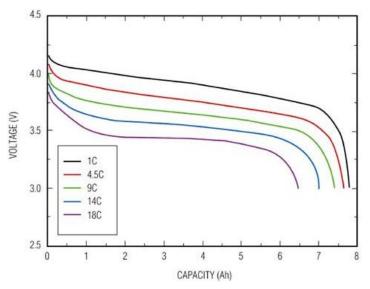


Figure 8 – Discharge curves graphic (Anon., 2006)

As seen in figure 8, the curve starts at the nominal voltage of the battery and decreases as the discharged capacity increases. At the end, the voltage drops and then, the battery stops

outputting when the limit cut-off voltage is reached. This curve differs depending on the discharge C-rate and for any type of battery but the principle is the same for all of them.

One of the characteristics that may differ between types of batteries is the depth of discharge, related to the cut-off voltage. When the load is disconnected from the battery, once the battery is discharged, the voltage rises again to the nominal voltage of the battery. Over-discharging the battery, may damage it and not let the voltage recover after it. This concept is known as depth-of-discharge (DoD) and is different in every battery type. For lead acid batteries the limit is at 1.75V/Cell, for nickel-based batteries it is at 1.00V/Cell, and for lithium-ion batteries it is at 3.00V/Cell. At this point, approximately 95% of the battery capacity is been discharged and the pre-set cut-off function stops the discharge process (Anon., 2019a). In some conditions the DoD needs to be adjusted (figure 9) because external conditions like temperature or heavy load might provoke a premature cut-off because they can provoke the voltage of the battery to be lower than usual when working.

End-of-discharge	Li-manganese	Li-phosphate	Lead acid	NiCd/NiMH
Nominal	3.60V/cell	3.20V/cell	2.00V/cell	1.20V/cell
Normal load	3.0-3.3V/cell	2.70V/cell	1.75V/cell	1.00V/cell
Heavy load or low temperature	2.70V/cell	2.45V/cell	1.40V/cell	0.90V/cell

Figure 9 – End-of-discharge reference values (Anon., 2020k)

4.4 Battery recharge

Those batteries that can be recharged are known as secondary batteries and work under the principal that electrochemical reactions at each of the electrodes are reversible. These batteries are recharged by reverting the process of discharge so the electrons flow is reversed and so it is for the ions in the electrolyte. When the power supply is transferring electricity the opposite way, the role of the materials changes in order to reach the initial status (figure 10). Thus, the material that acted as anode works as the cathode and in the process of recharge it is reduced, and the material that acted as cathode now works as anode and is oxidized in the process (Linden, 2011).

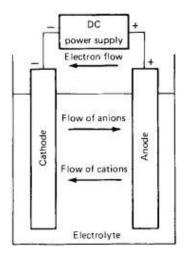


Figure 10 – Charge scheme (Linden, 2011)

In order to recharge the battery, the charger needs to be a specific one for each type of battery or the battery can be damaged in the process. This means that nowadays, except for some types of smart chargers that can adapt to the battery characteristics, each battery has its own charger and using another one could imply affecting the life span of the battery or its capacity.

In addition to that, several charging methods are used depending on the charger and the battery requirements. The differences between these charging methods are the charging rates which determines the amount of power is supplied to the battery per unit of time. Some of the main charging methods are discussed below:

• Constant voltage

Constant voltage allows the full current of the charger to flow into the battery until the power supply reaches its pre-set voltage. It is the simplest circuit structure to charge with easy control design. As the battery is being charged, the current will decrease until the voltage limit is reached and the battery is completely charged. At that point, if the battery is felt connected, the charger enters the float charging mode, that will recharge the minor energy loses due to self-discharge assuring that the battery is fully charged at any moment (Anon., 2020).

Constant current

Constant current charge varies the voltage level though out the charge to maintain the current level constant until the battery reaches the pre-set voltage indicating that is fully charged. This method can quickly charge the battery but the system must disconnect when the process is finished, if not a high constant current will overcharge the battery damaging the plates and shortening its lifespan (Anon., 2020).

• Mixed constant voltage and current

Mixing the constant voltage and constant current modes takes the advantages of each mode and tries to avoid the disadvantages of them. In the beginning of the charge, this method uses constant current at a high current charge. During the first half of the charge the battery is lowly charged and accepts better a high current which also charges it quickly. When a determined voltage is reached, the method is changed and then the voltage is constant until the end of the charge, and when the battery is fully charged the charger changes to the floating mode to assure that the battery is kept fully charged (Anon., 2020).

• Pulsed charge

Pulse charging method is used to increase the efficiency of the process. The battery is charged with periodic current pulses and the periods between the charging pulses, when the battery does not receive external energy, allows the electric energy to be completely converted to chemical energy and the chemicals of the plate to redistribute more uniformly, rising the overall efficiency of the charge (Anon., 2020).

4.5 Main parameters

In order to compare and understand the capability of each battery there are some important parameters that are characteristic of each battery, also within a type of battery. These parameters are a reference when a battery is needed and specific qualities are required, since batteries are used in all types of devices and for infinite purposes.

• Chemistry

As discussed in point 4.1, batteries are made of an extensive range of materials resulting in different capabilities and behaviors in the functionality of the battery. Most common ones are lead, nickel and lithium, each of them with different outputs and specific for some different purposes depending on the requirements (Anon., 2020a). In addition, the charger for each of these types is specially made for its type of battery and using other chargers will damage the battery and its capacity. (Anon., 2020b)

• Voltage

Voltage [V] is created by the potential difference of the materials that composes the positive and negative electrode in the electrochemical reaction. As explained in point 4.1, each material has specific Standard Potential, which means that different combinations can be made to obtain diverse voltages. Still, because most of the resulting voltages are around 2V, cells are connected in series to obtain more practical electrical potentials (i.e. 2V lead acid cells are connected in series to obtain a typical 12V battery).

To know the voltage of a battery, batteries are marked with nominal voltages which is the average voltage a cell outputs when is fully charged, but this may differ from the open circuit voltage (OCV) by a 5 to 7 percent (Anon., 2020c). And it will surely differ from the operating voltage or closed circuit voltage (CCV), which is the output voltage while the battery is being discharged during its use, due to equilibrium concentrations and polarization effects. In addition, some factors like low temperature can decrease the expected voltage output and increase with higher temperature, which is favorable for the electrochemical reactions.

To avoid batteries to discharge below a certain level which could cause damaging the battery, there is a voltage limit called Cut-Off Voltage. When the battery has delivered nearly all the contained energy, the operational voltage reaches the cut-off voltage limit and disconnects.

• Capacity

Battery capacity is measured in Ampere-Hour and is representative of the amount of charge that is stored in the battery. It is determined by the amount of active material contained and represents the maximum amount of electrochemical energy that can be extracted from the battery. It is not an exact value due to conditions and the amount of life cycles of the battery. So, in certain circumstances, battery capacity will differ and with time and use, which the major factor for the battery capacity, it will decrease, having to replace the battery at the end of the estimated charge/discharge cycles (Anon., 2020d).

Changes on the battery capacity can be easily seen when the battery is charged or discharged at different rates. If a battery is discharged using a high current, the capacity is reduced because the amount of active material that had time to react is less than would be if the discharge current was lower, letting the electrodes react more effectively with the electrolyte extracting more energy from the battery and therefore having a higher capacity. This is the reason why this value is given related to time, referred to the time that it takes to discharge a battery at certain current levels (Anon., 2020).

Another condition that affects the capacity of a battery is the operational temperature. Typically, at higher temperatures the performance of the battery is higher than at lower temperatures because the electrochemical reactions are less efficient and as a result the energy extracted is lower than expected.

• Cold Cranking Amps (CCA)

Cold Cranking Amps is referred to the capability for the starter batteries to start up and deliver a certain amount of energy in low temperature conditions. The value of CCA is determined by the amount of current that the starter battery can deliver in a -18°C (0 °F) temperature condition. SAE Standards specifies that a starter battery must maintain for 30 seconds a voltage greater than 7.2V in the low temperature conditions mentioned above. As an example, a battery with a CCA of 500A will deliver 500 amperes while meeting the requirements of the test (Anon., 2020e).

• Energy Density, Specific Energy

Energy density [Wh/kg] defines the amount of energy stored in a cell as a function of the mass of the cell. A battery that has high energy density is able to store a big amount of energy in a small amount of mass (Anon., 2018).

• Power Density, Specific Power

Power Density [W/kg] defines the amount of power that can be outputted at a time as a function of the mass of the cell. A battery that has high power density can deliver a big amount of energy in a short period of time having a small amount of mass. (Anon., 2019)

Since Energy Density and Power Density are similar concepts and can be confused, an example can clarify their meaning. A battery has high energy density but low power density since the energy is given slowly through a long period of time, on the other hand, a capacitator has low energy density but high power density since it delivers all its energy

in a short period of time. Similarly to water coming from a bottle, the flow rate at which the water comes out specifies the Power Density of the bottle, while the amount of water that the bottle contains and can be given represents the Energy Density of the bottle.

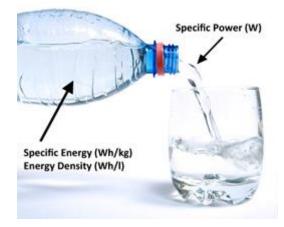


Figure 11 - Graphic explanation of Energy Density compared to Power Density (Anon., 2020a)

• C-Rates

C-Rate is used to express how fast a battery is discharged or charged. The energy contained in a battery can be discharged at different rates which means that the higher the discharge current is, the shorter the working time of the battery. In the same way, the lower the discharge current, the longer the time to discharge it completely will be needed. At 1C, the battery is discharged or charged completely at a current that the process is done in 1 hour. At 0.5C, the current used has been the half and the time needed has been the double. Differently, at 2C, the current has been the double and the time has been the half.

Ideally, changing the rate should not be a problem, but in reality, the efficiency changes and, as a result, when C-Rate is over 1C some energy is converted into heat and the efficiency will decrease and the battery capacity will not reach 100%. On the other hand, if the C-Rate is below 1C, the capacity of the battery could appear to be over 100% when charging process is finished. (Anon., 2020f)

• Load

The load $[\Omega]$ represents the external circuit or device that is connected to the battery causing it to work and extracting its energy in electrical form, thus, is the responsible for the current that is drawn from the battery. The discharge process of the battery will be done according to the power specifications and requirements of the load connected to it

causing the battery to discharge in different rates depending on the demand. At a certain point, the battery will not be able to satisfy the power demand of the load and before that happens, the battery disconnects from the load automatically at a specific voltage, known as end-of-discharge voltage, to avoid over-discharging the battery and causing internal damage.

• State of Health

The State of Health (SoH) is an indicator that represents the general condition of the battery and whether its original characteristics or specifications are being maintained or have deteriorated over time and use. It is inevitable that batteries will deteriorate over life cycles since some irreversible physical and chemical changes will take place. SoH is a measure of long term capability of the battery and indicates how much of the original energy stored in the battery when it was fully charged is no longer available when fully charged now. Therefore, it is a comparison between the current battery state and a fresh battery. (Anon., 2005a)

This 'measurement' it is not accurate and it is rather an estimation due to the different ways this procedure can be done and evaluated. Even though, the results should be similar and based on a consistent set of rules, also considering important factors like internal resistance, charge acceptance, voltage and self-discharge, which are some of the main indicators.

One of the most used procedures is the impedance and conductance test. Battery deterioration will cause impedance to increase and conductance to decrease providing a form to evaluate the 'health' of the battery over the life cycles (Panasonic, 2018).

• State of Charge

The State of Charge (SoC) indicates the amount of energy remaining in the battery before it needs to be recharged as a percentage of the total amount of energy that can be stored in the battery. It is a concept that people are used to it nowadays, but the reference that is considered as fully charged battery can create confusion. (Anon., 2005b)

As it is explained in the SoH concept above, with time and use batteries deteriorate and the total amount of energy that can be stored when the battery is new differs than the total amount of energy that can store after some life cycles. Some irreversible changes take place internally and the original capacity is affected by it. Accordingly, this entails two options when referring to a fully charged battery: use as reference the capacity rated when the battery is new or using the current capacity of the battery. If the first one is used, after some life cycles the battery will not be able to completely recharge since the current capacity would have decreased in comparison to the original one taken as reference. On the other hand, if the second option is used, the battery will be able to reach the 100% of capacity apparently but its actual capacity will not be the same as when it was new.

The chosen option should be the first one, the 100% reference should refer to the rated capacity instead of creating a false security sensation, when a battery still reaches the 100% charge but it is actually nearly at the end of its life.

Some of the methods used to know the value of SoC are Specific Gravity changes for Lead Acid batteries, Voltage changes for Lithium Ion batteries, particularly, and Coulomb Counting, which is the most reliable for any type of battery.

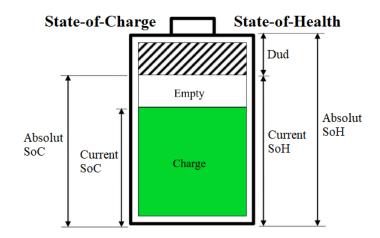


Figure 12 – SoC and SoH concepts compared. Modified from (Anon., 2020)

With the image above we can understand better what the meanings of State of Health and State of Charge are.

• State of Function

The State of Function (SoF) shows battery readiness comparing the evolution of the current energy stored (SoC) in the battery in relation to the available capacity. Depending on the external circuit or Load that is connected to, the State-of-Charge of the battery and the energy stored will evolve differently. The energy demand can vary and the battery needs to keep up with the continuous energy deliver. These factors can cause battery capacity to be affected in the long term creating uncertainty in the estimation of the

battery life span. To avoid that, SoF can be displayed throughout tri-state fuel gauges or fishbowl icons which are different form to represent the amount of energy that can be stored at the time in the battery also showing the amount of capacity lost over life cycles. (Anon., 2020a)

5 Types of Batteries

Despite the fact that most batteries work on the same principal, most of them have been created by different people that adapted that principal to their own idea or project. As a result, the amount of different types of batteries is really large, even though sometimes they just differ in minor aspects. This implies different materials, outputs, life cycles, manufacturing, costs, etc. and everything is considered when a battery is required, which means that this diversification have helped to evolve out technology because more possibilities were possible. In this section, the main types of batteries will be discussed and explained in detail from their creation to their current characteristics and applications.

5.1 Lead-acid batteries

The current lead-acid battery is the fruit of the research and development of many scientists and engineers in the field of electrochemistry. The first antecedents date back to the year 1800, when Alessandro Volta discovered the galvanic battery and began this line of research.

In 1780, Luigi Galvani, Volta's friend and scientist like him, claimed to have produced an electric current by bringing two different metals into contact with the muscle of a frog. Galvani sent a report of his discovery to Volta (Panasonic, 2018), who argued that the frog's muscle only carried the current, and that the current was produced by the metals themselves.

In 1800, Volta, professor of natural philosophy at the University of Pavia, demonstrated the operation of his electric battery, or voltaic cell, consisting of sheets of silver and zinc separated by dilute sulphuric acid, which produced an electric current. As interesting as these phenomena might seem, not much use was found for this type of storage device because the electric machines had not yet been invented. There were several scientists who were interested in this topic, and it was a 26-year-old French scientist, Gastón Planté (BAJ, 2015), who was the first to develop a device that laid the foundations for the leadacid cell, as we know it today. Its battery consisted of nine cells connected in parallel, since the emphasis was placed on obtaining a significant current, something that until then had not been possible with the primary cells. Each cell then consisted of two lead sheets, separated by bands. The entire assembly was wound in a spiral and immersed in a solution containing sulphuric acid diluted 10% in water.

In 1881, the French scientist Faure patented a process to paste the surface of the plates with a lead compound that was easily transformed into the active materials of the battery (Rand, 2016). Faure applied a layer of red lead oxide to the surface of pure lead plates. Subsequently, the plates were rolled up with an intermediate fabric separator. This type of cell proved to have a marked superiority in capacity and formation time over that of Planté. However, its weak point turned out to be the adherence of the active material to the lead base plate. From these improvements on the Planté works, the development of the plates and, also, it is essential to say it, due to the parallel development of the machines to generate electric current. As previously discussed, as long as there were no electrical machines, forming or charging a battery was very difficult.

At the beginning of the 20th century, the lead-acid battery was already a widely used product in many applications, from traction to lighting and telephony. But it was its incorporation as an indispensable element for the start of automobiles that led to the remarkable growth of the battery manufacturing industry.

We can find 2 main groups of Lead-Acid batteries:

- Flooded or ventilated electrolyte (from now on VLA) where the electrodes are submerged in excess of liquid electrolyte.
- Sealed or regulated by a valve (from now on VRLA) where the electrolyte is immobilized in an absorbent separator or in a gel.

In the vented lead-acid batteries (VLA) there are 3 groups:

• Traction or deep cycle: These types of batteries are designed to produce a constant and small discharge for long periods of time. These types of batteries are used in boogies and golf cars, electric cars, vehicles for reduced mobility and wheelchairs and radio control. There are also traction batteries for pallet trucks, forklifts and lifting platforms (BatteryUniversity, 2019).

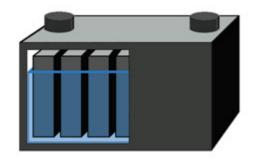


Figure 13 – Deep-cycle lead-acid battery (Anon., 2020m)

The traction battery has thick lead plates to achieve a specific capacity and a reasonably high number of cycles.

• Starter, lighting or ignition: They are designed to deliver the maximum current in a short space of time keeping the voltage constant, therefore, they have a very low internal resistance. These current discharges might be with strong temperature changes, which is why the weight, design and shape are characteristic. These types of batteries are usually frequent for starting cars and all types of diesel and gasoline vehicles. They are used in cars, motorcycles, trucks and buses. They are also used in agricultural and industrial machinery and for some aeronautical applications. (BatteryUniversity, 2019)

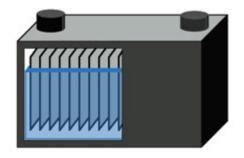


Figure 14 - Starter lead-acid battery (Anon., 2020m)

The starter battery does not allow deep cycles and it has many thin plates in parallel which provides low resistance with a high surface area.

A starter battery cannot be swapped with a deep-cycle battery or vice versa. Each type of battery is designed for a specific use and if we changed them, they would degrade quickly. This summary table compares the typical life of starter and deep-cycle batteries when deep cycled:

Depth of discharge	Deep-cycle battery	Starter battery
100%	150–200 cycles	12–15 cycles
50%	150–200 cycles	100–120 cycles
30%	1,000 and more cycles	130–150 cycles

Table 2 - Cycle performance starter and traction batteries (Anon., 2020m)

• Stationary: They are constantly being charged and special care must be taken so that they do not dry out. A classification of these batteries can be done according to the format in which they are found. It is possible to find stationary batteries that are characterized by presenting a high discharge depth (60 to 80%) and others less than about 50%. The electrolyte and electrode grid material are designed to minimize corrosion. Therefore, these types of batteries have a long service life and low maintenance. This type of batteries is used in the nautical industry and caravans or camper vans. It is also used for renewable energy, batteries for uninterruptible power supplies for computer use (UPS or UPS), telecommunications systems, alarms and emergency or signaling systems.

It must be clear about the purpose of the battery for. A traction battery is capable of starting an engine, but it is not designed for that use and we will miss its qualities. A starter battery can power an electrical device, but its useful life will be greatly affected.

The starter batteries give us a large dose of energy in a few seconds. From there, it will be the alternator of the vehicle responsible for maintaining the battery charge and supplying power to the vehicle. The traction batteries will have a greater requirement as the use we ask for will be more demanding and they operate for hours. And finally, of the stationary ones, we hope that it will provide enough energy supply in several hours. The battery will slowly discharge, so the chemical reaction will last much longer than in a starter battery.

Then, VRLA batteries, compared to the previous ones, have a shorter life cycle, high temperatures and high intolerance. It is a backup battery used in portable equipment, SAIS (uninterruptible power supply systems), factory automation equipment, small lighting devices, alarm systems, electric carts, rechargeable vehicles, etc. The point is that every battery during normal operation generates gasification, and if this is abundant, internal pressure is generated, therefore, it is not appropriate to completely seal a battery and therefore, VRLA batteries have rubber plugs that seal each cell. These plugs in case of excessive gasification, will open releasing internal pressure. That is, the safety plugs regulate the eventual gas leakage. We can divide them into two groups:

- Absorbed Glass Mat (from now on AGM) VRLA, where the electrolyte is maintained by an absorbent porous separator, usually made of fiberglass. The plates in an AGM battery may be any shape. Some are flat, others are bent or rolled. As with lead-acid batteries to maximize the life of AGM battery is important to follow charging specifications and a voltage regulated charger is recommended. There is a correlation between the depth of discharge (DOD) and the cycle life of the battery, with differences between 500 and 1300 cycles depending on depth of discharge.
- Gelled electrolyte VRLA, where a gelling agent is added to the liquid electrolyte so that it adopts the gel consistency. Gel batteries reduce the electrolyte evaporation, spillage (and subsequent corrosion problems) common to the wet-cell battery, and boast greater resistance to shock and vibration.

Table of characteristics:

Specification	Starter	Deep-cycle	AGM	Gel
Туре	A lot of thin plates to increase the surface for high current delivery	Less thick plates which gives high capacity and durability	Fine fiberglass material absorbs sulphuric acid	Electrolyte is suspended in silica type gel
Nominal voltage	2.00 v			
Specific energy	30-50wh/kg			
Charge rate	0.1-0.0	05c (16h charge time	to get for full saturati	on)
Discharge rate	High momentary current	Continuous moderate current	Moderate to high current	
Cycles life (full)	12-15	150-200, longer if not discharged lower than 60%		5-10 years for uninterruptible power supply (ups)
Maintenance	charge every 6 mo	looded needs water: 16 hours arge every 6 months to prevent sulfation		
Applications	Sli (starter, light, ignition) for vehicles	Ups, wheeled mobility	Military, aircraft, start- stop, racing, nascar, marine	Ups, wheeled mobility, busses, trucks, industry

Table 3 – Lead-acid batteries specifications compared (Anon., 2019c)

5.2 Nickel based batteries

Invented over 100 years ago, nickel based batteries was one of the most common in the last century and was used in almost all portables devices at the time. Nowadays, the emergence of other types of batteries makes the global market more competed but still, in other formulas, it is one of the most used batteries worldwide. Characteristics of the several types of nickel based batteries can be seen and compared in Table 4.

5.2.1 Nickel-cadmium (NiCd)

First appeared in 1899 and invented by Waldemar Jungner (Anon., 2014), the nickelcadmium batteries use electrodes made of nickel and cadmium in an alkaline bath of potassium hydroxide. They were the first rechargeable batteries used in a wide variety of portable devices after its development. Nickel-cadmium batteries were more advanced than the lead-acid batteries, which was its competitor at the time, in terms of resistance, both physically and chemically. Aside from that, the materials used in the nickelcadmium batteries were more expensive than lead-acid and thus, less used. But in 1932 some important advancements were made by Shlecht and Ackermann. They created the sintered pole plate and this material improvement resulted in higher load currents and improved longevity.

Some years later, in 1947, Georg Neumann successfully sealed a nickel-cadmium battery creating a useful and practical kind of battery for wider applications. To do it he had to prevent the raising of the pressure in the inside due to hydrogen and oxygen gases generated during the discharge. In order to avoid this, he increased the size of the negative electrode to eliminate the amount of gas produced and boost the efficiency of oxygen absorption. Since that moment, the commercialization of the nickel-cadmium battery was secure and practical, and the popularity to use it in various devices took off. Also, in late 1980s, the ultra-high capacity nickel-cadmium batteries were created, conceiving new opportunities with up to 60% more capacity despite the higher internal resistance and reduced cycle count (BatteryUniversity, 2020).

Nowadays, the applications of nickel-cadmium batteries are in small size portable devices such as power tools, toys, emergency lightning, medical instrumentation, industrial portable products, two-way radios or aviation (due to specific characteristics). It is used in small size products because their cost for low power applications is inexpensive but three to four time more expensive than lead-acid batteries for same capacity (Anon., 2016a).

5.2.2 Nickel-metal-hydride (NiMH)

Investigations started in Battelle-Geneva Research Center in 1967 but due to instabilities in the metal-hydride compound led to an alternative battery invention. Later, during the 80s, more research was done, and some new hydride alloys allowed to solve those instability problems enabling the correct function of the battery. Finally, in 1986, Stanford Ovshinsky patented it. It was based on the nickel-cadmium battery and, in this case, cadmium negative electrode was substituted by one of hydrogen absorbing alloys consisting on lanthanum and rare earth. Like in the nickel-cadmium battery, the electrolyte is alkaline potassium hydroxide. Finally, in the 90s, Group Effort commercialized the first nickel-metal-hydride battery and was the start for this kind of battery, that became one of the most used. During that time, portable electronic devices started to emerge, and nickel-metal-hydride is one of the reasons (BatteryUniversity, 2020).

The different format of the battery made it perfect for every device. In addition, the selfdischarge problem (one of the highest rates of all batteries in the beginning) was majorly solved and the memory effect is much less than nickel-cadmium batteries. With high specific energy and energy density (double of lead-acid and 40% more than nickelcadmium), high cycle life, low cost (expensive during first years of production), recyclability (cadmium is hazardous), and other qualities made it the most used battery and still nowadays is one of the most used. Its applications are much diverse: battery cells AA or AAA, cameras, old mobile phones, electric razors, medical instruments and equipment, high power static applications, and automotive batteries for electric cars (Anon., 2020).

5.2.3 Nickel-iron (NiFe)

When the invention of the nickel-cadmium battery echoed to the US, Tomas Edison started to investigate about it and about another possible combination that Waldemar Jungner already tested. That other formulation was nickel-iron but because of deficiencies with iron formulation Waldemar Jungner did not developed it. In 1901, Thomas Edison patented the nickel-iron battery and claimed to be "far superior than the

lead-acid batteries" promoting it for the starting engines of cars and electric cars at that time (Anon., 2020g). In fact, Tomas Edison and Ford Company worked together prior to WWI, but finally lead-acid batteries remained the common ones for starting engines in gasoline-powered cars and electric cars went out of production after gasoline-powered cars took over them. Still, nickel-iron batteries, despite having a high initial cost and high self-discharge percentage, had low operating cost, good resilience to overcharge and over-discharge, and a lifespan of 20 years or more, in addition to good resistance to vibrations and high temperatures. This made them the favorites for mining in Europe. They were also used for railway signaling, forklifts and stationary applications. During WWII, nickel-iron batteries powered the German V-1 flying bombs and V-2 rockets (BatteryUniversity, 2020).

Nowadays, with lots of improvements, nickel-iron batteries, has reduced significantly self-discharge problem, battery is practically immune to overcharge and over-discharge, and can last over 50 years. With a cost 4 times greater than lead-acid batteries, it competes with lithium-ion batteries in some fields.

5.2.4 Nickel-zinc (NiZn)

Just like nickel-iron, nickel-zinc was an alternative in the compounds of nickel-cadmium battery and was patented by Tomas Edison in US in 1901. As lead acid batteries were the chosen ones for automobile manufacture, nickel-based batteries were intended to specialize in specific fields such railways or mining due to its good resilience to vibrations and high temperature. Nickel-zinc batteries offered high power with great efficiency but short life cycle and high self-discharge percentage let them down (BatteryUniversity, 2020).

Today, some improvements have solved part of self-discharge problem and made them commercial in AA format. Low cost, high power output and good temperature range made them a respectable but rare option.

5.2.5 Nickel-hydrogen (NiH)

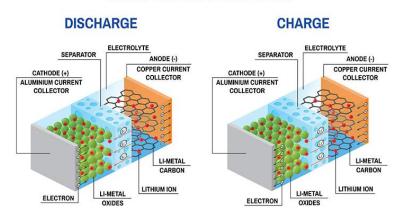
During 1967, while researchers were developing the nickel-metal-hydride battery, some problems with instability of metal-hydride compound led them to develop an alternative battery, which was nickel-hydrogen. Nickel-hydrogen batteries employ nickel-hydroxide for the positive electrode and alkaline potassium hydroxide as in nickel-cadmium batteries. For the negative electrode, instead of using Cadmium, it uses hydrogen in gaseous form as active material. The fact that hydrogen remains in gaseous form within the cells during charge process, enormously increases the pressure inside each cell. This oblige the cells to be hermetically sealed (BatteryUniversity, 2020). This kind of battery was intended to be used in satellites due to its qualities such light weight, very long lifespan, resistance to extreme low temperature and full discharge cycles, and maintenance free. But was not worth for its use in other fields on the earth because of its high cost production and low specific energy. Still nowadays some satellites are using this battery technology. (Anon., 2016b)

Table of characteristics:

Specification	Nickel- cadmium	Nickel-metal- hydride	Nickel- iron	Nickel- zinc	Nickel- hydrogen
Cell voltage (v) (nominal)	1.20	1.20	1.20	1.65	1.25
Specific energy (wh/kg)	45 - 80	60 - 120	50	100	40 - 75
Cycle life (80% dod)	1000	300 - 500	20 years in ups	200 – 300	> 70000
Self- discharge	High	Medium	Medium	Medium	Very low
Overcharging tolerance	Good	Bad	Very good	Bad	Bad
Temperature operating	Low temp	Wide range	Wide range	Wide range	Wide range
Toxicity	High	Low	Low	None	Low
Cost	Low	Low	High	Low	Very high

5.3 Lithium based batteries

The lithium ion batteries need an anode (negative electrode), a cathode (positive electrode) and an electrolyte as the conductor. The anode is made of porous carbon and the cathode is metal oxide. During the charging, the ions flow from the cathode to the anode and in the discharge, ions flow from the anode to the cathode through the electrolyte and the separator. We can see the process in the following figure:



LITHIUM-ION BATTERY

Figure 15 – Lithium-ion battery parts (Anon., 2020)

Diverse additives, including silicon-based alloys, have been tested to improve the performance of the graphite anode. One of the most common Lithium-batteries are Lithium Cobalt Oxide (LiCoO2), Lithium Manganese Oxide (LiMn2O4), Lithium Nickel Manganese Cobalt Oxide (LiNiMnCoO2), Lithium Iron Phosphate (LiFePO4), Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO2) and Lithium Titanate Oxide (Li2TiO3). All of them can be compared in the table of characteristics (Table 5)

5.3.1 Lithium Cobalt Oxide (LiCoO2)

In the 1980s a research group from the Oxford and Tokyo University discovered that the lithium cobalt oxide was quite useful as an intercalation electrode. It is possible to find particles of that compound (ranging from nanometers to micrometers) in some rechargeable lithium-ion batteries. During charging, the cobalt is partially oxidized with some lithium ions moving to the electrolyte. LiCoO2 batteries have very stable capacities, although its capacities are lower than those based on nickel-cobalt-aluminum (NCA)

oxides. The researches analyze that in terms of thermal stability, LiCoO2 are lightly better than other nickel-rich chemistries and this makes that batteries susceptible to thermal runaway in case of having a high temperature operation (over 130°C) or overcharging. If the temperature increases, LiCoO2 decomposition generates oxygen which reacts with the electrolyte of the cell and it could be a problem due to the magnitude of the high exothermic reaction. Currently, we can find this type of battery in mobiles phones, tablets, laptops and cameras (Anon., 2019b).

5.3.2 Lithium Manganese Oxide (LiMn2O4)

In 1983 the *Materials Research Bulletin* published the Li-ion with manganese spinel and in 1996, Moli Energy commercialized a Li-ion cell with lithium manganese oxide as cathode material. LiMn2O4 is one of the most studied manganese oxide-based cathodes because it contains inexpensive materials, the molecular structure lends itself to high rate capability during the charge and discharge of the battery by providing a well-connected framework for the de-insertion an insertion of Li⁺. A further advantage of spinel is enhanced safety and high thermal stability, but the cycle and calendar life are limited. This type of battery it is found in power tools, medical devices and powertrains (Anon., 2019b).

5.3.3 Lithium Nickel Manganese Cobalt Oxide (LiNiMnCoO2)

Lithium Nickel Manganese Cobalt Oxide battery, or NMC, was discovered at 2008 and nickel-manganese-cobalt is one of the most successful cathode combinations in the Liion systems. It can be tailored to serve as energy cells or power cell like Li-manganese. NMC batteries are used for power tools, e-bikes and other electric powertrains. The cathode combination is usually one-third nickel, one-third manganese and one-third cobalt and this distribution decreases the cost of the raw material, due to reduced cobalt content (Anon., 2019b).

5.3.4 Lithium Iron Phosphate (LiFePO4)

In 1996 a research group from the University of Texas published the use of LiFePO4 as a battery electrode. It has gained considerable market acceptance due to its low cost, its thermal stability, non-toxicity, the abundance of iron, safety characteristics and specific capacity. For the commercialization LiFePO4 particles were coated with conductive materials because its intrinsically low electrical conductivity was a barrier. That idea was developed by, Michel Armand and his co-workers but there were others approach that consisted of doping LFP with cations of materials like aluminums, zirconium and niobium (Anon., 2020).

Massachusetts Institute of Technology (MIT) introduced a new coating that allows the ions to move more easily within the battery. That battery can full charge a battery in under a minute by using a bypass system that allows the lithium ions to enter and leave the electrodes at a great speed. The applications in which we can find this type of battery are the devices which use high currents and endurance (Anon., 2019b).

5.3.5 Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO2)

In 1999, Lithium nickel cobalt aluminum oxide battery, or NCA, appeared in some special applications and it is similar to the NMC. It offers high specific energy, a long life span and a reasonably good specific power. Nevertheless, its weak points are the security, the high cost and the limited resources of cobalt and nickel. Nowadays, we can find this type of battery in medical devices, in the industry sector and some electrical vehicles (Tesla) (Anon., 2019b).

5.3.6 Lithium Titanate Oxide (Li2TiO3)

Batteries with lithium titanite were discovered in the 1980s. This type of battery is rechargeable and it is much faster to charge than other lithium-ion batteries because it uses lithium-titanite on the anode surface instead of graphite. Another advantage it is that this type of battery could be charged at low temperature and it has a good thermal stability under high temperature. However, LTO batteries are expensive and its capacity and

voltage is much lower than the conventional lithium-ion batteries. Currently, we can find this type of battery in electrical vehicles and in the solar street lighting (Anon., 2019b).

Table of characteristics:

Specificati on	Lithiu m cobalt oxide	Lithium mangan ese oxide	Lithium nickel mangan ese oxide	Lithium iron phosph ate	Lithium nickel cobalt aluminu m oxide	Lithiu m titana te oxide
Chemistry	Licoo ₂	Limn ₂ 04	Linimnco O2	Lifepo ₄	Linicoal O2	Li ₂ tio ₃
Nominal voltage	3.60v	~ 3.70v	~3.60v	~3.20v	3.60v	2.40v
Specific energy	150- 200wh/ kg	100– 150wh/k g	150– 220wh/k g	90– 120wh/k g	200- 260wh/k g	70- 80wh/ kg
Charge rate	0.7–1c (3h)	0.7–1c (3h)	0.7–1c (3h)	1c (3h)	1c	1c (5c max)
Discharge rate	1c (1h)	1c, 10c possible	1–2c	1c	1c	10c possib le
Cycle life (ideal)	500– 1000	300–700	1000– 2000	1000– 2000	500	3000– 7000
Maintena nce	Keep cool, store partially charged, prevent full charge cycles, use moderate charge and discharge currents					
Applicatio ns	Mobile phones, tablets, laptops	Power tools, medical devices, powertrai ns	E-bikes, medical devices, evs, industrial	Stationar y with high currents and enduran ce	Medical, industria l, Ev (tesla)	Ups, ev, solar street lightin g

Table 5 – Lithium based batteries specifications compared (Anon., 2020p)

5.4 Other types the batteries.

Sometimes and usually using other types of known proved batteries, new types of batteries are created. They are alternative options that work in a distinctive way other than the common ones, and often they have a specific purpose because of their naturality. These batteries have to be considered when talking about batteries because some of them cover a specific sector that has no other options or the alternatives would be too expensive or of difficult implementation. Some of them are explained in this section and compared in the Table 6:

5.4.1 Sodium Sulfide Battery

Thermal batteries appeared during World War II when Georg Otto Erb developed it for military applications for the German military (Anon., 1974). It consisted in cells that used a salt mixture as an electrolyte. Despite that the technology was never used in combat during WWII, United States obtained information about it, which made them investigate about the technology and develop it in order to use it for its own military in 1946. It was applied in fire and nuclear weapons.

A rechargeable version of the battery was requested and since mid-60s much research was done on the field to achieve a battery based on sodium as the negative electrode. Ford Motor Company successfully achieved to create a rechargeable sodium-sulfur battery at that time (Anon., 2011). Their intention was to use it for the electric cars of the moment but the invention did not result in a breakthrough and since then sodium-sulfur have been involved in different fields. In 1983, Japan was the leader in research of this technology and conducted the first large-scale energy storage field test in 1993. The test allowed to find possible improvements and by 2000, TEPCO and NGK, the leaders in the development of the technology, commercialized it (Anon., 2018). Also, NASA tested it successfully in 1997 to use it in high temperature environment but never operated in space. Requiring high temperatures to operate limits the field of application to large-scale stationary versions (Anon., 2010).

Nowadays, this technology is much used in military sector for one-shot guided missiles. Alternatively, sodium-sulfur batteries are used as large-scale energy storage to provide extra power to the power grid in some countries. Benefits of this technology are a large lifespan of 15 years, high voltage operation, high efficiency of 80%, high energy density and quick response in case of demand of energy (Anon., 2015).

5.4.2 Zinc-Air Battery

The effect of oxygen on metal was well known in the 19th century and after different experimentations, in 1932, George W. Heise and Erwin A. Schumacher of the National Carbon Company commercialized, for the first time, battery cells based on that principle (Anon., 1933). Inside the battery there was a porous body made of carbon with air access which collects the oxygen (active mass) coming from the surroundings. That was the positive electrode. The negative electrode consisted on zinc. The reaction was done in an aqueous solution of potassium hydroxide that worked as the electrolyte.

Thomas Edison also had its own battery cell based on zinc-air, larger than the one mentioned previously, and was used in railway signaling and remote communications. This type of battery is still used nowadays with the same technology, most of them in button size, used in watches and hearing aids. It provides high capacity at a very low cost and the voltage is limited so the lifespan achieved is longer.

Despite these advantages, this is a primary battery and cannot be recharged. It was not until 1996 when Miro Zorič commercialized the first rechargeable zinc-air battery (Anon., 2020). For larger units, the batteries could be mechanically recharged by physically substituting the zinc electrode and electrolyte. Doing it did not represent any major effort, it allowed to refuel the battery like would be done in a gasoline powered car, recharging the main substance for work (Anon., 2017). This was proven by Miro Zorič himself when installed this type of propulsor in buses in Singapore at that moment he was leading the national electrification program. These cells provided higher energy density and specific energy ratio, compared to the standard lead acid batteries used. Electrical recharge options are in development nowadays but since this evolution is in very prime stage, many years will be needed to achieve this technology.

5.4.3 Silver-Zinc Battery

Obtaining profitable results of this technology was not possible until 1920s, when Henri André developed a solution for the quick deterioration of the electrodes of the prototype (Anon., 2016). Later during WW2, the U.S. military worked on it and obtained good results, making this kind of primary battery profitable for their missiles or torpedoes. NASA took advantage of this technology in their first satellites also. In fact, this technology is still in use in both organizations for specific purpose. But NASA wanted this technology to be rechargeable.

In 1972, research was made by NASA in collaboration with Astropower Laboratory of Douglas Aircraft Company and achieved to create a rechargeable silver-zinc battery that could be recharged up to 500 times. That was a huge improvement compared to minor improvements made by NASA during 60s, but still far below the 10000 cycle-life that nickel-cadmium could offer at that time. Even though, the big save in space and weight in comparison with nickel-cadmium, convinced NASA to continue with the research. Throughout 70s, NASA increased the performance of the battery developing new chemistries but deep discharge-recharge cycles caused the failure of the battery quicker and, as a result, the technology was not much used by the association (Anon., 2016).

At that point, and after years of any improvement, another opportunity appeared for a company called ZPower (Anon., 2019). Using NASA's publicly available research about the topic as a starting point, in the 90s, this company evolved the rechargeable silver-zinc battery technology to made it commercial, and after more than 100 new patents, their achieved a battery able to survive more than 1000 cycles losing insignificant capacity. The company released its own rechargeable hearing aid battery in 2013 showing that this technology was about to expand and offer new and various opportunities in different sectors as it is doing now. Main qualities of it are the significant space and weight reduction, high energy density, recyclability and safety (unlike lithium-ion batteries, silver-zinc batteries are aqueous so there is no risk of fire).

5.4.4 Reusable Alkaline

All started in 1866, with the appearance of alkaline batteries in wet cell, which was not reusable and being wet meant that liquid electrolyte could be spelt. 20 years later, in 1888, dry cell was created with more durability than old ones and less probability of leaking, but still, these zinc-carbon cells were prone to leakage, corrosion and temperature variation. Finally, and some years later, in 1940s, Lewis Urry (Eveready Battery Company) invented the alkaline manganese battery and it became popular, replacing most of zinc-carbon batteries at the time. Even though the new technology was more expensive, it had more energy density, longer lifespan and less leakage. Corrosion and leakage were two major problems for batteries in 1920s and to prevent that, batteries were sealed with new and more efficient methods that became a problem for zinc-carbon batteries due to generation of corrosive hydrogen gas. To reduce it, researcher introduced mercury to inhibit undesired reactions (Anon., 2020).

After Minamata disaster (Anon., 2019), in Japan in 1956, industry decided to develop mercury-free batteries in late 1980s with the first laws by E.U. in 1991. But before that point was reached, first generation of reusable alkaline manganese batteries was introduced to the market in early 1970s by Union Carbide and Mallory. Alkaline batteries were one of most used types of battery, and at that time portable devices started to emerge, but the technology was not rechargeable (Anon., 2020).

In 1986, a second generation of the battery was produced by Battery Technologies Inc of Canada to market the product. It was based on the patents of the first generation. In 1995, improvements and reformulations were made to license RAM alkaline without mercury to satisfy new regulations (Anon., s.f.). Since mid 2000's RAM alkaline batteries had more energy density and suffered less self-discharge, but still was a kind of battery with lots of drawbacks such a 50% capacity drop in 2nd charge, risk of leakage or lifespan of less than 50 cycles. Some improvements were made since then, but nowadays, RAM batteries remain in the market because of their small environmental impact compared to other disposable cells, and NiMH batteries are taking over them.

Table of characteristics:

Specification	Sodium sulfide	Zinc-air	Silver- zinc	Reusable alkaline
Cell voltage (v) (nominal)	2.58	1.40 - 1.65	1.60	1.50
Specific energy (wh/kg)	90 - 120	300 - 400	250	200
Cycle life (80% dod)	3000	Infinite (manual recharge)	2 years	50
Self-discharge	Medium	High		Very low
Overcharging tolerance	Bad	Impossible to overcharge	Good	Bad
Temperature operating	High temp	Wide range	Wide range	Wide range
Toxicity	None	Low	Low	Medium
Cost	High	Low	Low	Low

Table 6 – Other types of batteries specifications compared (Anon., 2020q)

5.5 Future Batteries

A lot of development fruit of large investments from big technological companies is opening new opportunities to develop new types of batteries or simply, energy storage systems. Some of them are based in known batteries and others are innovative products that might be improved in the future to output more than what they can now. Some of these batteries are shown in this chapter.

5.6 Lithium-air

Originally was proposed in the 1970s although Lithium-air battery gained interest in the late 2000s, due to advancements in material science and the importance to find a better battery for the electric powertrain.

Scientist borrow the idea from fuel cell and zinc-air in making the battery "breathe" air. Lithium-air promises to be the Lithium battery which stores more energy than any other by using a catalytic air cathode which supplies oxygen, an electrolyte and a lithium anode (Anon., 2020h).

The specific power might be low at cold temperatures as with other air-breathing batteries and the air must be filtered because in some cities air it is not clean enough, the air purity it is a challenging factor. Nowadays, another problem is that this type of battery produces only 50 cycles due to the formation of a barrier of lithium peroxide films produced by the battery's lithium and oxygen (Anon., 2020h). This effect prevents electron movement and results in an abrupt reduction in the battery's storage capacity.

5.7 Lithium-metal

Lithium-metal can be classified as a future battery due to the good loading capability and its high specific energy. It can surpass the common lithium-ion battery in many ways. For example, it could hold at least a third more power than a lithium-ion battery (Anon., 2019). When the scientists will be able to control Lithium-metal batteries, they would have a lot of uses such as smartphones or electric cars. Nowadays, the main problem in this type of battery is the uncontrolled lithium depositions which causes dendrite growth that induces safety hazards by penetrating the separator and producing an electric short (Anon., 2020i). The research is focused on inhibit the growth of dendrite which can be possible by adding nanodiamonds as an electrolyte additive.

After various failed attempts to commercialize rechargeable lithium-metal batteries, it could be possible that in a few years a lot of devices bring them improving its benefits.

5.8 Solid-state Lithium

The solid-state battery is an evolution of the lithium-ion battery which its main development belongs to John B. Goodenough, who is considered the promoter of that type of batteries (Anon., 2020).

A solid-state battery works on the same principle as a lithium ion battery, the main difference is in the electrolyte. In the first case it is a liquid and in the second a solid material. As a solid material, Goodenough's team use a solid crystal electrolyte, to replace the liquid one. The crystal electrolyte allows the use of an alkaline metal anode which increases the charge density of the battery. It can store more energy than a lithium ion of the same size and prevents the formation of dendrites. In addition, the glass allows the battery to function even in ambient temperatures of -20°C.

In fact, a solid-state battery provides more autonomy, very short recharge time and it is more secure. According to John Goodenough's team, a solid-state battery can store three times more energy than a lithium-ion battery and recharges in less than an hour. In addition, in an accident it would not set fire (as it does with lithium-ion batteries) and the use of a crystal-based electrolyte would facilitate the serial manufacture of these batteries, and therefore would reduce its cost.

5.9 Lithium-sulfur

Lithium-Sulfur can be classified as a future battery because it offers a very high specific energy (three times that of Li-ion) and a respectable specific power. The battery's main ingredient is abundant available, it offers good cold temperature discharge characteristics (can be recharged at -60°C) and it is environmentally friendly (Anon., 2020j). However, the main drawback is the charging cycles of these batteries since they suffered a lot of stress after a time of use, which caused their useful life to be quite reduced.

Recently, at the University of Monash (Australia), they have managed to carry out tests and declare the patent for a new system that reduces such stress, as we mentioned above, which has allowed them to have batteries that have achieved more than 1,500 cycles of load.

As it is explained in the research, the key lies in adding a polymeric material in the carbon matrix responsible for passing electrons to the insulating sulphur. This polymeric material holds those two materials together, and stress during charging causes a break in this connection that causes rapid deterioration in battery performance. What these researchers have done to focus on this material and try to separate the sulphur particles (Anon., 2020).

Among the advantages we find a greater load capacity, which will allow greater autonomy for all the uses that may be given, whether in smartphones, cars or other devices that need a rechargeable battery for its operation. Also, another advantage that also includes the charging capacity is that we manage to have more powerful batteries, which could be good in some devices. Nevertheless, it is early to talk about their commercialization since they are still doing more tests to determine their behavior and right now, its high cost might be a disadvantage.

5.10 Sodium-ion (Na-ion)

Batteries made from sodium and solid ions are becoming a rational and efficient alternative for several reasons. Sodium is a virtually unlimited resource; it is as abundant as sea water (BatteryUniversity, 2020). However, sodium cannot be easily exchanged for lithium in the battery, because it has a larger ion and its chemical behavior is different. Lithium works well with carbon, but not sodium (EurekAlert, 2019).

At the Japanese NITech University, the expert Naoto Tanibata and his team have already identified a material that together with the graphite, serves to replace carbon, and allows to recharge a sodium battery in six minutes, compared to the hours required for one of lithium (EurekAlert, 2019).

In another article on the subject it is recognized that after many recharges the sodium battery is deteriorated, limiting its capacity in half. But it is also mentioned that with the same weigh, the capacity of sodium batteries is equal to seven times the lithium batteries. Solid sodium ion batteries are expected to be on the market by 2025 (Xhang, et al., 2019).

6 Project development

As has been previously mentioned, because of the pandemic situation, our work had to be a rethink and had to be done theoretically. However, in the future, the project can be tested and improved so our goal can be completed.

To reach the objectives of the thesis the project development part will be divided into two parts. A constant voltage battery charger will be designed and the different ways of estimating the discharge of a battery will be analyzed.

6.1 Constant voltage battery charger

In this section, a constant voltage battery charger has been designed (Figure. 16). A constant voltage allows the full current of the charger to flow into the battery until the power supply reaches its pre-set voltage (4.4).

The charger is used to charge a 12V DC battery with the 120/240 VAC (alternating current) supply found in every house. The system consists of a full-wave rectifier system (diodes D1 and D2 in the diagram). The resulting pulsating voltage (in the form of "m") is applied directly to the battery to be charged through the thyristor (SCR1).

When the battery is low on charge, the thyristor (SCR2) is in the cut-off state (it does not conduct and behaves like an open circuit). This means that a sufficient voltage level reaches the gate of the thyristor (SCR1) for the trigger and the current (current controlled by the resistor R1) also necessary to trigger it reaches it.

When charging is starting (the battery is low) the voltage at the potentiometer (P1) is also low. This voltage is too small to drive the 11-volt Zener diode. Then, the Zener diode behaves as an open circuit and SCR2 remains in the cut-off state.

As the battery charge increases (the voltage increases), the voltage at the potentiometer (P1) also increases, becoming a voltage sufficient to drive the Zener diode. When it conducts, it trips the thyristor (SCR2) which now behaves as a cut.

When the thyristor SCR2 conducts a voltage, division is created with the resistors R1 and R2. This causes the voltage at the anode of diode D3 to be too small to trigger the thyristor (SCR1) and the flow of current to the battery stops (no longer charging). So, the battery is fully charged.

If the battery is discharged again, the process starts automatically. Capacitor C is used to prevent possible unwanted tripping of the SCR2.

6.1.1 Potentiometer setting

The battery is fully charged when it has 1.7 volts across its terminals. When the battery reaches this voltage, the SCR2 should go into conduction and thus the SCR1 stops conducting. For that reason, it is important to set the potentiometer by following these steps:

- The voltage across the potentiometer is measured with a multimeter and adjusted until it measures 0 volts.
- Battery charging begins and the voltage at its terminals is monitored.
- When the battery voltage reaches 12.7 volts, adjust the potentiometer (P1) to drive the SCR2.

6.1.2 Charger Components

- 1 thyristor BT151 or similar (SCR1)
- 1 thyristor 2N5060 or similar (SCR2)
- 3 resistors of 47Ω (ohms), 2 watts (R1, R2, R4)
- 1 x 750 Ω (ohms), 2 watts (P1)
- 1 resistance of 1 K Ω (kilohms) (R3)
- 1 electrolytic capacitor of 50 uF, 25 V or more (C)
- 3 rectifier diodes of 3 amps (D1, D2, D3)
- 1 x 11 volt, Zener diode, 1 watt (Z1)
- 1 transformer with 24 Volt secondary, with center tap, 4 amps (T)

6.1.3 Battery charger's electric schema

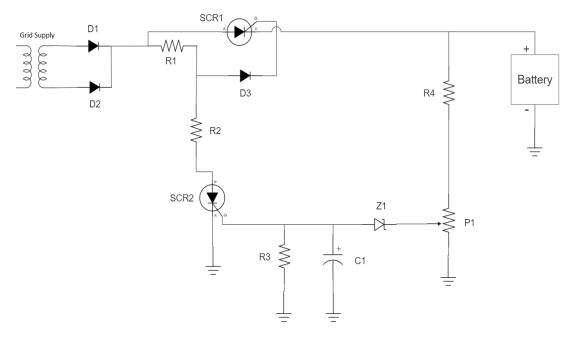


Figure 16 - Constant voltage battery charger schema.

6.2 Battery discharge estimation

It is important to highlight that the information on how much charge a battery has does not give us much by itself. In a car, knowing that there are 10 liters of gasoline left does not tell me how many kilometers I can travel, since the autonomy that those 10 liters give me depends on the type of vehicle, its efficiency and the way the user drives.

For that reason, it is necessary to decide how the information is given, if it is given in Ampere-hours or in percentage and the user has left the responsibility of estimating how long a device can be used, or an estimate is provided in minutes or hours of the charging time you have available.

There are different methods for calculating the state of charge of a battery, depending on battery type, system conditions, etc. The most important are explained below:

• Direct measurement:

It is a theoretical and hypothetical method since it is based on the hypothesis of a constant current discharge. This value is multiplied by the total discharge time of the battery, obtaining the capacity of the battery cell. As it is easy to guess, it is about a method that is not feasible in practice, since the discharge current is variable.

• Measurement of specific gravity:

This method is also known as relative density measurement, and to use it is needed to access to the battery's internal liquid electrolyte. The relationship between the density of water and that of an electrolytic substance decreases linearly with the discharge of the battery cell. Therefore, by measuring the density of the electrolyte, gets an estimate of the cell's SOC (state of charge). Although this is a fairly accurate method, it is not able to determine the total capacity of the battery.

• Internal impedance:

With the charge and discharge cycles, the composition of the internal chemical components changes and that produce a variation of the internal impedance of this battery. This parameter is also an indication of the state of charge, but its measurement becomes very difficult during the actual operation of a battery. In addition, this parameter is highly dependent on temperature, which makes it even more difficult to use.

• Voltage-based estimates:

This method is based on the existence of a direct relationship between the current-voltage of the battery and the capacity of the battery. This is an inaccurate method due to the non-linear behavior of many types of batteries. In the graph below you can see how there is a voltage drop as the full discharge state approaches.

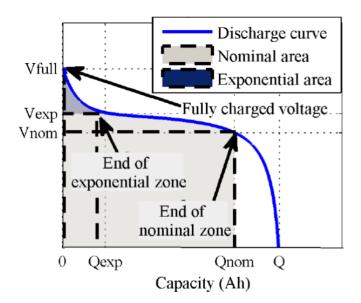


Figure 17 - Nominal current discharge characteristic (Edrington, 2011).

It is known that when a computer or a device runs out of battery, the hard drive can be damaged and that is why companies needed to predict the moment before that happened to perform a scheduled shutdown, giving time to disconnect the equipment from the safe way. For this reason, it is vitally important to have great precision in estimating the voltage before the low battery shutdown.

• Estimation based on intensity:

This method is also called Coulomb Counting and consists of the integration of the incoming and outgoing current of the battery. The method integrates in time the intensity that the cells charge and discharge and its result is the charge stored inside the cells. This method is rated as the most accurate for estimating the battery's state of charge because, as its name suggests, it counts the charges entering and leaving the battery cells.

6.2.1 Peukert's Law

Peukert's Law (BatteryStuff, 2020) explains a phenomenon that occurs in batteries that, apart from being a phenomenon that is not at all obvious, is not fulfilled in some of the discharge models. It consists of a relationship between the state of charge of a battery and its discharge rate: the higher the discharge rate, the lower the battery capacity. Peukert's equation is as follows:

$$C_p = I^k \cdot t \ (6.2.1)$$

Where:

- C_p: Battery capacity discharging to 1 amp (h).
- I: Real discharge current (A).
- t: Real discharge time (h).
- k: Peukert's constant (dimensionless).

The above equation can be reformulated considering H the theoretical discharge time battery:

$$t = H \cdot (\frac{C}{I \cdot H})^k (6.2.2)$$

Theoretically, if we have a battery with a capacity of 40 Ah (Fig. XX), if we discharge it at an intensity of 10 A, we will have a duration of 4 hours.

However, if we consider Peukert's Law, the calculation is not so direct. If we assume that the battery has a Peukert constant of 1.2 (a lead-acid battery has a k between 1.1 and 1.3) and we discharge it at 20 A, we obtain:

$$t = 4 \cdot \left(\frac{40}{20 \cdot 4}\right)^{1,2} = 1.74 \ h$$

So, in this case, if the theoretical calculations had been applied, with a battery with a capacity of 40 Ah and a discharge of 20 A, t = 2 h would have been obtained. However, that is not feasible in practice, since the discharge current is variable, as it has been seen in section 4.3.

7 Discussion

In this chapter, it will be discussed if the initial objectives are achieved, the validity of the results, the limitations of the study and the consistencies and inconsistencies of it.

The first objective of the thesis was to investigate the principles and the evolution of the battery types and determine the most potential future batteries in order to have deep knowledge about this topic. To meet this objective, the first part of the project collects information about the technology, operating methods (charge-discharge), implementation and properties of the different types of batteries, as well as their main uses and their history. Besides, the advantages and disadvantages of each type of batteries were determined and new advances in the industry were presented showing the most important batteries of the future.

The second objective was to analyze the different kinds of estimation at the discharge process and compare them. This objective has been met in the second part of the project development and special emphasis has been placed on the Peukert's Law which proves that theoretical calculations are not the real ones. It is common to suppose a constant current discharge and this method is not feasible in practice since the discharge current is variable. Among the existing methods, some are very precise, but they are complicated to implement them.

The last objective was to design a schematic prototype of a battery charger. Despite the difficulties of coronavirus, it had been possible to have a small approximation in the design of a "smart" charger by designing a constant voltage battery charger which it has to be tested by future students. If the charger works well, the availability of this circuit would avoid the need to visit a specialized workshop to charge the battery as it will charge a 12V DC battery with a 120/240 VAC power supply. However, as it has been presented in the theoretical part, there are other more efficient and complex charging methods which would increase the battery life.

To sum up, the objectives were achieved successfully. This thesis consists of a main theoretical part, drawn from the most recent research articles and a project development part which can be improved by future students. As has been previously mentioned, we had the limitations of the pandemic situation (COVID-19) so our work had to be rethought and unfortunately, we could not test the battery charger presented in the project development part. So, we hope it can be tested and improved so our initial goal can be completed.

Although the difficulties produced by the pandemic situation, thanks to the knowledge in energy technology, electronics and renewable energies acquired in the degree courses, it has been easier to solve the different problems that presented while developing the project.

8 Conclusions

Related to the conclusions, several concepts should be highlighted. The first of these is the importance of having a good method to estimate the state of charge and discharge of the batteries. There are different methods for calculating that and it is important to identify the battery type, system conditions and battery usage. As it has been proved, direct theoretical calculations sometimes are not as accurate as of reality, so it is necessary to use other more complicated methods to achieve better results.

The world trend is that we increasingly depend more on electrical energy sources, and a clear example of this is the electric car. Therefore, it is essential to be able to have batteries with high capacity and reduced weight, and being able to precisely determine the state of charge allows them to take advantage of their potential much more. Battery critical points such as complete filling (to increase the batteries life) and the point closest to complete discharge (to be able to perform a controlled shutdown of the device and avoid possible loss of information or damage to the batteries) are of vital importance. For this reason, smart chargers are very useful in the state of charge because they use charging models to increase battery life and improve performance. Besides, consumer would save money (with the battery life prolongation) and it is more environmentally friendly.

Summarizing, this thesis has allowed entering the world of the batteries, whilst further deepening and improving theoretical knowledge both in the battery discharge estimation and the assembly of electronic circuits applied in the design of the battery charger.

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