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# ANALYSIS AND SYNTHESIS OF AN INNOVATIVE, TEMPERATURE DEPENDENT RUN TIME MODEL FOR THE PERFORMANCE ESTIMATION OF BATTERIES FOR ELECTRIC TRACTION APPLICATIONS

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To my family

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### Abstract

The research activity of this Ph.D. Thesis is about study and definition of innovative methodologies and technologies for the estimation of State of Charge and State of Health of energy storage systems. The specific target of the activities done was to find proper technological and methodological solutions for efficiency and optimization of energy storage systems for what concerns storage capacity, performances in time, number of charge and discharge cycles and prediction and extension of useful life. The solution found and validated in this Ph.D. Thesis is based on an innovative, dynamic, circuital model which allows to accurately represent the functioning of a battery (in charge and discharge) in function of its state of charge (SoC), state of health (SoH)and temperature (T). This model let to determine the battery's internal state and its evolution, if the parameters of the model are known. Model's characterization was made through tests in laboratory on three different sets of  $LiFePO_4$  batteries at the ambient temperature setpoints of  $0^{\circ}C$ ,  $25^{\circ}C$  and  $50^{\circ}C$ . Once the tests were completed, data obtained have been analyzed in the frequency domain to obtain the parameters of the capacitance - resistance model of the battery. So, with non linear interpolation techniques between known points, it was found a relation for each parameter, that highlights its dependence on: temperature, state of charge, state of health and number of cells. The model was finally validated by performing tests on new batteries in different ambient temperature conditions and comparing the data provided by the model with the data obtained from the measurements. Finally, it was identified an ideal room temperature range for the type of batteries under examination, in order to improve their performance over time in terms of energy efficiency and extension of useful life.

### **Energy Storage Systems**

Energy storage systems are electric energy tanks. They are mainly used for the storage of energy produced by renewable sources, for electric traction and to power mobile devices. They produce electric energy by the electrochemical reaction which has place between the two electrodes: cathode and anode, and the electrolyte solution in which they are immersed. The redox reaction which involves the active agents produces a potential difference between the two electrodes, so whether they are connected to an external circuit a current will flow. The open circuit voltage drop between the two electrodes of the battery is function of time, temperature, state of charge, and the story of the battery. It is affected also by the kind and concentration of the agents involved, then as soon as a battery is discharged, the concentration of the agents decreases and so does the voltage drop between the electrodes.



How a Battery Works

Fig. 1.1: Operating principles of an electrochemical cell.

The manufacturers of energy storage systems usually provide discharge curves, which indicate the battery behaviour over time under specific conditions. A battery is also identified by the ability to supply charge: this capacity, indicated with the symbol C, is expressed in Ampere-hours (Ah). However the capacity, even for a new battery is not an absolute quantity, but is function of the supplied current. If a battery is discharged at a low current, the discharge process is slow and the capacity to supply charge is higher. Due to that, the C symbol is often followed by a subscript which indicates the number of hours of the discharge process (for example  $C_{10}$  indicates the capacity to supply charge referred to a process of ten hours) [1].

The basic configuration described is an elementary cell, one or more cells connected in series, in parallel or in a mixed configuration constitute a battery. The series connection (Figure 1.2(a)) is used to have an higher voltage at the terminals of the battery pack, however the main risk of this configuration is the inversion of polarity: if a cell is more damaged than the others it can be inverted during a discharge process, causing venting, electrolyte losses and in worst case flames. For that reason it is highly recommended to replace all the cells of a battery pack if necessary. The parallel configuration (Figure 1.2(b)) otherwise is used to increase the battery capacity. It is a dangerous configuration too, in fact if a cell is damaged, it can absorb current which is supplied by the other cells. Due to that it is recommended to insert a protection diode in series to each cell. Moreover this configuration is ill-judged for charge processes because it introduces uncertainty in the distribution of charge between cells [2].



(c) Mixed configuration

Fig. 1.2: Battery pack configurations

A macro-distinction can be done between primary cells, which are not rechargeable, and secondary cells, which are rechargeable [2]. As it is easily understood, for applications of energy storage are used the secondary cells, because with a charge process it is possible to have the inverse reaction of that described before, and so to restore the initial concentration of the reagents. In that way it is possible to convert electric energy in chemical energy, which is (losses apart) suitable for a re-conversion in electric energy when it is needed. For this reason, in this document only the secondary cells will be discussed in detail, analyzing the aspects related to the various construction technologies, the charge and discharge processes and their uses.

#### 1.1 Technologies of energy storage systems

The first electrochemical accumulator in history was the lead acid accumulator, built for the first time in 1859. The oldest technologies of batteries, and also the most utilized until some years ago, were the lead acid and the Nickel-Cadmium(Ni-Cd), with different characteristics. The presence of heavy metals in these kinds of accumulators, and their environmental impact, had stimulated the research and development of other cleaner technologies, like Nickel-Metal-Hydride(Ni-Mh) and Lithium-ions (Liion). The last one is nowadays the most widespread technology of batteries over market [3]. The construction technologies and the operating principle of the main storage systems will be illustrated below.

#### 1.1.1 Lead Acid Accumulators

Lead Acid accumulators were the first systems to be used for energy storage applications, and still nowadays are widespread mainly as starter batteries, but also for stationary storage and electric traction applications. The great advantage of this kind of accumulators is the low price for Wh, on the other hand they have a low energy density in relation to the weight, so they are preferred in all those applications where the presence of heavy and large accumulators does not generate problems.

Each elementary lead acid cell supplies a nominal voltage of 2, 16V. In each cell it can be triggered a reversible redox reaction, through which it is possible to accumulate and withdraw electrical energy. The "galvanic cell" of a lead accumulator consists in a container inside which is located an electrolyte consisting of an aqueous solution of sulfuric acid  $H_2SO_4(S)(1.32g/cm^3)$  in which two electrodes are immersed at a short distance from each other. The positive electrode is a lead dioxide plate  $(PbO_2)$ , while the negative electrode is made of pure metallic lead (Pb). The electrolyte by its nature is able to carry electric charges through the movement of anions (negatively charged ionized particles) and cations (positively charged ionized particles). In the case of sulfuric acid,  $H^+$  cations and  $SO_4^{2-}$  anions are produced by its ionization. These ions reacting at the contact surface with the electrodes, trigger a redox reaction which at the equilibrium determines a potential difference. The reaction that takes place at the positive electrode is as follows:

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longleftrightarrow PbSO_4 + 2H_2O \tag{1.1}$$

while at the negative electrode the reaction is:

$$Pb + SO_4^{2-} \longleftrightarrow PbSO_4 + 2e^-$$
 (1.2)

Cumulating 1.1 and 1.2, the total reaction is:

$$PbO_2 + Pb + 2H_2SO_4 \longleftrightarrow 2PbSO_4 + 2H_2O \tag{1.3}$$

The reaction evolves in its natural direction from left to right during the discharge phase, while in the charging phase, following the action of an external force impressed by a generator, it evolves in the direction that goes from right to left. As can be seen in figure 1.3, during the discharge process, the electrons flowing through the external circuit from the negative electrode to the positive one, cause in this latter the dissociation of the  $PbO_2$  molecules into  $Pb^{4+}$  and  $2O^{2-}$  and the consequent reduction of  $Pb^{4+}$  ions in  $Pb^{2+}$  ions. These, reacting with the  $SO_4^{2-}$  ions present in the electrode to the Pb molecules in  $Pb^{2+}$ , which by reacting with the  $SO_4^{2-}$  ions, form lead sulfate. Therefore, as the accumulator is discharged, both the electrolyte concentration and the availability of active material will decrease.



Fig. 1.3: Chemical reaction in a lead acid cell during discharge process

In the charge process, the electron flow is inverted due to the the action of an external generator. In this case the inflow of electrons at the negative electrode causes the ionization of  $PbSO_4$  in  $Pb^{2+}$  and  $SO_4^{2-}$  and the reduction of the  $Pb^{2+}$  in Pb, while the  $SO_4^{2-}$  ions will react with the  $H^+$  ions present in solution, releasing sulfuric acid. At the positive electrode the electron extraction causes the ionization of  $PbSO_4$  and the oxidation of  $Pb^{2+}$  in  $Pb^{4+}$ , that reacting with the  $O^{2-}$  ions present in solution will form  $PbO_2$ . The  $SO_4^{2-}$  ions will react with the hydrogen ions releasing sulfuric acid. Once the initial concentration of electrolyte is restored, the further supply of energy to the battery will have no effect on the charge of the same, but will cause further ionization of the water molecules in its components of hydrogen and oxygen, which being inflammable gases, at high concentrations can create a risk condition. This phenomenon is called "gassing". For this reason the charge of lead-acid batteries must always be carried out in well-ventilated rooms, taking care not to overload the battery.

The open circuit potential difference between the two electrodes is the sum of the potentials of the single semi-reactions, whose value depends essentially on the reduction potentials of the two reactions and on the concentration of the electrolyte in the solution, instead it does not depend on the shape and size of the electrodes. In lead-acid cells, as said before, the nominal open circuit voltage between the two electrodes is 2, 16V and this is valid for an electrolyte concentration of  $1,32g/cm^3$ . While the discharge process goes on, the electrolyte concentration decreases and so does the open circuit voltage. The voltage value can be determined by the Nernst Equation if the electrolyte concentration is known:

$$V_{OC} = 0,84 + D\left[\frac{g}{cm^3}\right] \tag{1.4}$$

The open circuit voltage is always different by the voltage under load, because the current flow through the *series resistance* of the battery causes a voltage drop across it. The value of the series resistance increases as the battery is discharged, because the lead sulfate has a much higher resistivity than the lead dioxide and the pure lead. The typical voltage profile during a discharge process at a constant current is showed in figure 1.4. At the startup the voltage decreases steeply due to the formation of a thin layer of lead sulfate on the electrodes; after that there is a long phase in which the voltage is kept almost constant, since the electrolyte molecules that reacts to the contact surface of the electrodes are immediately replaced by other electrolyte molecules present in solution, so that the concentration of the electrolyte near the contact surface remains almost constant. Once a large part of the useful contact surface has been covered with lead sulphate, the voltage will start to decrease steeply, until the end of discharge condition. This type of accumulator must not be discharged below a certain threshold, which is 1,7V in open circuit conditions. Theoretically the discharge process could continue, but in reality, when this threshold is reached, most of the active material has been converted in lead sulfate. Continuing in the discharge



process would further increase the amount of lead sulfate creating a layer so thick as to hinder the reversibility of the process.

Fig. 1.4: Discharge profile of a lead acid cell discharged at a constant current

This happens because the lead sulfate is chemically a salt and therefore tends to "crystallize" by nature, that is to deposit on the electrodes in an irreversible way in the form of salt crystals. That process is called "sulfation" and causes irreversible damage to the electrodes, since the salt crystals are very difficult to be converted into active material. The salt crystals will take some time to form and settle, so the more  $PbSO_4$ to be disposed of and the time the battery will be kept in even partial discharge conditions, the more sulfation will be. Temperature increases the risk of sulfation, especially in the long periods of battery inactivity, as it favors the slow process of self-discharge, which is a cause of sulfation. However it is suggested to keep lead acid batteries under a small charge current during long periods of inactivity, in order to counteract the self-discharge process and with it the risk of sulfation.

The sulfation process, which happens partially in every discharge process, affects battery life, which is declared by the manufacturer, as a certain number of discharge and charge cycles. Manufacturers declare the number of cycles in function of the depth of discharge, for each kind of battery.

A distinction has to be made between cyclic batteries, which are made of thick and compact electrodes, and starter batteries, which are made of thin and porous electrodes. Taking a cyclic battery and a starter battery with the same capacity, the last one will be able to supply higher currents than the first one, because there is more contact surface with the electrolyte and then the reaction is faster. On the other hand these kinds of electrodes have a lower mechanical and structural strength compared to those of the cyclic batteries, so they can less tolerate deep and repeated discharges, which could cause irreversible mechanical and structural alterations.

#### 1.1.2 Nickel-Cadmium Accumulators

The Nickel-Cadmium accumulator was presented for the first time in 1889, and until some years ago, it was the main competitor of the lead acid accumulator. It was widespread because it had some advantages over the lead acid accumulator, including: longer battery life, more strength and reliability, better performances at low temperatures [4]. Anyhow the production of these accumulators was stopped because of the environmental problem related to the presence of Cadmium, the scarcity of disposal centres and the issuance of several European directives that direct towards the prohibition of the use of cadmium. Although Ni-Cd accumulators are going to be totally replaced by the younger and more environmental-friendly Nickel-Metal-Hydride accumulators, they still cover an important role and their principle of operation cannot be ignored in a discussion about batteries.

A Nickel-Cadmium cell is made of two electrodes immersed in an aqueous solution of potassium, sodium or lithium hydroxide. The positive one is made of trivalent Nickel oxy-hydroxide (NiO(OH)), while the negative one is made of metal Cadmium (Cd). The redox reaction which involves the positive electrode is:

$$2NiO(OH) + 2H_2O + 2e^- \longleftrightarrow 2Ni(OH)_2 + 2OH^-$$
(1.5)

while at the negative electrode the reaction is:

$$Cd + 2OH^{-} \longleftrightarrow Cd(OH)_{2} + 2e^{-}$$
 (1.6)

Cumulating 1.5 and 1.6, the total reaction is:

$$Cd + 2NiO(OH) + 2H_2O \longleftrightarrow 2NiO(OH)_2 + Cd(OH)_2$$
 (1.7)

The reaction evolves in its natural direction from left to right during the discharge phase, while during charge, following the action of an external force impressed by a generator, it evolves in the direction that goes from right to left. The concentration of electrolyte is almost constant either during charge and discharge, and so, unlike the lead acid batteries, its measure can not be used as a state of charge indicator.

The nominal open circuit voltage of a Nickel-Cadmium cell is 1, 2V and it can reach 1, 35-1, 4V, the cell can be considered completely empty when its open circuit voltage drops at the value of 1V. Anyhow, to discharge further this kind of cell is not dangerous or very harmful, so they are well suited for applications in which repeated deep discharges are required. During the charge process, some reactions cause the production of gases, especially at the approach of full charge condition, when oxygen is produced at the positive electrode and hydrogen at the negative one. In order to avoid the condition of creating an explosive mix of these flammable gases, the negative electrode



Fig. 1.5: Discharge profile of Nickel based cells discharged at a constant current [2]

is built with an higher capacity than positive one, so that just oxygen under pressure is produced in case of overcharge condition. When the pressure exceeds 3, 5*atm*, cadmium hydroxide is formed at the negative electrode and recycled as water inside the cell. For this reason Nickel-Cadmium batteries can tolerate weak and prolonged overcharges. On the other hand this condition causes a loss of charge and energy, and in vented cell batteries can cause a loss of liquid and therefore the need for periodic top-ups with water. There are two construction technologies of Nickel-Cadmium cells:

- Pocket plate, in which the electrodes are built up of flat pockets of perforated steel strips to hold the active materials and allow the penetration of the electrolyte. The strips are nickel plated to prevent "iron poisoning" of the active materials [4].
- Sintered plate, in which the electrodes are made of Nickel and Cadmium powders compressed and dried in a reducing atmosphere at 800 - 1000°C, in order to be porous. This technology has better performances in terms of energy and power density, and a lower internal resistance [5].

The main advantages of that technology are: an higher energy density (until 60 - 80Wh/kg) and the capacity to withstand deep discharges and repeated overcharges. On the other hand the main disadvantages are: the high rate of self-discharge (a Nickel-Cadmium cell can lose all its charge in few weeks, even if not used), and the memory effect. This phenomenon comes up when batteries are partially discharged: if a Nickel-Cadmium battery is charged before a complete discharge cycle, it loses its capacity to supply all the stored energy. For this reason it is highly advisable to completely discharge these batteries before a charge process.

#### 1.1.3 Nickel Metal Hydride Accumulators

Nickel Metal Hydride accumulator was born from the Ni-Cd one, replacing the Cadmium electrode with one made of a mixture of metal hydrides. This allows to overcome the environmental problems related to the usage of cadmium. Ni-Mh accumulators were presented for the first time in 1967, but the first prototypes were chemically unstable, so they were not used for a long time. The discover of new hydrides in 80s led to a new development stage of that technology, which is widely spread nowadays mainly for consumer electronics. Nickel-Metal hydride batteries inherit the characteristics of their Nickel-Cadmium "older sisters", though they have some differences. They have an high energy density (until 40-85Wh/kq), an higher capacity to supply charge than the Ni-Cd ones, no toxicity, and a low operating internal pressure. Furthermore, the negative pole acts as a catalyst on which hydrogen and oxygen, that can develop with an overcharge, are recombined. When this happens (not valid for charge currents higher than  $C_{10}$ ), the temperature of cell increases considerably, and this indicates that the end of charge condition is reached. The Nickel Metal Hydride batteries also suffer of self-discharge, but the optimization of these systems has recently led to the patent by Sanyo of the so-called "Encloop" or "hybrid" technology that solves this problem; the memory effect, instead, is less present than in the Ni-Cd batteries [6]. The main disadvantage of this technology is the weakness of negative electrode materials, which consequently does not tolerate overcharging.

The positive electrode is made of Nickel Hydrate Oxide, as in the Nickel-Cadmium cell, while the negative electrode is made of metal alloys (M) capable of absorption and accumulation of hydrogen, with the consequent formation of metal hydrides (MH). The electrolyte is alkaline (an aqueous solution of potassium, sodium or lithium hydroxide).

The reaction at the positive electrode is:

$$Ni(OH)_2 + OH^- \longleftrightarrow NiO(OH) + H_2O + e^-$$
 (1.8)

and at the negative electrode:

$$H_2O + M + e^- \longleftrightarrow OH^- + MH \tag{1.9}$$

Cumulating 1.8 and 1.9, the total reaction is:

$$Ni(OH)_2 + M \longleftrightarrow MH + NiOOH$$
 (1.10)

The reaction evolves in its natural direction from left to right during discharge, while during charge, following the action of an external force impressed by a generator, it evolves in the direction that goes from right to left. The nominal voltage of the NiMH accumulators is the same as the Ni-Cd ones, an so is the discharge curve (Figure 1.5).

#### 1.1.4 Lithium Ions Accumulators

Lithium technology is definitely the one that has had the greatest rise in the last 20 years. Nowadays Lithium-ions batteries are a standard "de facto" for mobile devices, laptop and high technology, and cover a very important role too in electric traction and stationary storage applications. They have much better performances than their competitors (Nickel and Lead-Acid technologies), but better performances mean an higher cost, mainly due to the cost of Lithium. Lithium is the lightest metal in nature, it has the highest electrochemical potential and the highest specific energy in relation to weight. Therefore these accumulators have an high energy density related to weight, which make them perfect for usage in mobile devices. There are three types of Lithium



Fig. 1.6: Energy Density related to weight, a comparison between Li-ion, NiMH and Ni-Cd technologies [2]

accumulators:

- Metal-Lithium accumulators;
- Lithium-ions accumulators;
- Lithium-ion polymers accumulators.

The first type has the positive electrode made of a lithium ions acceptor material, and the negative electrode made of metal lithium. These kinds of cells are intrinsically unstable, such that in 90s the idea of marketing them quickly was abandoned. However, the research activity focused in the realization of stable Metal-Lithium accumulators is still active.

Lithium-ions accumulators are more stable and safe, for this reason they became a standard "de facto" for high technology applications. They have a common structure: the anode is made of graphite, while the cathode is usually made of a lithium oxide of a transition metal (for example cobalt oxide, iron phosphate, etc...), which guarantees a layered or tunneled structure where lithium ions can be easily inserted and extracted, as showed in figure 1.7(a). Electrolyte is liquid and consists of lithium salts in organic solution. Electrolyte allows the conduction of lithium ions between the positive and negative electrodes, which are separated from each other by a suitable electronic insulating layer usually consisting of polyolefin. Electrochemical reactions vary depending on the different typologies of cells. In the first Lithium-ion batteries the anode was made of porous carbon, then it was substituted by graphite, which ensured a more flat and regular discharge curve(Figure 1.7(b). Open circuit nominal voltage is 3, 6V and the gravimetric energy density is lower than for lithium metal batteries [7] [8].

The general electrochemical reaction is at the negative electrode:

$$Li_x C_6 \longleftrightarrow C_6 + xLi^+ + e^-$$
 (1.11)

while at the positive electrode:

$$Li_{1-x}MO_2 + xLi^+ + e^- \longleftrightarrow LiMO_2 \tag{1.12}$$

cumulating 1.11 and 1.12, the total reaction is:

$$Li_{1-x}MO_2 + Li_xC_6 \longleftrightarrow LiMO_2 + C_6$$
 (1.13)

where  $C_6$  is graphite, x the number of moles, and M a metal.

The reaction evolves in its natural direction from left to right during discharge, while during charge, following the action of an external force impressed by a generator, it evolves in the direction that goes from right to left. As it can be seen in 1.13, the concentration of electrolyte doesn't change during charge and discharge processes. However they don't tolerate overcharge and over-discharge conditions. Even small perturbation of the optimal operating conditions can trigger processes such as thermal escape, gassing and "venting with flame", which are harmful to the cell and can create dangerous conditions for the operator that uses the battery. For this reason Li-ion batteries are often equipped with an electronic control circuit (BMS - Battery Management System), which has the rule to monitor and control voltage, current and temperature on the cells. The BMS control the charge process and has to intervene promptly if the functioning parameters exceed the limits. Furthermore, for safety reasons, the cells are often placed inside metal containers. For the particular sensitivity of this type of accumulator, precautions must be taken also for series and parallel connections in the battery packs. The presence of electronic monitoring and control systems have an impact upon battery reliability, but also on its cost. Anyway, since lithium-ion batteries are used in applications where small size and reliable batteries are essential, the cost increase due to the control circuitry is then acceptable.



(a) Structure of a Li-ion cell



(b) Voltage - State of Charge curve of a Li-Ion cell

Fig. 1.7: Internal structure and discharge curve of a Li-ion cell [8]

Lithium ion polymers cells , developed since 1999, have the same structure of the Lithium ion ones except for the usage of solid electrolytes made of a solid compound polymer (polyethylene oxide, polyacrylonyl), across which lithium ions move. Instead of Lithium-ion cells, which are enclosed in rigid metal containers, polymeric cells have a flexible and often folding foil structure. For this reason, they adapt to almost all the forms required by the various electronic devices, and permit a simpler, and in perspective less expensive, manufacturing process. Furthermore polymeric cells have the advantage to be less thick than the Li-ion ones. They are in general considered more safe than the Li-ion ones, because their gel electrolyte is less reactive than the liquid electrolyte, and it is not released even in case of an overcharge or an over-discharge. Therefore, a reduced need for strict control systems makes them competitive from an economic point of view [9].

All Lithium technology cells suffer of the self-discharge problem, even tough in much smaller quantities than their Nickel competitors, furthermore they don't have the memory effect. Cycle life of a Lithium battery depends logarithmically on discharge deepness, and it is strongly reduced by overcharge and over-discharge operative conditions. One of the disadvantages of Lithium batteries is their progressive degradation, which means a progressive capacity reduction, starting from the moment of manufacture, regardless of the number of charge and discharge cycles, so even if they are not used.

#### 1.1.5 Molten Salten Accumulators

Molten salt accumulators were used for the first time in the second world war by Germans. These are high temperature batteries, since their operative temperatures are between  $400^{\circ}C$  and  $700^{\circ}C$ , and in the most recent types between  $245^{\circ}C$  and  $300^{\circ}C$ . These accumulators have not toxic elements, have an high energy density versus weight (about three times that of lead-acid ones), a much longer cycle life than the competitors and do not contain rare metals, so they are not too much expensive. Obviously, having such high operating temperatures, they need enclosures which minimize the heat exchange with the outside, and an internal heating system in order to meet the thermal specifications. Thanks to these characteristics, molten salt batteries are increasingly used for stationary storage, for electric traction and for special uses such as in submarines, space probes, etc...

Molten salt technologies include:

- Sodium-Sulfur accumulators;
- Sodium-Nickel Chloride accumulators (ZEBRA);
- Liquid metal accumulators.

As said in [9] Sodium-Sulfur batteries are mainly used for stationary storage applications. The positive electrode is made of sulfur and the negative one is made of sodium, and they are in the molten state. Electrolyte is solid and is made of a ceramic separator of beta-alumina, which being a perfect electronic insulator guarantees the absence of self-discharge. The cell capacity does not depend on the discharge rate and temperature. In general, the battery performance is not influenced by the ambient temperature, as a consequence of the high thermal insulation.

ZEBRA accumulators are similar to sodium-sulfur, but they are intrinsically safer, which is why sodium sulfur is mainly used in stationary accumulation, while ZEBRA is used for electric traction, where the greater the probability of mechanical stress. In ZEBRA batteries the positive electrode is made of nickel chloride, while the negative one is made of sodium. They are in the molten state and are separated by a layer of beta-alumina, and immersed in a liquid electrolyte solution of sodium tetrachloraluminate. The nominal voltage at the terminals of a ZEBRA cell is 2,58V at a temperature of  $300^{\circ}C$ , and it does not depend on the state of charge. In order to obtain a homogeneous and reliable structure, the elementary cell is generally small, and consequently has a small capacity. Therefore, to obtain batteries with higher capacities and higher voltages, series-parallel configurations must be used with the aid of BMI circuits, which are included in the packages together with the heating systems. Liquid metal accumulators are a newer technology and are the result of a research project carried out at MIT. They use molten metals as electrodes, separated by an electrolyte made of a mixture of molten salts. In the first prototypes, the positive electrode consisted of an antimony and magnesium alloy, and the negative one of lithium. Subsequently, the magnesium has been replaced by lead, which is less expensive and allows to lower the operating temperature of the cell, extending its useful life.

#### 1.1.6 Future storage systems: Flywheel batteries

Flywheel batteries are completely different from all the energy storage systems mentioned above. They are electro-mechanical accumulators, which store energy in the form of rotational kinetic energy of a flywheel with magnetic suspension, placed inside a vacuum chamber in order to reduce its friction. These storage systems are coupled with reversible electric machines, which let to the stored energy to be fed into the power grid. In particular, the electric machine acts as a motor during the charge process, increasing the number of rotations of the flywheel up to the nominal value, while during discharge it acts as a generator at the expense of the flywheel rotation energy, whose speed then decreases. The amount of stored energy is given by:

$$W = \frac{1}{2}J\omega^2 \tag{1.14}$$

where W is the stored energy, J the moment of inertia of the rotating mass, expressed in  $[kg * m^2]$ , and  $\omega$  is the angular velocity expressed in [rad/s].

In the equation 1.14 it can be seen how increasing the flywheel rotation speed also the stored energy increases. As a consequence it is theoretically possible to obtain accumulators with a very high energy density versus weight. Very important features of these accumulators are the low self-discharge, the high efficiency (over 90%), a very long cycle life (about  $10^5 - 10^7$  discharge and charge cycles) and very fast charge processes: it is possible to completely charge a flywheel battery in few minutes. These characteristics make them particularly interesting especially for electric traction applications. However, they have still many problems, especially with regard to safety and high costs. Such systems were tested in Formula 1 cars, where a KERS system recovered the kinetic energy in braking, subtracting it from the rotation energy of the crankshaft and storing it in a flywheel battery, which would then return it when required [9].

#### 1.2 Energy Storage Applications

Energy storage systems are nowadays essential in many applications, from high technology, to consumer electronics, to automotive applications. The increasing demand for smartphones, laptops, tablets has led to an increasing need for small and safe accumulators, with an high energy density. Just think about the features that have been added to a simple cell phone over the last twenty years and how much these cost in terms of energy. For this reason Lithium-ion batteries, which have an high energy density versus weight (140 - 180Wh/kg), have become a standard de facto for high technology. Thank to them it was possible to add ever more features to the mobile devices and at the same time to reduce their dimension and weight. In low cost consumer electronics applications, instead, the high cost of Li-ion batteries is not acceptable, so primary cells (one time usable) and Ni-MH cells are more used. One of the classic sectors where the use of storage systems has been indispensable for decades is the automotive sector. The classic starter battery is a 12 Volt lead-acid battery, capable of delivering high currents for a few seconds, such as to allow the engine to start. These accumulators, if used properly, do not sustain deep discharge cycles, and once the engine is started, they are kept in charge by the alternator, which has the function to convert mechanical energy in electric energy for the battery. In new generation cars and vehicles, the battery does not have just the starter function, but also has the task of supplying all the integrated electronics in the vehicle (on-board computer, car radio, GPS, etc...).

In the following paragraphs are discussed more in detail the electric traction and stationary storage applications.

#### 1.2.1 E-Mobility

The E-Mobility sector comprises many sub-sectors, from private transport, to public transport, to intralogistics. The first electric car was made in the late 800s, but the lack of efficient and ergonomic energy storage systems has inhibited the diffusion of this technology for traction applications. With the improvement of the energy storage systems, carried out with the high technology, the E-mobility sector too has had a

huge development, tough it still is not widely spread on market, especially for what concerns the vehicles on the road. The main problems in this field are the high cost, long charge times and low autonomy. Autonomy depends on the type of battery used, and, as ever, better performances mean higher costs. The electric cars that today mount lead acid accumulators have a maximum autonomy after the charge that does not exceed 100 - 130 km (obviously this is an indicative rate, actually it depends on the car's load and the speed at which the car is carried during the march), those that mount Ni-MH accumulators have a maximum autonomy up to 200 km at the cost of a much higher price. Without doubt Lithium-ion technology is the most expensive, but also the most effective in order to achieve high performances, Li-ion batteries can guarantee a maximum autonomy up to 400-500km, though they have a big problem, which is that of the progressive degradation of the battery. Lithium-ion accumulators lose about 20-40% of their capacity to supply charge every year, even if not used, so that the battery pack must be substituted every 2-3 years regardless of the kilometres travelled. Another problem with this technology is given by the very long charging times compared to the refueling times for a car with an internal combustion engine. The batteries can be charged directly in the box, or at appropriate charging stations. Recently, public parking areas have been set up to encourage the spread of electric cars, where in each place electricity can be used to charge the vehicle's batteries.

A battery of a car can be charged in conductive mode, by connecting the battery to the grid through an external power supply, or in inductive mode, by inserting the primary winding (adequately protected) into a slot in the vehicle, where it couples with the secondary winding. With this last kind of connection, the risk of electrocution is eliminated since there are no live parts accessible. Obviously in this case the power electronics related to the power supply is integrated in the car. Charge processes are slow, and although the time required for a complete charge depends on the battery technology, it can be quantified in hours. There are many methods of fast charging, that feed the battery with an high current rate to speed up the process, but they are not able to completely charge the battery, and, furthermore, the high current rates imply mechanical and thermal stressful conditions with the risk of damaging the battery or reducing its useful life. These problems, together with the lack of an adequate incentive for the purchase of electric cars, have greatly limited their diffusion, especially in Italy, where it is much lower than the European average. However the use of electric vehicles for public transport in cities is increasing, with car sharing services and buses, that, being intended for urban use, do not require extensive autonomy, and can safely be loaded overnight to be operational during the day. A separate discussion is to be done for hybrid vehicles with double "electric-thermal" power. They combine an electric motor with an internal combustion engine, so they don't

suffer of low autonomy and long charge problems, or even they do not limit the usage of the vehicle. Hybrid cars are able to travel over 700km after a full charge and a full tank of fuel. The internal combustion engine in most hybrid cars is automatically activated only at the start and at high speeds, or when the battery is low. Furthermore a battery of an hybrid car is charged while travelling by a KERS system, which recovers the kinetic energy in braking by transferring it from the drive shaft to the battery through a motor-generator that converts mechanical energy into electrical energy. In addition, the battery is continuously charged while travelling by a motor-generator that burns fuel to produce electrical energy. Obviously hybrid cars do not have zero  $CO_2$  emissions, but still much lower than any car with an internal combustion engine. Both purely electric and hybrid vehicles have some benefits, such as free access to city centres, restricted traffic areas and paid parking. These facilities are part of the incentive plan for the purchase of electric vehicles, which is driven by the European Union's restrictions on  $CO_2$  emissions. The European target, in the last "Clean Mobility Package", is a 30% reduction of the average  $CO_2$  emissions in 2030 compared to 2021, an unthinkable threshold to reach for a car with an internal combustion engine. Anyway, it's not true to say that electric vehicles do not involve  $CO_2$  emissions, since most of the electric energy comes from thermoelectric power plants. So looking at the entire production-charge-discharge chain, there are big advantages on the environment only if the use of electric vehicles is combined with the use of renewable sources to charge the batteries of the vehicles. Energy sharing could be another solution, it implies that the energy could be taken according to a priority criterion from other storage systems, among which, other electric vehicles connected to the grid. However, neither the spread of electric vehicles nor the Energy sharing culture is today mature enough to allow the adoption of such a solution. Other advantages that are not related to the environmental sensibility are the cost of electricity and the efficiency of electric motors: with a petrol engine it is possible to have an efficiency of 25 - 28%which rises to 40% with a diesel engine, while with an electric motor it is possible to have efficiency tips of 90% or more (a value that in any case does not take into account losses in the production process of electricity). However, nowadays the lower consumption costs are not able to amortise the initial costs that remain very high compared to the corresponding internal combustion engine vehicles.

Another discussion is to be done with regard to the sectors of industrial and intralogistics mobility, in fact, a growing number of companies are adopting policies which take care of the environmental issues and of the health of its employees, by reducing the  $CO_2$  emissions. In these applications the main problems related to the e-mobility are acceptable and economic revenues are also more tangible than in the case of electric cars. In fact, especially in big companies, which need an high number of forklifts, the saving of money due to the lower cost of energy, not only amortise the initial cost of the electric vehicles, but also produces a profit. Furthermore, in most cases electric forklifts equipped with lead-acid batteries (which are not very expensive) are able to guarantee the daily autonomy in working hours. Also the request for long charge times is not a problem in this case, as the batteries can be left in charge during "rest" times, to be operative during working hours. In the worst case, if the vehicles are used continuously, it would still be possible to use a spare battery to be alternated.

The advantages related to the use of electric vehicles are: the possibility to use them safely even in closed rooms, the quietness, a longer life than those with fossil fuel engines and a lower cost of maintenance.

#### 1.2.2 Stationary Storage

Stationary Storage refers to the use of storage systems to store energy produced from renewable sources. These sources, like wind energy and solar energy, are not constant and regular, but they have production peaks alternated with phases in which they produce little or nothing. For example a photovoltaic system produces energy only during the daytime hours and not always in the same way, as the angle of incidence of the sun's rays on the surface of the panel changes. Furthermore, production is strongly influenced by meteorological phenomena, such as the presence or absence of cloudiness. A typical daily production curve (Peak Power - time) of a photovoltaic system in a sunny day has the shape of a bell, whose peak power value and its time distribution varies with the size and efficiency of the system, and it also depends on the area where the system is located (both geographical and topographic). During peak hours, if the plant is well sized, there is an overproduction of energy compared to the needs of the user. This surplus energy can be fed into the grid and sold, or can be stored in storage systems and then reused when the photovoltaic production is no longer sufficient to guarantee the needs of users. While the first solution is available only with grid connected systems, the second one is available even for those people who want to get away from the national supplier and be energetically autonomous. In fact, in the first case, the amount of energy sold to the grid covers the expenses due to the request for energy from the grid during the hours when the plant does not produce; however, in the second case, the use of storage systems makes it possible to reuse the energy produced, thus increasing the self-consumption. If the user does a good management of loads and consumption, he can become autonomous and independent of the grid. Obviously, this implies some limitations in use of the loads, which must absorb more in the hours of maximum production. The self-consumption is an index of how much of the energy produced is consumed by the user, and in a plant with well dimensioned energy storage should ideally tend to 100%.

In reality self-consumption never reach the 100%, because of losses in the inverter and in energy storage systems which cause a loss of efficiency. For both the inverter and the energy storage, it is declared a peak value of efficiency, which is reached only when they work in their optimal conditions. Since in traditional systems the energy flows are determined by the needs of the user, the inverter and the batteries will rarely work at their point of maximum efficiency, so the maximum efficiency of the entire system drops below the 70%, even with high quality inverter and batteries. These performances can be significantly improved with an Energy Management System, which has the rule to carefully manage the energy flows to and from the batteries and to the loads, in order to make the batteries and the inverter work as close as possible to their point of maximum efficiency.

The most used batteries for Stationary Storage applications are the lead acid batteries because of their better quality-price rate. Anyhow the lithium ion batteries are widespread too, even though the cost is higher. In fact, with the same stored energy, lithium batteries are smaller, so much so that some manufacturers of solar inverters integrate them inside the inverters themselves. In USA even flywheels batteries are used in some huge photovoltaic power plants of last generation.

The main limits to the use of storage in such systems are logistic and economic. In fact, for big plants it is necessary to have special ventilated chambers where the batteries must reside. Furthermore, storage requires an higher initial investment, and considering that the batteries have a limited life in terms of charge and discharge cycles, it is not always profitable. Earnings in economic terms can be increased through an increase in efficiency and self-consumption.

#### 1.3 Charge process of the Energy Storage Systems

#### 1.3.1 Charging the Lead Acid Batteries

In paragraph 1.1.1 it was discussed the charge process of a Lead Acid accumulator from an electrochemical point of view, and how it causes the decomposition of the lead sulphate molecules created during the discharge process, and the restoration of the initial concentration of sulfuric acid. It is necessary to provide a higher voltage than that of the float charge, in order to be able to fully charge the battery. Doing that, the flowing current is able to ionize the lead sulphate. The charge voltage of a lead acid cell is 2, 4V, but it is advisable to not supply such a voltage for a long time in order to not damage the cell. So it is necessary, in order to completely charge a battery avoiding any damage, to use a stage regulating system to monitor and control voltage and current on the cells according to target values of each stage.

The traditional battery chargers are designed to perform a constant voltage charge,

whose value is usually that of the float charge (2, 21V/cell). So the power supply will try to regulate that voltage, and the current that will flow through the battery is given by Ohm's law:

$$I_{batt} = \frac{V_{CC} - V_{BAT}}{R_{BAT}} \tag{1.15}$$

where  $V_{BAT}$  is the potential difference at the battery terminals and  $R_{BAT}$  is the internal resistance of the battery (which is variable). If the battery is low, the current can be too high and the electromechanical stress can damage the electrodes. In order to avoid that, it is necessary to limit the current which flows across the battery. The range of allowed currents for lead acid batteries is 0, 15 - 0, 3C. In that manner, during a charge process, if a low battery tries to absorb an high current, the power supply will go in current limitation mode. During charge, both  $V_{BAT}$  and  $R_{BAT}$ increase, and when their value is such as to have a lower current than the maximum current delivered by the power supply, the charge continues at a constant voltage of 2, 21V/cell and the flowing current will have a decreasing trend as the battery charges. The constant current phase is much slower, the more charge current is low. In this phase the battery is charged up to 50-60% of its nominal capacity in about 2-3 hours. To carry the battery up to the 80% of its nominal capacity, it is necessary to supply the battery with constant voltage for 3-4 hours more. Continuing to power the battery will not bring more benefits, which can instead be obtained with the use of a multi-stage charging system. A multi-stage charger monitors and controls voltage and current on the battery in each phase of charge. The first stage is at constant current which is 0, 15 - 0, 3C, until the voltage rises up to 2, 4V/cell, which is the absorption voltage. When this condition is reached, the battery is at the 90% of its charge. The second stage is at constant voltage, the system supplies the battery with a voltage of 2, 4V/cell until the current absorbed decreases to a lower value than 0, 03C. In that condition the 100% of charge is reached and then the next stage is the float charge in which the regulator keeps the voltage indefinitely at a value of 2,21V/cell.

Some battery chargers implement another stage of "final charge" at a constant current, which is triggered when the current drops below 0,05-0,06C (as showed in picture 1.8). In this stage the battery is supplied with a constant current of 0,05-0,06C until the voltage increases to a value of 2,65V/cell, then the charge is stopped. In this stage the charge process is accelerated, but almost all energy supplied is converted in "gassing", which comports an increase in the temperature of the cells. If the battery can not accept more charge, it could happen that the voltage value never reach 2,65V/cell and all the energy introduced is converted in "gassing".



Fig. 1.8: A multi-stage charge profile for a lead acid cell

#### 1.3.2 Charging Nickel Batteries

Nickel batteries need a different charge system than that of the lead acid ones. Nickel Cadmium and Nickel Metal Hydride are similar, then the charge process is almost the same for these two types of batteries, even though there are little differences. Since the Ni-MH batteries require some small additional measures, in this section will be discussed first the charging process of Ni-Cd batteries and then that for Ni-MH.

New Ni-Cd batteries need some slow charge cycles before they can be properly used. These charge cycles are made at a low current for a long time (16-24 hours) and their aim is to equally distribute the charge between cells. In fact, the new cells of a battery pack are certainly in a state of imbalance among themselves. Moreover, the electrolyte tends, due to inactivity, to settle on the bottom of the cell, and the settling charges also serve to equally spread it inside the cell. Once finished these first slow charges, the Ni-Cd batteries have better performances if charged at high current rates. In fact, by charging a Ni-Cd battery at rates of 1C or more, a charge efficiency of 91% is achieved, while with a rate of 0, 1C a charge efficiency of 71% is achieved and the memory effect also comes up. To determine the end of charge condition it is possible to monitor the temperature, it keeps almost constant until the battery can accept more charge, then it will rapidly rise because of gassing. Some low quality battery chargers use a temperature sensor to determine the end of charge condition when the temperature rises to  $40 - 50^{\circ}C$ . This technique as well as being inaccurate, does not work well if the charge process is not continuous: if the battery is repeatedly disconnected and connected to the charger, the temperature drops and, despite the battery is already charged, it needs some time to reach again the target temperature. During this time the battery will be overloaded with a deleterious effect on its useful life. Other chargers check the temperature variation (dT/dt) and the end of charge condition occurs when
the temperature rises by at least  $1^{\circ}C$  per minute. This happens because if the battery can not accept more charge, all the energy absorbed will be converted in heat (due to gassing). If the rate of  $1^{\circ}C$  per minute is not reached, the charger nevertheless has a safety threshold set at  $60^{\circ}C$ , after which the charge is stopped. Although these chargers are more fast and accurate, they still may overcharge the battery if it is disconnected and re-connected repeatedly to the charger. The overcharge condition has an harmful effect on useful life of the batteries, even tough it is not as relevant as for Lead Acid and Lithium ion ones. The most advanced chargers check the variation in battery voltage to detect the end-of-charge condition. When the battery is full the voltage characteristic has a peak followed by a decrease in voltage up to its nominal value, so the negative voltage delta indicates the end of charge condition. This delta is even more pronounced as the charge current is higher. Also for this reason chargers of this type do not work as slow chargers, as they would not have adequate sensitivity. Typically a battery charger react to a voltage drop of 10mV/cell at a current rate of 0, 5C or higher. The NDV method is usually combined with a system for detecting the flattening of the voltage curve: that is, if the voltage remains for a long time at the same level without having the standard characteristic with peak and drop, it can be assumed that the charge is over. For safety reasons these chargers have also a temperature control system and a timer that will terminate the charge after a certain time [10].

Charge currents higher than 1C are not harmful for Nickel Cadmium batteries, rather



Fig. 1.9: Charge profile of Nickel Cadmium cell [10]

they are necessary in order to effectively charge the batteries. Up to 70% of the state of charge it is possible to obtain an efficiency close to 100%. Over that threshold, the gassing phenomenon is triggered, with a consequent increase in pressure and temperature inside the cell. So it can be useful to charge the battery with different current rates, reducing the current rate as the state of charge increases over a certain threshold, in order to have better efficiency and reduce gassing.

Nickel Metal Hydride batteries have similar charge specifications, but they less tolerate overcharges, so that to charge them properly it is highly recommended a system which uses NDV technology to detect the end of charge condition. In this case, the delta V is smaller and the sensitivity threshold of the battery charger must be less or equal than 5mV/cell. As a consequence, Ni-Cd battery chargers can not be used for Ni-MH batteries, while those designed for Ni-MH accumulators can be safely used for Ni-Cd batteries [11].

Battery chargers for nickel technologies can also charge the batteries with high current pulses, and this is even healthier because the temperature delta will be lower. Once the charge is finished it is a good practice to keep the Nickel batteries under a small charge current (0, 05 - 0, 1C) in order to compensate for the self-discharge, but in any case it is not advisable to keep them in this state for more than a few days.

#### 1.3.3 Charging Lithium batteries

A multi-stage battery charger, similar to that used for lead acid technology, is necessary to charge properly Lithium cells, anyhow Lithium batteries have different voltage and current thresholds and, moreover, they do not tolerate even little overcharges. A small overcharge can trigger in a lithium cell an instability condition inside the cell, which can be dangerous. Moreover, once charged, these cells do not tolerate a float charge.

A typical Lithium ion cell has a nominal open circuit voltage in the range 3, 6 - 3, 8V/cell, depending on the materials, but the phosphate-based lithium-ion has a nominal cell voltage of 3, 20V and 3, 30V; lithium-titanate is 2.40V. This voltage difference makes these chemistries incompatible with regular Li-ion in terms of cell count and charging algorithm [12]. Of course each battery has its charger which fits the specifications given by the manufacturer. In this paragraph will be discussed the charge process for a battery of 3, 6V Li-ion cells, the same considerations can be made for the other ones, by adapting the voltage levels.

Li-ion batteries are charged at a constant current (first stage) in range 0, 5 - 1C, anyway manufacturers advise to not exceed 0, 8C for an optimal charge. When the voltage reach the threshold of 4, 2V/cell (or the value specified by the manufacturer), the battery charger must keep it constant until the current drops below 3% of the rated current, or it will no longer fall. Since lithium cells do not tolerate overcharges, each battery needs a BMS system properly designed. Lithium cells, unlike the lead acid ones, do not need to be fully charged, indeed keeping the voltage at the maximum threshold reduces their useful life. A full charge on the other hand has some advantages in terms of battery capacity at the expense of service life. Which of the two aspects to prefer depends on the intended use and the choice of the battery charger manufacturer. Some manufacturers choose to not use the 100% of the battery's potentiality, they just carry out a fast charge at constant current until the reach of the threshold. At the end of this stage, the battery will be charged to about 70% of its nominal capacity. Another option is to continue the charge process at constant voltage lower than maximum [13]. Figure 1.10 shows a typical charge profile for a Li-ion cell and how the capacity varies as the battery is charged. Li-ion cells, as said before,



Fig. 1.10: Charge profile of a typical Lithium ion cell [13]

do not tolerate a maintenance charge at all. Some chargers to keep the battery full against the self-discharge problem, apply a "Topping Charge" when the voltage drops below a certain threshold (lower than 4V), and keep it until the voltage does not dates back to the value of 4,05V/cell.

### Battery modeling

The need for battery modeling comes from the needs of applications where these systems are used. As seen in Chapter 1, Energy storage systems are mainly used to power high technology and mobile devices, to store energy from renewable sources, to improve the power quality and to power electric vehicles. Since accumulators are not ideal systems, their behaviour and their characteristics change, depending on the operating conditions and the current state. For many of the applications mentioned above it is essential to know the current state of the battery (and for others very useful), in order to know what to expect from the battery in present and future use. The most important indicators of the battery's state are: the State of Charge and the State of Health (SoC, SoH). The first one is to indicate the amount of charge available in the battery (in a moment of its life) related to the nominal.

Many mathematical and circuital models are used to statically and dynamically describe batteries, and to determine their state during operations. The optimization of the models still covers an important role in many activities of research.

#### 2.1 State Indicators

#### 2.1.1 State of Charge

The State of Charge is an indicator of the quantity of charge available in a certain moment. In some applications, such as those mentioned above, it is important to estimate how much energy the battery can supply in certain conditions, in order to avoid unexpected malfunctions or harmful conditions for the battery. A new full battery has a nominal capacity expressed in Ah at a given current rate and temperature (specified by the manufacturer). If a load tries to absorb more energy, the battery's voltage will drop down, and if the discharge is prolonged, the polarity of some cells can be inverted. This is a very harmful condition especially for Lead acid and Lithium ion cells, as seen in Chapter 1. Manufacturers often give discharge curves at different

current rates and temperatures, in fact the relation between capacity, current rate and temperature is not linear. In general, assuming the ambient temperature constant in nominal conditions, the relation between effective capacity and current rate is expressed by the *Peukert's law*:

$$C_{eff} = \frac{C_{nom}}{i^{n-1}} \qquad i \neq 0; n > 1$$
 (2.1)

where  $C_{eff}$  is the effective capacity of the battery,  $C_{nom}$  the nominal capacity, *i* is the current and *n* is a number that depends on the specific battery. If the battery is ideal n = 1 and then the effective capacity is equal to the nominal capacity at every current rates. In reality typical values of *n* are between 1, 2 and 1, 5.

The state of charge, which is the ratio between the residual charge in a certain moment t, and the capacity of the battery, is also function of current rate and temperature:

$$SoC(i,T) = \frac{Q_t}{C_{eff}(i,T)}$$
(2.2)

If the operating conditions, in terms of temperatures and currents are well defined in a certain range, it is possible to refer to the discharge curves given by the manufacturers or to characterize the battery in order to determine the effective capacity.

The most simple and common method used for the on-line state of charge measurement is the *Coulomb Counting* technique, which consists in the measurement and integration of the current flow across the battery, starting at a moment  $t_0$  when the initial conditions  $(SoC(t_0))$  are well known. Doing that and assuming that temperature and current rate are constant the 2.2 becomes:

$$SoC(t) = SoC(t_0) - 100 \int_{t_0}^t \frac{i(\tau)}{C_{eff} * 3600} d\tau$$
(2.3)

The 2.3 is still valid for small variations of current and temperature. In literature there are many solutions that consider the Peukert's effect on the Coulomb Counting technique [14] [15] [16] [17].

The main disadvantage of this method is the cumulation of the error: as it can be seen in equation 2.3, even a little error in the measurement of current, can lead to a relevant error in the measurement of SoC after a long time. Furthermore this technique doesn't take into account losses for Joule's effect and for self discharge. Assuming that after a complete charge process SoC = 100% (see section 1.3), it is possible to reset the error and start a new measurement. In all those applications where a periodic reset of the measure is not possible, Coulomb Counting is not an effective method for the measurement of SoC.

Another option is to measure the open circuit voltage at the battery terminals, anyhow in order to do that, the battery must have long rest times. In fact as seen in section 1.1 charge and discharge processes involve two phenomenons: charge transfer and diffusion, which are not instantaneous. When the current flow is stopped, battery will need a certain time to exhaust transients and reach its equilibrium condition. Open circuit voltage( $V_{oc}$ ) can be measured at the terminals only when the battery is in its equilibrium condition. This is necessary, but not sufficient to relate  $V_{oc}$  with SoC, in fact, to add more complexity,  $V_{oc}$  is also function of temperature, and dependence on both SoC and T is not linear (see Figure 2.1).



Fig. 2.1: Dependence of  $V_{oc}$  on SoC and T for a  $LiFePO_4$  cell [17]

After a characterization of the battery, if the ambient temperature is known and constant, it is possible to measure the  $V_{oc}$  and to obtain a SoC estimation.

Another more used solution for the measure of  $V_{oc}$  is a combination of the two techniques mentioned above: the *Coulomb Counting* technique is used for on-line measurements, and the  $V_{oc}$  measurement is used to periodically reset the measure during the rest times. Obviously this solution is good just for those applications which have long rest times, in fact the time needed to exhaust the transients depend on the specific battery, and sometimes can be very long (hours or fractions of hours). If transients are still present, the voltage measured at the terminals differs from the open circuit voltage, and can lead to an error in the SoC estimation up to 30%.

A more complex, but also accurate and flexible method to estimate SoC is based on the measurement and characterization of the internal impedance of the battery, which will be discussed later in this document.

#### 2.1.2 State of Health

The State of Health is an indicator of the performance degradation of the battery over time. Manufacturers define a useful life for each battery in terms of discharge and charge cycles. This is because, as seen in Chapter 1, not all the material that reacts at the electrodes can be converted back in active material, with the consequence of a loss of capacity. Furthermore extreme conditions such as overcharges and deep discharges cause mechanical stress on the electrodes, reducing so their useful life. As a consequence the "Cycle life" is also function of the deep of discharge, in fact most manufacturers guarantee a certain number of cycles specifying the operating conditions. Moreover each battery has a minimal, but constant degradation over time since the moment of production, even if not used, caused by internal irreversible processes. This problem is much more relevant for Lithium-ion batteries. Manufacturers often declare a "Shelf life" for their products which is similar to a date of expiry for foods. Also operating and storage temperature, and even SoC at which the batteries are kept during standby periods, affect more their useful life. So it is possible to say that the battery ageing depends on its history [18] [19].

The SoH or State of Health is an index in percentage of the battery ageing and it can be measured as a ratio between the real capacity of the battery and its nominal capacity. Nominal capacity is often defined by the manufacturer, who specifies that it is valid in certain (well defined) operating conditions. This quantity has a certain tolerance, so it is advisable to measure nominal capacity for the specific battery at the start of life, by performing a complete discharge cycle in nominal conditions of temperature and current rate. Capacity is measured with the Coulomb Counting technique, and it is the maximum quantity of charge that the battery can supply. This measurement can be repeated in each moment of the battery life in order to measure its current capacity. Having defined the nominal capacity  $C_n$  and the capacity at a certain moment  $C_t$ , the State of Health is:

$$SoH = 100 \frac{C_t}{C_n} \tag{2.4}$$

In reality, some new batteries need a certain number of "training" cycles before they reach their best performances. In this case the nominal capacity is to be measured when the battery has reached its maximum performances.

It is a common practice to consider that the end of life condition is reached when the

battery has lost a 20% of its nominal capacity.

In some applications, such as hybrid vehicles, the *Coulomb Counting* technique can not be used to measure capacity, since complete charges and discharges are never performed.

Another method that can be used to measure the State of Health of a battery is the *impedance spectroscopy*. It is demonstrated in [20] that the real part of the impedance at 1kHz for Lithium ion batteries is almost the same when the battery is full or low. Otherwise it increase by a 58% after 230 discharge and charge cycles, when the battery has lost a 14% of its capacity.

#### 2.2 Mathematical and Circuital Models

In literature there are many models of electrochemical cells, and with the growth of batteries market, nowadays many activities of research are focused in optimization and discover of new models. Electrochemical cells models are mainly of two types: mathematical [21] [22] and circuital-impedance based [23]. Some models are used for on-line estimation of the battery state [24] [25] and are adapted to the specific operating conditions [26].

#### 2.2.1 Mathematical Model of a battery

A mathematical model describes the electrochemical cell behaviour in terms of mathematical concepts and language. Due to its historical importance it is to mention the Shepherd model, which is a voltage-current model for discharge processes of primary and secondary cells. The Shepherd equation gives the cell potential during discharge as a function of discharge time, current density, and many other factors. It makes possible a complete description of cell discharge characteristics, using a minimum of experimental data and at the same time pinpointing experimental errors [27]. Its expression is:

$$E = E_s - K\left(\frac{Q}{Q - it}\right)i - r_0i + Ae^{-BQ^{-1}it}$$
(2.5)

$$it = \int_0^t i(\tau) \mathrm{d}\tau \tag{2.6}$$

where  $E_s$  is the open circuit voltage, K is the polarization coefficient  $[\Omega cm^2]$ , Q is the available amount of active material per unit area, i is the current density and  $r_0$  is the internal resistance per unit area. The last term is to model the initial potential drop, and A and B are empirical constants. In a number of cases the initial drop in potential is too rapid to be included in the observed experimental data and consequently, the value of  $Ae^{-BQ^{-1}it}$ , being negligible, could be ignored.

$$SoC = 100 \left( 1 - \int_0^t \frac{i(\tau)}{Q} d\tau \right)$$
(2.7)

it is possible, by ignoring the last term of the 2.5, to re-write the Shepherd equation as a function of the State of Charge:

$$E = E_s - \left(\frac{100K}{SoC}\right)i - r_0i \tag{2.8}$$

Another important analytical model is the Rakhmatov and Vrudhula [28]. That model describes the diffusion process of the active material in the battery. The diffusion is considered to be one-dimensional in a region of length w. C(x,t) denote the concentration of active material in a finite region at time  $t \in [0, L]$  at distance  $x \in [0, w]$ from the electrode. Assuming that the initial concentration  $C(x, 0) = C^*$  is the same for every x, the model is interested in the variation of active material concentration at the electrode surface C(0, t). When C(0, t) drops below the cutoff level  $C_{cutoff}$  at time t = L, the battery is no longer able to supply charge.

The one-dimensional diffusion process is described by Fick's laws:

$$\begin{cases} -J(x,t) = D \frac{\partial C(x,t)}{\partial x} \\ \frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial^2 x} \end{cases}$$
(2.9)

where J(x, t) is the flux of active material at time t at distance x, and D is the diffusion coefficient.

In accordance with the Faraday's law, the flux at the left boundary of the diffusion region (the electrode surface) is proportional to the current i(t), The flux at the right boundary (x = w) is zero. This lead to the following boundary conditions:

$$\begin{cases} \frac{\partial C(x,t)}{\partial x}|_{x=0} = \frac{i(t)}{\nu FA}\\ \frac{\partial C(x,t)}{\partial x}|_{x=w} = 0 \end{cases}$$
(2.10)

where A is the area of the electrode surface, F is Faraday's constant, and  $\nu$  is the number of electrons involved in the electrochemical reaction at the electrode surface. It is possible to obtain an analytical solution from these differential equations and boundary conditions using Laplace transforms. From the solution one can obtain the following expression relating the load, the battery lifetime (L) and the battery parameters [29]:

$$\alpha = \int_{0}^{L} \frac{i(\tau)}{\sqrt{L-\tau}} d\tau + 2 \sum_{m=1}^{\infty} \int_{0}^{L} \frac{i(\tau)}{\sqrt{L-\tau}} e^{-\frac{\beta^{2}m^{2}}{L-\tau}} d\tau$$
(2.11)

where  $\alpha = \nu FA\sqrt{\pi D}C\rho(L)$ ,  $\rho(L) = 1 - \frac{C(0,L)}{C^*}$  and  $\beta = \frac{w}{\sqrt{D}}$ .

Parameters  $\alpha$  and  $\beta$  are extracted from experimental data. By the knowledge of these parameters, with equation 2.11 one can predict the cycle lifetime, if the discharge current profile is known.

In some other more recent solutions, charges and discharges are considered as stochastic and complex processes, so algorithms as Kalman Filter [30] [31], particle filter [32] [33] and others are used to simulate the batteries behaviour. Anyhow these algorithms are not a subject of this thesis.

Each mathematical model can be implemented in Matlab or another analytical software in order to simulate the behaviour of the physical system and then to compare the results with the experimental data.

#### 2.2.2 Circuital Model of a battery

Circuital models use elements such as voltage sources, current sources and passive components in order to describe the behaviour of a battery. In figure 2.2 are shown the main categories of circuital models.

As said in [34], Thevenin model (Fig. 2.2 (a)) [35] [36] is the simplest one, it is made of a voltage generator, which represent the  $V_{OC}$ , a resistance  $R_0$  and an R-C group, which models the dynamic processes. This model assumes that the open-circuit voltage ( $V_{oc}(SoC)$ ) is constant. Unfortunately, this assumption prevents it from capturing steady-state battery voltage variations (i.e., DC response) as well as runtime information. Furthermore one R-C group is not sufficient to accurately describe transients, which must be described by an higher order circuit.

Impedance-based models, shown in Fig. 2.2 (b), uses the method of electrochemical impedance spectroscopy to obtain an ac-equivalent impedance model in the frequency domain, and then uses a complicated equivalent network ( $Z_0$ ) to fit the impedance spectra. The fitting process is difficult, complex, and non-intuitive. In addition, impedance-based models only work for a fixed *SoC* and temperature setting [37], and therefore they cannot predict DC response or battery runtime.

The last one (Fig. 2.2 (c)), which is the Run-time model proposed in [34], is an intuitive and comprehensive electrical battery model. On the left, a capacitor  $(C_q)$  and a current-controlled current source, model the capacity, SoC, and runtime of the battery. The RC network, similar to that in Thevenin based models, simulates the transient response. To relate SoC to open-circuit voltage, a voltage-controlled voltage source is used. That model can simultaneously predict runtime, steady-state, and transient response accurately and either capture all the dynamic electrical characteristics of batteries: usable capacity  $(C_q)$ , open-circuit voltage  $(V_{oc})$ , and transient response (R - C network).

Actually not just the controlled voltage source, but even the parameters of the R-C network are function of SoC, SoH and temperature.

The parameter  $R_0$  is to model contact resistance, and it is responsible of the instantaneous voltage drop at the start up stage of a discharge(or charge) process; R - C



(c) Circuital Runtime-based model

Fig. 2.2: Circuital models of a battery

groups are to model the dynamic response due to reaction times, diffusion and other parasitic phenomenons. The more are the R-C groups taken into account, the more accurate and complex is the model. In order to have a good trade-off between accuracy and complexity, a good practice is to consider just two R-C groups, so the circuit in figure 2.2 (c) becomes that represented in figure 2.3: where all parameters are function of SoC, SoH and T.

More in detail:  $V_{oc}$  is the open circuit voltage at battery terminals in steady state condition,  $R_{ohm}$  is to model contact and separator resistances,  $R_{ct}$  (charge transfer resistance) is to model losses due to the slow rate of chemical reaction,  $C_{dl}$  (double layer capacity) is to model the dynamic due to the reaction rate,  $R_{diff}$  (diffusion



Fig. 2.3: Run-Time Thevenin Model with two R-C groups

resistance) represents losses due to charge diffusion and  $C_{diff}$  (diffusion capacitance) is to model dynamics due to charge diffusion.

Discarding the self discharge phenomenon, which is negligible for short time measurements,  $V_{SoC}$  is given by equation 2.12 and SoC is given by equation 2.3.

$$I_{batt} = -C_q \frac{\mathrm{d}V_{SoC}(t)}{\mathrm{d}t} \to V_{SoC}(t) = V_{SoC}(0) - \frac{1}{C_q} \int_0^t I_{batt}(\tau) \mathrm{d}\tau$$
(2.12)

Once parameters are extracted from experimental data, the model can be used to predict battery behaviour in run-time and to esteem SoC and SoH by the knowledge of parameters value and dynamics.

# Advanced Algorithms for the Estimation of SoC and SoH

In applications such as electric traction and stationary storage, models and algorithms for SoC and SoH estimation cover an important role. They are used in run-time, in order to determine what to expect from battery in future use, and how to properly use it and optimize its performances [38] [39] [40]. In chapter 2 the most important parameters to take into account have been defined, moreover were discussed the most important mathematical and circuital models of a battery. In this chapter will be examined some advanced algorithms, for the estimation of SoC and SoH, off-line and in run-time condition.

#### 3.1 Algorithms for the estimation of SoH

In literature there are many models for State of health estimation. As said in section 2.1.2, *SoH* is defined as an indicator of the performance degradation of the battery over time and its value is given by equation 2.4. Battery ageing depends on many factors, such as discharge/charge cycles, deep of discharge, charge conditions, storage, etc... moreover ageing triggers a chain reaction, since the more battery is damaged, the faster is ageing process.

An heuristic method for the estimation of SoC takes into account many factors, combining them in a polynomial function. These are:

- a battery usage time
- b temperature throughput
- c number of charge/discharge cycles
- d current throughput
- e number of starts

in the polynomial function 3.1 each of these terms are properly weighted depending on the application and on the specific battery.

$$SoH[\%] = 100(1 - w_a a - w_b b - w_c c - w_d d - w_e e)$$
(3.1)

The main advantage of an heuristic method is low complexity, on the other hand it can be trusted only in the early stage of battery life, since its accuracy decreases after a certain time of battery usage.

Another method, mentioned in section 2.1.2, consists in the measurement of real capacity at a certain moment: SoH is defined as the rate between capacity available at time t and the capacity at the start of life:

$$SoH[\%] = 100 \frac{C_t}{C_n} \tag{3.2}$$

The main advantage of this technique is that once defined the operating conditions, it gives an accurate measure of SoH, on the other hand it requires full discharge and charge cycles in order to complete the measurement.

Another method widely used in some applications is the internal resistance measurement at high frequency. As showed in figure 2.12 each battery can be represented with such a model. The open circuit voltage  $V_{oc}$  has a very slow dynamic (on the order of mHz) and the dynamic of R-C groups is slow too (fractions of Hz), so exciting battery with current pulses at high frequencies (hundreds of Hz) it can be isolated and measured the  $R_{ohm}$  which models contact resistance and separator resistance, which increases with battery ageing. This method allows to have fast and accurate measures of the battery's SoH, but it must be defined in certain operating conditions, since  $R_{ohm}$  does not depend only on SoH, but also on SoC and temperature. Another disadvantage of this technique is the requirement for a more complex hardware-software, which must allow a synchronous high frequency sampling (on the order of kHz) of Iand V, and the analysis in frequency domain.

It is possible to have an analysis in time domain by measuring the rate between the variation of voltage and current during fast transients. In order to do that, rise and fall time of current must be much lower than the dynamic of  $V_{oc}$  and R - C groups. The expression of  $R_{ohm}$  is:

$$R_{ohm} = \frac{\mathrm{d}V}{\mathrm{d}I} \tag{3.3}$$

Once measured  $R_{ohm}$  in well defined operating conditions, SoH can be expressed with the 3.4

$$SoH[\%] = 100 \frac{2R_{new} - R_{ohm}}{R_{new}} \Big|_{\substack{SoC = SoC_i \\ T = T_j}}$$
(3.4)

where  $R_{new}$  is the internal resistance of the new battery, which can be measured at the start of life if not defined in cell's datasheet.

#### 3.2 Algorithms for the Estimation of SoC

In this section are presented two methodologies used for the estimation of the State of Charge of a battery. Both these methodologies are proposed in [41] and [42] and are based on the circuital model of figure 2.3.

#### 3.2.1 Estimation of SoC with a genetic algorithm

Genetic algorithms (GAs) are heuristic search and optimization techniques inspired by natural evolution. They have been successfully applied to a wide range of realworld problems of significant complexity. In the case of study, a genetic algorithm is used to estimate the five parameters of the circuital model of figure  $3.1 : R_{ohm}, R_{ct},$  $C_{dl}, R_{diff}, C_{diff}$ . By the knowledge of these parameters, it is possible to estimate the State of Charge, power dissipation and state of health of the battery.



Fig. 3.1: Run-Time Thevenin Model with two R-C groups

By using the Ohm's law, the capacitor characteristic equation and the Kirchoff's voltage law,  $V_{b-est}$  is:

$$V_{b\_est}(t) = V_{oc} - R_{ohm}(t)I_b(t) - R_{ct}(t) * \left(I_b(t) - C_{dl}(t)\frac{\mathrm{d}V_{ct}}{\mathrm{d}t}\right)$$
$$-R_{diff}(t) * \left(I_b(t) - C_{diff}(t)\frac{\mathrm{d}V_{diff}}{\mathrm{d}t}\right)$$
(3.5)

The parameters values are time dependent since they are also function of State of Charge and Temperature. By choosing a time window  $T_w$  short enough to consider the five parameters as constants, the equation 3.5 becomes:

$$V_{b\_est}(k) = V_{oc} - R_{ohm} I_b(k) - R_{ct} * \left( I_b(k) - C_{dl} \frac{V_{ct}(k) - V_{ct}(k-1)}{T_k} \right) - R_{diff} * \left( I_b(k) - C_{diff} \frac{V_{diff}(k) - V_{diff}(k-1)}{T_k} \right)$$
(3.6)

By using a minimization technique based on a genetic algorithm and finding the best fit between the measured voltage at battery terminals and the estimated voltage, one can obtain an estimation of the parameters value. If  $V_{ct}(k)$  and  $V_{diff}(k)$  are rewritten as:

$$V_{ct}(k) = \frac{V_{ct}(k-1)C_{dl} + I_b(k)T_k}{\frac{T_k}{R_{ct}} + C_{dl}}$$

$$V_{diff}(k) = \frac{V_{diff}(k-1)C_{diff} + I_b(k)T_k}{\frac{T_k}{R_{diff}} + C_{diff}}$$
(3.7)

Using the 3.7, the equation 3.6 can be rewritten as:

$$V_{b\_est}(k) = V_{oc} - R_{ohm} I_b(k) - V_{ct}(k) - V_{diff}(k)$$
(3.8)

The algorithms operates in runtime, assuming the initial condition of

 $V_{ct}(0) = 0$  and  $V_{diff}(0) = 0$ . By indicating with  $V_b(k)$  the measured voltage at battery terminals at the *k*-th step, with  $V_{b\_est}(k)$  the estimated voltage at battery terminals at the *k*-th step, and with N the number of samples in a time window  $T_w$ , the cost function  $F_w$  can be written as:

$$F_{w} = \sum_{k=(w-1)N+1}^{wN} (V_{b\_est}(k) - V_{b}(k))^{2} \Longrightarrow \min_{\substack{V_{oc}(w) \\ R_{ohm}(w) \\ R_{ct}(w) \\ C_{dl}(w) \\ R_{diff}(w) \\ C_{diff}(w) \end{bmatrix}} F_{w}$$

$$(3.9)$$

with:

$$V_{oc\_min} \leq V_{oc}(w) \leq V_{oc\_max}$$

$$0 \leq R_{ohm}(w) \leq R_{ohm\_max}$$

$$0 \leq R_{ct}(w) \leq R_{ct\_max}$$

$$0 \leq C_{dl}(w) \leq R_{dl\_max}$$

$$0 \leq R_{diff}(w) \leq R_{diff\_max}$$

$$0 \leq C_{diff}(w) \leq R_{diff\_max}$$

$$(3.10)$$

where the maximum and minimum values depend on the battery technology and configuration.

Once known the estimated values for the circuital parameters in run time, it is possible, by using a look-up table, to have an estimation of the SoC and SoH of the battery.

#### 3.2.2 Estimation of SoC with a frequency domain algorithm

The technique discussed in this section is proposed in [41] and [42], and it is a starting point for this thesis work.

It is based on the circuital model of figure 2.3 and uses a Frequency Domain Identification Algorithm (FDIA) to identify the circuital parameters. Provided that the algorithm operates in frequency domain, it is necessary, in order to identify static and dynamic behaviour with its time constants, to excite battery with a pulsed current profile, such as to alternate steady state conditions and transients.

The current profile applied to the battery I(t) and the voltage profile measured at battery terminals  $V_m(t)$  are converted with a *FFT* operation in  $\overline{I}(j\omega)$  and  $\overline{V}_m(j\omega)$ . The voltage drop across battery impedance is:

$$\overline{V}_{z}(j\omega) = \overline{V}_{oc}(j\omega) - \overline{V}_{m}(j\omega)$$
(3.11)

where  $V_{oc}$  is the open circuit voltage.

Using Ohm's law, battery's associated impedance is:

$$Z(j\omega) = \frac{\overline{V}_{oc}(j\omega) - \overline{V}_{m}(j\omega)}{\overline{I}(j\omega)}$$
(3.12)

and rewriting the equation 3.12 using the circuital model of figure 2.3, we have:

$$Z(j\omega) = \frac{\overline{V}_{oc}(j\omega) - \overline{V}_m(j\omega)}{\overline{I}(j\omega)} = \left[ R_{ohm} + \frac{R_{ct}}{1 + s\tau_{ct}} + \frac{R_{diff}}{1 + s\tau_{diff}} \right]_{\substack{s = j\omega \\ SoC = SoC_i \\ T = T_i}}$$
(3.13)

where  $\tau_{ct} = R_{ct}C_{dl}$  and  $\tau_{diff} = R_{diff}C_{diff}$ . Separating real part and imaginary part in 3.13 after a few steps we have:

$$Z(j\omega) = \frac{a(\omega) + jb(\omega)}{d(\omega)}$$

$$\begin{cases}
a(\omega) = \omega^{2} \left( \omega^{2} \tau_{ct}^{2} \tau_{diff}^{2} R_{ohm} + \tau_{ct}^{2} (R_{ohm} + R_{diff}) + \tau_{diff}^{2} (R_{ohm} + R_{ct}) \right) & (3.14) \\
+ R_{ohm} + R_{ct} + R_{diff} \\
b(\omega) = -\omega \left( \tau_{ct} R_{ct} + \tau_{diff} R_{diff} + \omega^{2} \tau_{ct} \tau_{diff} (\tau_{ct} R_{diff} + \tau_{diff} R_{ct}) \right) \\
d(\omega) = 1 + \omega^{2} (\omega^{2} \tau_{ct}^{2} \tau_{diff}^{2} + \tau_{ct}^{2} + \tau_{diff}^{2})
\end{cases}$$

If temperature is constant the identification algorithm works as follows:

1. Battery's State of charge (SoC) is measured with Coulomb Counting Technique, whose expression is that of 3.15.

$$SoC(t) = SoC(t_0) - 100 \int_{t_0}^t \frac{i(\tau)}{C_{eff} * 3600} d\tau$$
(3.15)

2. The open circuit voltage  $V_{oc}$  is measured in steady state condition, with  $I_b = 0$ and  $dV_m/dt = 0$ . This condition is reached when all dynamic effects due to long transients are exhausted. The time needed to exhaust transients depends on the specific battery technology and capacity. So battery is kept in an idle state for a certain amount of time, after which, voltage at battery terminals is almost constant and equal to the open circuit voltage. Indicating with  $t_0$  the instant of time when the current flow through the battery is stopped, and with  $\Delta t^*$  the amount of time needed to exhaust transients, we have:

$$V_{oc}(t_0 + \Delta t^*) \approx V_m(t_0 + \Delta t^*)|_{SoC(t_0 + \Delta t^*) = SoC(t_0)}$$
(3.16)

By using equation 3.16, the open circuit voltage is measured by measuring the voltage at battery terminals after a certain rest time.

- 3. With the methods seen in items 1 and 2 we define a look-up table which relates  $V_{oc}$  and SoC for a specific battery:  $V_{oc} = f(SoC)$
- 4. The voltage drop across battery internal impedance is measured as

$$V(t) = V_{oc}(t) - V_m(t)$$
(3.17)

- 5. V(t) and  $I_b(t)$  are transformed with an *FFT* operation and evaluated in the frequency domain.
- 6. Using the 3.12, 3.13 and 3.14 the cost functions for module and phase are built:

$$\begin{cases} F_m(\omega) = \frac{\sqrt{a(\omega)^2 + b(\omega)^2}}{d(\omega)} |I(\omega)| - |V(\omega)| \\ F_p(\omega) = \arctan(\frac{b(\omega)}{a(\omega)}) + \arg(I(\omega)) - \arg(V(\omega)) \end{cases}$$
(3.18)

By minimizing the cost functions in 3.18, the result gives an estimation of the five unknown parameters:  $R_{ohm}$ ,  $R_{ct}$ ,  $C_{dl}$ ,  $R_{diff}$ ,  $C_{diff}$ , which can be directly related, through a look up table, to a specific SoC condition if SoH and T are well defined. It is really important that the parameters domain, and their initial values are of the same order of magnitude as the nominal values for the same types of batteries, in order to let the algorithm converge to a suitable solution.

In figure 3.2 it is represented the block diagram of the FDIA Algorithm.

## 3.3 An innovative, temperature dependent Run-Time Model for the estimation of SoC and SoH

The models and algorithms presented above faithfully represent discharge processes of energy storage systems in nominal operating conditions of ambient temperature. However there are two open problems:

- They are not able to represent both charge and discharge processes, this because the parameters trend in function of *State of Charge*, *State of Health* and *Temperature* is not the same for discharge and charge processes;
- The models and algorithms mentioned above don't consider the dynamics of parameters as due to temperature variations.



Fig. 3.2: Block Diagram of the FDIA Algorithm [41]

The solution proposed in this Ph.D. Thesis is based on an innovative double R - C group, directional circuital model, which can represent faithfully the battery in both discharge and charge processes, using an improved FDIA Algorithm which allows the identification of circuit parameters and their dynamics in function of State of Charge, State of Health and Temperature.

The circuital model proposed is represented in figure 3.3, where all parameters are function of SoC, SoH and T.



Fig. 3.3: Run-time directional circuital model with two R-C groups

The parameters are:  $V_{oc}$ , which is the open circuit voltage at battery terminals in steady state condition;  $R_{Dohm}$  and  $R_{Cohm}$  which are to model contact and separator resistances respectively in discharge and charge processes;  $R_{Dct}$ ,  $C_{Ddl}$ ,  $R_{Cct}$  and  $C_{Cdl}$ which are to model losses and dynamics due to the chemical reaction rate respectively in discharge and charge processes;  $R_{Ddiff}$ ,  $C_{Ddiff}$ ,  $R_{Cdiff}$  and  $C_{Cdiff}$  which represent losses and dynamics due to charge diffusion respectively in discharge and charge processes; Diodes are ideal diodes, and their function is to fix the only available current direction across each branch of the circuit.

The impedance for each branch is:

$$\begin{cases} Z_D(j\omega) = \frac{\overline{V}_m(j\omega) - \overline{V}_{oc}(j\omega)}{\overline{I_D}(j\omega)} \\ Z_C(j\omega) = \frac{\overline{V}_m(j\omega) - \overline{V}_{oc}(j\omega)}{\overline{I_C}(j\omega)} \end{cases}$$
(3.19)

where:

$$\begin{cases} Z_D(j\omega) = \frac{\overline{V}_m(j\omega) - \overline{V}_{oc}(j\omega)}{\overline{I_D}(j\omega)} = \left[ R_{Dohm} + \frac{R_{Dct}}{1 + s\tau_{Dct}} + \frac{R_{Ddiff}}{1 + s\tau_{Ddiff}} \right]_{s = j\omega} \\ s_{oC} = s_{oC_i} \\ T = T_i \\ Z_C(j\omega) = \frac{\overline{V}_m(j\omega) - \overline{V}_{oc}(j\omega)}{\overline{I_C}(j\omega)} = \left[ R_{Cohm} + \frac{R_{Cct}}{1 + s\tau_{Cct}} + \frac{R_{Cdiff}}{1 + s\tau_{Cdiff}} \right]_{s = j\omega} \\ s_{oC} = s_{oC_i} \\ T = T_i \\ \end{cases}$$
(3.20)

Using equation 3.20, the equation 3.14 becomes:

$$Z_{D}(j\omega) = \frac{a_{D}(\omega) + jb_{D}(\omega)}{d_{D}(\omega)}$$

$$\begin{cases} a_{D}(\omega) = \omega^{2} \left( \omega^{2} \tau_{Dct}^{2} \tau_{Ddiff}^{2} R_{Dohm} + \tau_{Dct}^{2} (R_{Dohm} + R_{Ddiff}) + \tau_{Ddiff}^{2} (R_{Dohm} + R_{Dct}) \right) \quad (3.21) \\ + R_{Dohm} + R_{Dct} + R_{Ddiff} \\ b_{D}(\omega) = -\omega \left( \tau_{Dct} R_{Dct} + \tau_{Ddiff} R_{Ddiff} + \omega^{2} \tau_{Dct} \tau_{Ddiff} (\tau_{Dct} R_{Ddiff} + \tau_{Ddiff} R_{Dct}) \right) \\ d_{D}(\omega) = 1 + \omega^{2} (\omega^{2} \tau_{Dct}^{2} \tau_{Ddiff}^{2} + \tau_{Dct}^{2} + \tau_{Ddiff}^{2}) \end{cases}$$

for the branch which represents discharge processes, and:

$$Z_{C}(j\omega) = \frac{a_{C}(\omega) + jb_{C}(\omega)}{d_{C}(\omega)}$$

$$\begin{cases} a_{C}(\omega) = \omega^{2} \left( \omega^{2} \tau_{Cct}^{2} \tau_{Cdiff}^{2} R_{Cohm} + \tau_{Cct}^{2} (R_{Cohm} + R_{Cdiff}) + \tau_{Cdiff}^{2} (R_{Cohm} + R_{Cct}) \right) \quad (3.22) \\ + R_{Cohm} + R_{Cct} + R_{Cdiff} \\ b_{C}(\omega) = -\omega \left( \tau_{Cct} R_{Cct} + \tau_{Cdiff} R_{Cdiff} + \omega^{2} \tau_{Cct} \tau_{Cdiff} (\tau_{Cct} R_{Cdiff} + \tau_{Cdiff} R_{Cct}) \right) \\ d_{C}(\omega) = 1 + \omega^{2} (\omega^{2} \tau_{Cct}^{2} \tau_{Cdiff}^{2} + \tau_{Cct}^{2} + \tau_{Cdiff}^{2}) \end{cases}$$

for the branch which represents charge processes.

The algorithm used for parameters identification is an improved version of the FDIAAlgorithm of paragraph 3.2.2: the steps from 1 to 6 are the same as those seen in paragraph 3.2.2 and the characterization is made in different operating conditions of ambient temperature. The cost functions of the 3.18 become respectively for discharge and charge processes:

$$\begin{cases} F_{Dm}(\omega) = \frac{\sqrt{a_D(\omega)^2 + b_D(\omega)^2}}{d_D(\omega)} |I_D(\omega)| - |V(\omega)| \\ F_{Dp}(\omega) = \arctan(\frac{b_D(\omega)}{a_D(\omega)}) + \arg(I_D(\omega)) - \arg(V(\omega)) \end{cases}$$

$$\begin{cases} F_{Cm}(\omega) = \frac{\sqrt{a_C(\omega)^2 + b_C(\omega)^2}}{d_C(\omega)} |I_C(\omega)| - |V(\omega)| \\ F_{Cp}(\omega) = \arctan(\frac{b_C(\omega)}{a_C(\omega)}) + \arg(I_C(\omega)) - \arg(V(\omega)) \end{cases}$$
(3.23)
(3.24)

The cost functions in 3.23 and 3.24 are minimized with the Least Squares Optimization Technique and the result gives an estimation of the unknown parameters for each branch of the circuit model. In this mode, by repeating the previous steps in different operating conditions of ambient temperature, we have a set of points for each parameter. By interpolating known points with a *polynomial fitting technique* we obtain a relation for each parameter which is function of SoC, SoH, T and the number of cells of the battery:

$$\begin{split} V_{oc}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} v_{ij}(SoH, n) * SoC^{i} * T^{j} \\ R_{Dohm}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} a_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ R_{Cohm}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} a_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ R_{Dct}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} b_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ R_{Cct}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} b_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Ddl}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} c_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdl}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} c_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ R_{Ddiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} d_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ R_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} d_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Ddiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} d_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Ddiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} d_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Ddiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} d_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Ddiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Dij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} \sum_{j=0}^{m} e_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Cij}(SoH, n) * SoC^{i} * T^{j} \\ C_{Cdiff}(SoC, SoH, T, n) &= \sum_{i=0}^{m} \sum_{j=0}^{m} \sum_{j=0}^{m} E_{Cij}(SoH, n) * SoC$$

where the values  $v_{ij}$ ,  $a_{Dij}$ ,  $a_{Cij}$ ,  $b_{Dij}$ ,  $b_{Cij}$ ,  $c_{Dij}$ ,  $c_{Cij}$ ,  $d_{Dij}$ ,  $d_{Cij}$ ,  $e_{Dij}$  and  $e_{Cij}$  are experimentally found and are function of the number of cells (*n*) and the *State of Health* of the battery (*SoH*). The block diagram of the algorithm proposed is shown in figure 3.4.



Fig. 3.4: Block Diagram of the improved FDIA Algorithm

Model and algorithm are validated in different operating conditions of ambient temperature, by comparing the measured voltage at battery terminals and the voltage obtained from the equivalent circuit model stimulated with the same current of the battery. The accuracy of this modeling technique is evaluated by measuring the relative error with the equation 3.26.

$$E_r = \frac{|V_m - V_{model}|}{V_m} \tag{3.26}$$

### **Experimental Activities**

Once the model and the parameter identification algorithm have been chosen, there was a need to conduct some laboratory tests in order to characterize the batteries and to validate the overall procedure. This required the realization of an automated test platform (SCADA System) for the monitoring and control of discharge and charge processes of lead acid, Nickel Metal Hydride and Lithium ion batteries. Experimental activities consisted in:

- Configuration, wiring and engineering of the test platform;
- Project and implementation of an algorithm for the automated control of standard charge and discharge processes and of pulsed charge and discharge processes of lead acid, nickel and lithium batteries;
- Test activities in climatic chamber at the target temperatures of  $0^{\circ}C$ ,  $25^{\circ}C$ ,  $50^{\circ}C$ .

#### 4.1 Configuration, wiring and engineering of the test platform

In order to perform the testing and measurement activities mentioned above, it was built an automated experimental platform, which can monitor and control constant current discharge and standard charge processes of lead acid, Nickel based and Lithium ion batteries. Furthermore this platform is able to perform discharge and charge processes with pulsed current profiles. It is made of a fast switching power supply, a programmable fast switching electronic load, a power analyzer, two acquisition modules, current and temperature transducers. All the instruments are connected through a communication bus to an *Energy Storage Management System* implemented in LabVIEW which has the rule to monitor and control charge and discharge processes. The automated platform, whose configuration is showed in figures 4.1 and 4.2 consists of the following instrumentation:

- Power Supply Ametek SGI 15/801,
- Programmable Electronic Load Amrel PLA 10K-60-1500,
- Power analyzer Yokogawa WT1800,

- Data Acquisition Switch Agilent 34970A (for temperature measurements),
- NI CompactDAQ with the acquisition module NI9233,
- A Type J thermocouple,
- A current transducer LEM CT 10-T,
- Climatic Chamber Angelantoni Discovery DY 250.

The power supply has the function to feed current to the battery during charge processes, and it is in open circuit mode during discharge processes. On the other hand the programmable electronic load has the rule to absorb current from the battery during discharge processes. Power analyzer Yokogawa WT1800 monitors at a rate of 20S/s the following quantities:

- Current [A];
- Battery voltage [V];
- Single cells voltage [V];
- Charge [Ah];
- Instantaneous power [W];
- Energy [Wh].

The Data Acquisition Switch has the rule to monitor Temperature [°C] with a Type-J thermocouple at the same rate. Only in pulsed and fast switching charge and discharge processes some quantities are monitored with the NI CompactDAQ and the acquisition module NI9233, at the frequency rate of 2kS/s in order to capture fast transients. These quantities are:

- Current [A];
- Battery voltage [V];
- Single cells voltage [V].

A current transducer LEM CT 10-T is used to convert current in voltage at the rate of 10A/5V, in order to have a quantity measurable by the NI9233 module. Climatic chamber is used to set and maintain the ambient temperature in which batteries operate. Target temperatures used for the characterization of the batteries under test are:  $0^{\circ}C$ ,  $25^{\circ}C$  and  $50^{\circ}C$ .

The effects of wire resistance have been minimized thanks to an accurate dimensioning, but also by taking a measure of the voltage drop across each cell of the battery and by taking the measurement points as near as possible to each cell terminals. Although taking measurements at the cell's terminals is a good practice in order to avoid that the measure is soiled by the voltage drop over wires and contacts, it is not enough to guarantee an accurate and stable control in open loop, this because the instrumentation sensing needs low wire resistances to work properly. The limitation on wire resistance is imposed by the programmable electronic load Amrel PLA 10K-60-1500, and



Fig. 4.1: Configuration of the Automated Test Platform

the Power Supply Ametek SGI 15/801, which can compensate with sensing contacts a maximum voltage drop across wires of 1V. The wires were dimensioned taking into account two Italian standards: the CEI-UNEL 35024/1,Ec and the CEI-UNEL 35023. The CEI-UNEL 35024/1,Ec standard says that the cable flow  $(I_z)$  must be higher than the current of use $(I_b)$  of the same, this in order to avoid overheating. It is possible to calculate the minimum  $(I_z)$  needed for the wires through the following formula:

$$I_z = I_{0_{30}} * k_1 * k_2 \tag{4.1}$$

where  $I_{0_{30}}$  is the standard flow in air at a temperature of  $30^{\circ}C$ ,  $k_1$  is a corrective parameter which takes into account the ambient temperature and  $k_2$  is a corrective parameter which takes into account the installation condition (in air, in bundles or layers, etc...). The condition chosen for the installation was the laying in free air. To achieve this goal, however, precise prescriptions must be observed, especially useful not to prevent the natural phenomenon of convection in the air. Cable must be laid at a distance of at least 0, 3 times its diameter with respect to the wall or, if laid on the catwalk, this has to be pierced for more than 30% of its surface. As for with concerns the minimum distance between wires, it has to be at least equal to the outer diameter of the upper section cable. The standard CEI-UNEL 35023 define some tables for the calculation of voltage drop over wires. These tables provide the impedance values of



Fig. 4.2: Automated Test Platform

the cables and the voltage drop values for unit current and length. The formula for the calculation of the voltage drop over a wire is:

$$\Delta V = K * I * L * (R_L \cos \phi + X_L \sin \phi)$$
(4.2)

where K = 2 for single phase lines and  $K = \sqrt{3}$  for three phase lines; I is the operating current, L the wire length and  $R_L$  and  $X_L$  are respectively the resistance and the reactance of the line per unit length  $[\Omega/km]$ . In the case of interest the line is single phase and a DC current has to be supplied to the batteries, while 3 meters of cable are needed to connect all the instrumentation and the units under test. A project choice was to guarantee the platform operations up to a DC current rate of 50A, which is also the maximum current that can be measured with a direct measurement by the Power Analyzer Yokogawa WT1800. So, for a  $50mm^2$  single pole EPR cable we have from the CEI-UNEL 35023 that  $R_L = 0, 49\Omega/km$  and  $X_L = 0,085\Omega/km$ . For the case of study we have:

$$\Delta V = 2 * 50A * 0,003km * (0,49\Omega/km * 1 + 0,085\Omega/km * 0) = 0,147V$$
(4.3)

From the CEI-UNEL 35024/1, Ec we have that the maximum current flow for that cable at  $30^{\circ}C$  is 197A, and  $k_1 = 0,71$  at  $50^{\circ}C$  and  $k_2 = 1$ , so using the equation 4.1, the maximum current flow is:

$$I_z = 197A * 0,71 * 1 = 139,87A \tag{4.4}$$

So the specifications  $I_b < I_z$  and  $\Delta V < 1V$  have been satisfied, and the cables seem to be oversized, but this is a good thing, because it leaves a margin for other contact resistances due to the connectors, that are not taken into account in the calculations made above.

#### 4.2 Algorithm for the automated control of the platform

All the instrumentation described above is controlled by an *Energy storage management system* algorithm implemented in LabVIEW whose function is to monitor and control constant current and pulsed current discharge processes and standard and pulsed current charge processes. The control algorithm is the core of the platform because it manages times, acquires measurements, makes decisions and gives instructions to each instrument through the IEEE 488.2 bus. The flowchart of the *Energy Storage Management System* is represented in figure 4.3. It is a state machine with four main states, each state is designed for a well defined test profile. These are: Constant current Discharge, Standard Charge, Pulsed Discharge Profile, Pulsed Charge Profile.



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Fig. 4.3: Flowchart of the Energy Storage Management System Algorithm

In the Constant current Discharge state, the instrumentation is managed to extract from the battery a constant current rate set by the user until the cutoff condition is reached. In the Standard Charge state the instrumentation is managed to perform constant current, constant voltage and mixed charge processes as defined from the standard for the specific technology of accumulators (the platform is designed to charge and discharge Lead acid, Nickel and Lithium batteries). In the Pulsed Discharge Profile and Pulsed Charge Profile states, the instrumentation is managed respectively to extract and to feed current with pulsed profiles.

Each state has a *Scan For instruments* process: this is to automatically search the instrumentation in the platform. The research is made by requesting the Identification number to all the instruments connected to the bus. The ID numbers are then compared with those of the instruments which have to build the platform. If they match, the instrumentation needed is present on the bus and so the operations can go on, otherwise the program returns an error with the name of the instruments that are not present. The user has to verify that all the instruments are operative and then can trigger a new search. In figure 4.4 it is represented a portion of the LabVIEW code related to the automatic research of the instruments.



(a) Scan For Instruments subVI.



(b) Scan For Instruments - detail of the code.

Fig. 4.4: Automatic research of the instruments

If instrumentation is found the program can go on, getting the user settings and setting the instrumentation.

For the Constant Current Discharge state the user settings are:

- Battery technology;
- Number of cells;
- Capacity [Ah];
- Current rate [% of C];
- Cutoff Voltage [V];
- Ah to extract [Ah].

The program creates a new ".csv" file to log measurement data, sets the Power Analyzer and Data Acquisition Switch full-scale and measurement ports, puts the Power Supply in an idle state and then sets a starting point at zero current absorption for the electronic load. The next step of the program consists in the measurements acquisition from the the Power Analyzer and Data Acquisition Switch (fig. 4.5). Then the program performs a closed loop control on the current rate (fig. 4.6): it compares the current measured and the set point and calculates the error function e. The error is multiplied with a constant control K and added to the previous set point, in order to adjust it until the error is close to zero. In this way the algorithm implements a closed loop control with a first order dynamics.



Fig. 4.5: Measurement Acquisition code for the YOKOGAWA WT1800



Fig. 4.6: LabVIEW code for the control loop of the DC Discharge state

The next steps provide to update the display and to log the last measurement data to a new row in the file log previously created. The program shows on the display the time trend of the following quantities (fig: 4.7):

- Voltage of the single cells [V];
- Battery Voltage [V];
- Battery Current [A];
- Charge [Ah];
- State of Charge [%];
- Temperature  $[^{\circ}C]$ ;

while the quantities recorded in the file log are:

- Time [*s*]
- Voltage of the single cells [V];
- Battery Voltage [V];
- Battery Current [A];
- Charge [Ah];
- State of Charge [%];
- Power [W];
- Energy [Wh];
- Temperature  $[^{\circ}C]$ .

The algorithm then verifies if the "end of discharge condition" is reached, and if it is the case stops the instrumentation, otherwise it loops back to an arbitrage state which manages times in order to guarantee that a new measurement is acquired every two seconds and than it triggers the measurement-control chain again. The end of discharge condition is determined by the user settings: it can be either extraction of



the desired amount of charge or the reach of the cutoff voltage.

Fig. 4.7: LabVIEW code for the Display Update

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For what concerns *Standard Charge* state instead, user settings are:

- Battery technology;
- Number of cells;
- Capacity [Ah];
- Current rate [% of C];
- Charge Voltage [V];
- Ah extracted in last discharge [Ah];

and just for lead acid technology:

- Final charge current [% of C];
- Maximum Voltage on battery [V];

this because, as said in section 1.3, Nickel Cadmium and Nickel Metal Hydride batteries have to be charged at a constant current, Lithium Ions and Lead acid batteries require a first stage of charge at a constant current and a second one at a constant voltage, but some lead acid batteries can have a final charge stage at a constant current of 0,05-0,06C until the battery reaches a maximum voltage threshold.

So the program gets user settings, creates a new ".csv" file to log measurement data, sets the Power Analyzer and Data Acquisition Switch full-scale and measurement ports, puts the Electronic Load in an idle state and then sets a starting point for the power supply at I = 0 and V = 0.

The next step of the program consists in the measurements acquisition from the the Power Analyzer and Data Acquisition Switch (as represented in figure 4.5). Then the program goes into the specific state related to the battery technology and performs

a closed loop control on battery voltage in order to have the I - V profiles described in section 1.3. The program sets a current limit for safety reasons and then it compares the current and voltage measured and the set point in order to calculate the error function e. The error is multiplied with a dynamic control K and added to the previous set point, in order to adjust it until the error is close to zero. Control Khas a maximum value and it decreases as the error decreases, this let to have a more stable control and a better fit around the I - V set point than the case of constant K. In Ni-MH state the error is calculated by comparing the measure of current and the desired current set point and it serves to compute a new set point of voltage; in Lead acid state the error is calculated by comparing the measure of current and the desired current set point in the constant current stage and final charge stage, while it is calculated by comparing the measure of voltage and the desired voltage set point in constant voltage stage. In all the three stages the error serves to compute a new voltage setpoint. In *Li-ion*, as for Lead acid the error is calculated by comparing the measure of current and the desired current set point in the constant current stage, while it is calculated by comparing the measure of voltage and the desired voltage set point in constant voltage stage. In both stages the error serves to compute a new voltage setpoint (fig. 4.8). In this way the algorithm implements a closed loop control with a first order dynamics. For all technologies the switch condition between stages and the end of charge condition are determined by the reach of the relative thresholds plus a certain hysteresis margin, as discussed in section 1.3.

The next steps provide to update the display and to log the last measurement data to a new row in the file log previously created. The program shows on the display the time trend of the following quantities (fig: 4.7):

- Voltage of the single cells [V];
- Battery Voltage [V];
- Battery Current [A];
- Charge [Ah];
- State of Charge [%];
- Temperature  $[^{\circ}C]$ ;

while the quantities recorded in the file log are:

- Time [s]
- Voltage of the single cells [V];
- Battery Voltage [V];
- Battery Current [A];
- Charge [Ah];
- Overcharge factor;



(a) Constant current stage.



(b) Constant Voltage stage.

Fig. 4.8: LabVIEW code for Standard Charge Control of Li-Ion batteries

- State of Charge [%];
- Power [W];
- Energy [Wh];
- Temperature  $[^{\circ}C]$ .

where Overcharge factor is :

$$OC = \frac{Charge[Ah]}{Ah \ extracted \ in \ last \ discharge \ [Ah]} \tag{4.5}$$

The algorithm then verifies if the "end of charge condition" is reached, and if it is the case stops the instrumentation, otherwise it loops back to an arbitrage state which manages times in order to guarantee that a new measurement is acquired every two
seconds and then it triggers the measurement-control chain again.

For the Pulsed Discharge Profile and Pulsed Charge Profile cases the structure of the algorithm is a bit different and it is based on a mixed architecture which uses the the "Producer - Consumer" structure for measurement and file logging, and the "Master-Slave" structure for control, data analysis and to update the display. These architectures are used because in these cases data acquisition is faster than the other operations and the program can't operate in a sequential mode, so a parallel architecture must be used. "Producer - Consumer" and "Master-Slave" design patterns are used for synchronization reasons:

- The Master/Slave pattern consists of multiple parallel loops. Each of the loops may execute tasks at different rates. Of these parallel loops, one loop acts as the master and the others act as slaves. The master loop controls all of the slave loops, and communicates with them using messaging architectures [43].
- As with the standard Master/Slave design pattern, the Producer/Consumer pattern is used to decouple processes that produce and consume data at different rates. The Producer/Consumer pattern's parallel loops are broken down into two categories: those that produce data, and those that consume the data produced. Data queues are used to communicate data between loops in the Producer/Consumer design pattern. These queues offer the advantage of data buffering between producer and consumer loops [44].

In this application there is only one Event based Master/Producer loop for data acquisition and instrumentation control, a Slave loop for data analysis, a Slave loop for display update and a Consumer loop for data logging.

As the automatic research of the instruments is complete, the program gets user settings, which are:

- Battery technology;
- Number of cells;
- Capacity [Ah];
- Current rate [% of C];
- Cutoff Voltage [V];
- Ah to extract [Ah].

for the Pulsed Discharge Profile state; and:

- Battery technology;
- Number of cells;
- Capacity [Ah];
- Current rate [% of C];

- Charge Voltage [V];
- Ah extracted in last discharge [Ah];

for the Pulsed Charge Profile state. Then the program triggers a subroutine for high frequency data acquisition which runs in parallel to the main program, creates a new ".csv" file to log measurement data and sets the Power Analyzer and Data Acquisition Switch full-scale and measurement ports. In Pulsed Discharge Profile state it puts the Power Supply in an idle state and then sets a starting point at zero current absorption for the electronic load, while in Pulsed Charge Profile state it puts the Electronic Load in an idle state and then sets a starting point for the power supply at I = 0 and V = 0. The High Frequency Logger subroutine is triggered through an asynchronous call in LabVIEW and then runs in parallel to the main program and creates a series of files where it logs voltage and current data acquired with NI CompactDAQ and acquisition module NI9233, at a sampling frequency of 2kS/s. Figure 4.9 and 4.10 show flowchart and code for the High Frequency Logger subroutine.

After the instrumentation has been set, the algorithm provides to acquire standard measurements from Power Analyzer and Data Acquisition Switch (as represented in figure 4.5). New measurement data are provided by the Master/Producer loop every 50ms, as showed in figure 4.11. Slave loops use last data to update display and to determine the next control operations, while the consumer loop takes data from the FIFO queue and logs them to the file previously created. Quantities displayed and saved for *Pulsed Discharge Profile* and *Pulsed Charge Profile* are the same respectively as for *Constant Current Discharge* and *Standard Charge* cases.

The control slave loop does not algorithmically implement a closed loop control, as opposed to Constant Current Discharge and Standard Charge cases. This because, although a closed loop control is the best choice in order to have an high accuracy, it slows down the operations and it is not well suited for Pulsed Discharge/Charge operations where fast transients are needed. Actually it is not an open loop control, in fact as said before, it is just algorithmically open loop, since the control over the I-Vset-point is automatically implemented by the power supply Ametek SGI 15/801 and by the programmable electronic load Amrel PLA 10K-60-1500 through their sensing contacts. This allows to have a good trade-off between response accuracy and rate. The algorithm just controls when to switch the current feed/absorption on and off: it verifies if the current flow has been switched to zero and if it is the case, keeps the power supply and the electronic load in an idle state for the time needed by battery to exhaust transients (as said in chapters 2 and 3 this settling time depends on battery technology. In this work settling time used is 1800s). After that time has passed, the control algorithm sets a new current set point, equal to the current rate previously chosen by the user and passes it to the Master loop through a "Generate User Event"



Fig. 4.9: Flowchart of the High Frequency Acquisition Subroutine



(a)Code for subroutine call in main VI.



(b) Code of the High Frequency Acquisition subroutine .

Fig. 4.10: LabVIEW code for High Frequency Acquisition



Fig. 4.11: LabVIEW code for Measurement acquisition in Producer Loop

function. This function in LabVIEW is used to programmatically generate events in programs with Event driven Master/Slave or Producer/Consumer architectures. The Master, which receives the user event, serves it and sets the instrumentation as shown in figure 4.12(a) (the power supply in *Pulsed Charge Profile* case and the electronic load in *Pulsed Discharge Profile* case). After that, the algorithm repeatedly verifies if the end of discharge/charge condition (determined by the relative thresholds) is reached and if it is the case generates a new *User Event* to stop the instrumentation and end the program, otherwise it verifies if the battery has been discharged (in *Pulsed Discharge Profile* case) or charged (in *Pulsed Charge Profile* case) by a 10% (fig. 4.12(b)). If this last condition is reached the control slave loop generates a new user event to put power supply and electronic load in an idle state, so switching

the current to zero. After that, the program loops back to verify if the current has switched to zero and to wait that the settling time has passed.

Figure 4.13 shows the user interface of the application created.



(a) User Event Handling Code.



(b)A portion of the control slave loop code.

Fig. 4.12: LabVIEW code for Control operations in Pulsed Discharge Profile state

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(a) Find Instrumentation and User settings pane.



(b) Run Time Monitoring pane.



# 4.3 Test activities in climatic chamber

Once the automatic platform has been developed and validated, it has been used to perform the test activities described in this section. Since the final target is to characterize and validate the innovative model proposed in section 3.3 for electric traction applications, the type of accumulators chosen for these test operations is  $LiFePO_4$ , which is a widely used technology nowadays in electric vehicles, as said in Chapter 1. The unit under test is made in scale respect to the batteries of electric vehicles, and it is built of two of the  $LiFePO_4$  cells showed in figure 4.14.



Fig. 4.14: A cell of the Unit under Test: NX26650  $LiFePO_4$  battery

The characteristics of the  $LiFePO_4$  cell under test specified by datasheet are described in table 4.1, while in figure 4.15 are represented the declared discharge curves at different operating temperatures.



Fig. 4.15: Discharge curves at different operating temperatures

Brand Name	NX
Technology	Lithium Iron Phosphate
Voltage	3, 2V
Dimension	$26, 2(d) \ X \ 65, 6(H) \ mm$
Weight	80g
Standard Capacity	2300mAh at $0, 5C$
Maximum Charge Voltage	$3,65\pm0,05V$
Inner Resistance	$\leq 15 m \Omega$
Maximum Discharge Voltage	2V
Cycle Characteristic	1500(C/5) - 300(10C)
Max Continuous Discharge Current	46 <i>A</i>
Pulse Discharge Current	70A  for  10s
Working Temperature	Charge: 0 to $55^{\circ}C$
	Discharge: $-20$ to $60^{\circ}C$
Storage Temperature	$-20$ to $45^{\circ}C$

Table 4.1: Datasheet Characteristics of the  $LiFePO_4$  cell under test

The test profiles applied are such as to excite the resistive-capacitive behaviour of the battery. This allows to identify the parameters of the circuital model and their evolution, by using the procedure described in section 3.3. Tests are performed in climatic chamber at different temperature set points, in order to observe the temperature effects on battery's performances and life. The procedure is as follows for each new set of battery:

- 1. Set the ambient temperature in climatic chamber at  $25^{\circ}C$
- 2. Precharge single cells: fully charge each cell before to connect them in series in order to avoid charge unbalances.
- Perform 4 settling discharge and charge cycles: these are not deep discharge cycles, battery is discharged down to a 20% of SoC and then re-charged.
- 4. Set ambient temperature in climatic chamber at  $25^{\circ}C$  and keep it constant for at least two hours before to start the parametric test.
- 5. Parametric Test: execute a full discharge cycle followed by a full charge cycle. Cycles are: Constant Current Discharge cycle at a current rate of 1C (fig. 4.16) and Standard Li-Ion Charge Cycle at a current of 0, 5C (fig. 4.17). Measure the initial capacity with the Coulomb Counting Technique. SoH is assumed to be 100%.











(c) Single cells voltage profile.

Fig. 4.16: Parametric Test - Constant Current Discharge



(a) Current profile.







<sup>(</sup>c) Single cells voltage profile.

Fig. 4.17: Parametric Test - Standard Charge

- 6. Set climatic chamber to set and maintain the target temperature desired for test operations and keep it constant for at least two hours before to start the test operations.
- 7. Perform a pulsed Discharge Profile: Fully discharge the battery with 2C current pulse train, each current pulse extracts from battery a 10% of charge and it is followed by a rest time of 1800s after which we measure  $V_{oc}$  (fig. 4.18).









Fig. 4.18: Pulsed Discharge Profile

- 8. Perform a pulsed Charge Profile: Fully Charge the battery with 0.5C current pulse train, each current pulse feed to battery a 10% of charge and it is followed by a rest time of 1800s after which we measure  $V_{oc}$  (fig. 4.19).
- 9. Perform a topping charge (Standard charge), to complete the charge operation with the constant voltage stage, as defined from the state of art.



(a) Current profile.





Fig. 4.19: Pulsed Charge Profile

- 10. Repeat points from 7 to 9 for 10 times.
- 11. Set ambient temperature in climatic chamber at  $25^{\circ}C$  and keep it constant for at least two hours before to start the parametric test.
- 12. Parametric Test: execute a full discharge cycle followed by a full charge cycle. Cycles are: Constant Current Discharge cycle at a current rate of 1C (fig.4.16) and Standard Li-Ion Charge Cycle at a current of 0, 5C (fig. 4.17). Measure the residual capacity with the Coulomb Counting Technique and calculate the battery's *SoH* with the equation 2.4.
- 13. Repeat points from 6 to 12 for 3 times.

As mentioned in previous section, the control loop of the *Constant Current Discharge* and *Standard Charge* cycles is a closed loop control algorithmically implemented, this let to have a more accurate control over the I - V set point. The maximum relative error observed between the measured and the desired current is:

$$Max(E_r) = \frac{|I_m - I_{setpoint}|}{I_m} = \frac{|2,265A - 2,3A|}{2,265A} = 0,015$$
(4.6)

Conversely for *Pulsed Discharge Profile* and *Pulsed Charge Profile* the control loop is algorithmically open loop in order to have fast transients. A closed loop control is automatically implemented by the Power Supply and Electronic Load, which is faster but less accurate. The maximum relative error observed between the measured and the desired current in this case is:

$$Max(E_r) = \frac{|I_m - I_{setpoint}|}{I_m} = \frac{|4,85A - 4,6A|}{4,85A} = 0,051$$
(4.7)

which is higher but still acceptable in order to have a good trade off between rate and accuracy.

The test procedure described is repeated with 3 sets of new batteries at the target temperatures of  $0^{\circ}C$ ,  $25^{\circ}C$  and  $50^{\circ}C$ . The final target of these tests is to obtain informations about the battery's run time behaviour and its lifetime evolution in different operating conditions of ambient temperature. Data obtained from the tests were processed with the algorithm described in section 3.3 and the results obtained are presented in the next chapter.

# Results

Data obtained by the test operations described in Chapter 4 were processed and analyzed using the algorithm described in section 3.3. In this way it was made a characterization of the resistive-capacitive model of the battery in function of its State of Charge (SoC), State of Health (SoH) and temperature T. Furthermore an analysis of the internal resistance evolution over time at the same condition of SoC allows us to determine the operating temperature impact on battery life. The model was finally validated by performing new test operations as those described in Chapter 4 on two sets of new batteries at different set points of temperature than those used for characterization. Validation was made by a comparison between the voltage provided by the model and that measured at battery terminals (the model is stimulated with the real current data), and with the evaluation of the relative error. Tools used for these operations are NI LabVIEW, Wolfram Mathematica and Pspice A/D for circuital simulations.

### 5.1 Characterization of the model

The characterization of the model of figure 3.3 was made by processing and analyzing data obtained by the test operations with the algorithm described in section 3.3. For what concerns internal resistances  $R_{Dohm}$  and  $R_{Cohm}$ , the points experimentally found were affected by contact resistance due to the connectors. The contact resistance  $R_{contact}$  was measured at the target temperatures with the fall of potential method.

$$R_{contact} = \begin{cases} 0,0230\Omega & T = 0^{\circ}C \\ 0,0190\Omega & T = 25^{\circ}C \\ 0,0165\Omega & T = 50^{\circ}C \end{cases}$$
(5.1)

 $R_{contact}$  was subtracted from the experimentally found points in order to find  $R_{Dohm}$ and  $R_{Cohm}$  points and functions.

In this section are reported the parameters functions obtained and their graphical representation in function of Temperature and State of Charge: •  $V_{oc}$  :

$$V_{oc}(SoC, SoH, T, n) = \sum_{i=0}^{m} \sum_{j=0}^{m} v_{ij}(SoH, n) * SoC^{i} * T^{j}$$
(5.2)

The result obtained for SoH = 1, number of cells n = 2 and with an approximation of the series for m = 3 are represented in figure 5.1, while the  $v_{ij}$  values are reported in table 5.1 in matrix form. Figure 5.1 shows how the open circuit voltage depends on State of Charge and Temperature:  $V_{oc}$  increases as the State of Charge increases, but it has also a strong dependence on temperature, in fact in the same condition of SoC,  $V_{oc}$  increases with temperature with a maximum point between 30 and  $40^{\circ}C$  (it depends on the battery SoC).



Fig. 5.1:  $V_{oc}$  trend in function of SoC and T

	$v_{i0}$	$v_{i1}$	$v_{i2}$	$v_{i3}$
$v_{0j}$	6,16053	0,00104607	$-3,61575*10^{-6}$	$-3,70973*10^{-7}$
$v_{1j}$	1,74411	0,00146021	0	0
$v_{2j}$	-2,56144	0	0	0
$v_{3j}$	1,33982	0	0	0

Table 5.1:  $v_{ij}$  values with m = 3 approximation

•  $R_{Dohm}$  :

$$R_{Dohm}(SoC, SoH, T, n) = \sum_{i=0}^{m} \sum_{j=0}^{m} a_{Dij}(SoH, n) * SoC^{i} * T^{j}$$
(5.3)

The result obtained for SoH = 1, number of cells n = 2 and with an approximation of the series for m = 5 are represented in figure 5.2, while the  $a_{Dij}$  values are reported in table 5.2 in matrix form. Figure 5.2 shows how the internal resistance on the discharge branch depends on State of Charge and Temperature. An higher internal resistance means more losses and so a lower efficiency in transferring charge.  $R_{Dohm}$  is lower when battery is full and increases as the battery

is discharged and the State of Charge decreases. It has also a strong dependence on temperature, in fact  $R_{Dohm}$  increases as temperature decreases, which means that battery does not operate well at very low temperatures.



Fig. 5.2:  $R_{Dohm}$  trend in function of SoC and T

	$a_{Di0}$	$a_{Di1}$	$a_{Di2}$	$a_{Di3}$	$a_{Di4}$	$a_{Di5}$
$a_{D0j}$	1,63538	-0,108625	0,000875382	0,0000301917	$2,05981 * 10^{-7}$	$-9,93146 * 10^{-9}$
$a_{D1j}$	-12,3857	0,964587	-0,0084666	-0,000280891	$-1,87841 * 10^{-6}$	$9,28734 * 10^{-8}$
$a_{D2j}$	44,5787	-3,71971	0,0340606	0,00110769	$7,26716 * 10^{-6}$	$-3,70212*10^{-7}$
$a_{D3j}$	-78,7311	6,95541	-0,0662047	-0,00211342	-0,0000135552	$7,1625*10^{-7}$
$a_{D4j}$	67,1001	-6,25569	0,0617904	0,00193792	0,0000121344	$-6,66523 * 10^{-7}$
$a_{D5j}$	-22,0717	2,16773	-0,0221687	-0,000683956	$-4,18137*10^{-6}$	$2,38627 * 10^{-7}$

Table 5.2:  $a_{Dij}$  values with m = 5 approximation

•  $R_{Dct}$  :

$$R_{Dct}(SoC, SoH, T, n) = \begin{cases} \sum_{i=0}^{m} \sum_{j=0}^{m} b_{1Dij}(SoH, n) * SoC^{i} * T^{j} & SoC < 0, 4\\ \sum_{i=0}^{m} \sum_{j=0}^{m} b_{2Dij}(SoH, n) * SoC^{i} * T^{j} & 0, 4 < SoC < 0, 7\\ \sum_{i=0}^{m} \sum_{j=0}^{m} b_{3Dij}(SoH, n) * SoC^{i} * T^{j} & SoC > 0, 7 \end{cases}$$
(5.4)

For  $R_{Dct}$  because of the discontinuous trend between the known points the best fit result was found by cutting the function in three parts determined by three different ranges of SoC. The result obtained for SoH = 1, number of cells n = 2and with an approximation of the series for m = 5 are represented in figure 5.3, while the  $b_{1Dij}$ ,  $b_{2Dij}$  and  $b_{3Dij}$  values are reported in tables 5.3, 5.4, 5.5 in matrix form. Figure 5.3 shows how the charge transfer resistance on the discharge branch depends on State of Charge and Temperature. This resistance represents losses due to the electrochemical reaction, its minimum values are in the range of SoCbetween 80 - 50% and nominal temperature condition. Than it increases as the battery is discharged and the State of Charge decreases.







(b)  $R_{Dct}$  trend with 0.4 < SoC < 0.7.



(c)  $R_{Dct}$  trend with SoC > 0.7.

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	$b_{1Di0}$	$b_{1Di1}$	$b_{1Di2}$	$b_{1Di3}$	$b_{1Di4}$	$b_{1Di5}$
$b_{1D0j}$	0,033216	0,00030167	$1,1287 * 10^{-6}$	$-3,8832 * 10^{-8}$	$-1,4175*10^{-9}$	$-3,47686*10^{-11}$
$b_{1D1j}$	-0,022598	-0,00095691	$-5,7211 * 10^{-6}$	$5,5991 * 10^{-8}$	$2,9104 * 10^{-9}$	$7,62043 * 10^{-11}$
$b_{1D2j}$	-0,16354	-0,0036471	-0,000019423	$2,8816 * 10^{-7}$	$1,2857 * 10^{-8}$	$3,2837 * 10^{-10}$
$b_{1D3j}$	-0,2806	-0,0044996	-0,000021362	$4,3714 * 10^{-7}$	$1,779 * 10^{-8}$	$4,4653 * 10^{-10}$
$b_{1D4j}$	0,13697	0,0096951	0,000061438	$-4,583 * 10^{-7}$	$-2,6914*10^{-8}$	$-7,1678 * 10^{-10}$
$b_{1D5j}$	2,7768	0,080666	0,0004574	$-5,5018 * 10^{-6}$	$-2,6379*10^{-7}$	$-6,820*10^{-9}$

Table 5.3:  $b_{1Dij}$  values with m = 5 approximation

	$b_{2Di0}$	$b_{2Di1}$	$b_{2Di2}$	$b_{2Di3}$	$b_{2Di4}$	$b_{2Di5}$
$b_{2D0j}$	0,0389602	0,00461839	0,0000209955	$-4,77898 * 10^{-7}$	$-1,89485 * 10^{-8}$	$-4,7314*10^{-10}$
$b_{2D1j}$	-0,0958573	-0,012397	-0,0000548032	$1,3316 * 10^{-6}$	$5,20147*10^{-8}$	$1,29479 * 10^{-9}$
$b_{2D2j}$	-0,0275716	-0,007654	-0,0000362915	$7,45068 * 10^{-7}$	$3,02949 * 10^{-8}$	$7,60312 * 10^{-10}$
$b_{2D3j}$	0,223932	0,0195658	0,0000817433	$-2,25072*10^{-6}$	$-8,56127*10^{-8}$	$-2,11917*10^{-9}$
$b_{2D4j}$	0,292457	0,0338712	0,000148396	$-3,68018 * 10^{-6}$	$-1,43105 * 10^{-7}$	$-3,55892 * 10^{-9}$
$b_{2D5j}$	-0,589087	-0,041874	-0,000167719	$5,04364 * 10^{-6}$	$1,88577*10^{-7}$	$4,65038 * 10^{-9}$

Table 5.4:  $b_{2Dij}$  values with m = 5 approximation

	$b_{3Di0}$	$b_{3Di1}$	$b_{3Di2}$	$b_{3Di3}$	$b_{3Di4}$	$b_{3Di5}$
$b_{3D0j}$	0,0020664	0,000286	$6,9687 * 10^{-6}$	$1,4831 * 10^{-7}$	$3,0262 * 10^{-9}$	$6,095 * 10^{-11}$
$b_{3D1j}$	0,0037923	-0,00019554	$-2,8350*10^{-6}$	$-4,0844*10^{-8}$	$-6,3951 * 10^{-10}$	$-1,0953 * 10^{-11}$
$b_{3D2j}$	0,0043632	-0,00049961	$-9,55 * 10^{-6}$	$-1,7674 * 10^{-7}$	$-3,3426 * 10^{-9}$	$-6,4707*10^{-11}$
$b_{3D3j}$	0,0030137	-0,0004486	$-9,7530*10^{-6}$	$-1,9567 * 10^{-7}$	$-3,8742*10^{-9}$	$-7,686 * 10^{-11}$
$b_{3D4j}$	-0,0008891	0,0001126	$-4,3159 * 10^{-7}$	$-4,1252*10^{-8}$	$-1,1607*10^{-9}$	$-2,6550*10^{-11}$
$b_{3D5j}$	-0,007791	0,001299	0,00002067	$3,2894 * 10^{-7}$	$5,6081 * 10^{-9}$	$1,0199 * 10^{-10}$

Table 5.5:  $b_{3Dij}$  values with m = 5 approximation

•  $C_{Ddl}$  :

$$C_{Ddl}(SoC, SoH, T, n) = \sum_{i=0}^{m} \sum_{j=0}^{m} c_{Dij}(SoH, n) * SoC^{i} * T^{j}$$
(5.5)

The result obtained for SoH = 1, number of cells n = 2 and with an approximation of the series for m = 5 are represented in figure 5.4, while the  $c_{Dij}$  values are reported in table 5.6 in matrix form. Figure 5.4 shows how the double layer capacitance on the discharge branch depends on State of Charge and Temperature. Together with  $R_{Dct}$  models the dynamics due to the chemical reaction.  $C_{Ddl}$ does not vary too much with SoC, except at high temperatures, so, during a discharge process there are not huge variations in  $C_{Ddl}$ . Conversely it has a strong dependence on temperature, in fact  $C_{Ddl}$  increases with temperature, and at high



temperatures it decreases while the battery is discharged. This means that the dynamic due to the chemical reaction is slower at high temperatures.

Fig. 5.4:  $C_{Ddl}$  trend in function of SoC and T

	$c_{Di0}$	$c_{Di1}$	$c_{Di2}$	$c_{Di3}$	$c_{Di4}$	$c_{Di5}$
$c_{D0j}$	-20682, 3	1975, 88	16,6483	0,0361313	-0,00242741	-0,0000803674
$c_{D1j}$	227450	-14007, 4	-146,654	-1,15472	-0,00400321	0,000113876
$c_{D2j}$	-754361	30883, 5	474,066	7,2763	0,12049	0,00214872
$c_{D3j}$	$1,14596*10^{6}$	-17314, 8	-695,436	-17,5639	-0,385862	-0,00804555
$c_{D4j}$	-775276	-16670	460, 12	18,5443	0,465428	0,0102406
$c_{D5j}$	177608	15418, 3	-106, 178	-7,12761	-0,193849	-0,00438612

Table 5.6:  $c_{Dij}$  values with m = 5 approximation

•  $R_{Ddiff}$  :

$$R_{Ddiff}(SoC, SoH, T, n) = \sum_{i=0}^{m} \sum_{j=0}^{m} d_{Dij}(SoH, n) * SoC^{i} * T^{j}$$
(5.6)

The result obtained for SoH = 1, number of cells n = 2 and with an approximation of the series for m = 5 are represented in figure 5.5, while the  $d_{Dij}$  values are reported in table 5.7 in matrix form. Figure 5.5 shows how the diffusion resistance on the discharge branch depends on State of Charge and Temperature. This resistance represents losses due to the diffusion of carriers.  $R_{Ddiff}$  is higher at higher temperatures and does not vary too much during a discharge process, except near to the end of discharge condition.



Fig. 5.5:  $R_{Ddiff}$  trend in function of SoC and T

	$d_{Di0}$	$d_{Di1}$	$d_{Di2}$	$d_{Di3}$	$d_{Di4}$	$d_{Di5}$
$d_{D0j}$	-0,00284819	0,00448249	0,0000282401	$-2,17079*10^{-7}$	$-1,2566 * 10^{-8}$	$-3,34034*10^{-10}$
$d_{D1j}$	0,119093	-0,0452777	-0,000287569	$2,12003 * 10^{-6}$	$1,25214 * 10^{-7}$	$3,3372 * 10^{-9}$
$d_{D2j}$	-0,318786	0,182429	0,00114449	$-8,98618 * 10^{-6}$	$-5,1499*10^{-7}$	$-1,36714 * 10^{-8}$
$d_{D3j}$	0,283606	-0,35606	-0,00218679	0,000019014	$1,03996 * 10^{-6}$	$2,74318 * 10^{-8}$
$d_{D4j}$	0,0586174	0,333851	0,00200062	-0,00001939	$-1,01197 * 10^{-6}$	$-2,65131 * 10^{-8}$
$d_{D5j}$	-0,135583	-0,120147	-0,000702344	$7,53177 * 10^{-6}$	$3,77258 * 10^{-7}$	$9,82246 * 10^{-9}$

#### Table 5.7: $d_{Dij}$ values with m = 5 approximation

•  $C_{Ddiff}$  :

$$C_{Ddiff}(SoC, SoH, T, n) = \sum_{i=0}^{m} \sum_{j=0}^{m} e_{Dij}(SoH, n) * SoC^{i} * T^{j}$$
(5.7)

The result obtained for SoH = 1, number of cells n = 2 and with an approximation of the series for m = 5 are represented in figure 5.6, while the  $e_{Dij}$  values are reported in table 5.8 in matrix form. Figure 5.6 shows how the diffusion capacitance on the discharge branch depends on State of Charge and Temperature. Together with  $R_{Ddiff}$  models the dynamics due to the diffusion of carriers, which is slower than that due to the chemical reaction.  $C_{Ddiff}$  (as  $C_{Ddl}$ ) does not vary too much with SoC, except at high temperatures, so, during a discharge process there are not huge variations in  $C_{Ddiff}$ . Conversely it has a strong dependence on temperature, in fact  $C_{Ddiff}$  increases with temperature, and at high temperatures it decreases while the battery is discharged. This means that the dynamics due to the diffusion of carriers is slower at high temperatures.



Fig. 5.6:  $C_{Ddiff}$  trend in function of SoC and T

	$e_{Di0}$	$e_{Di1}$	$e_{Di2}$	$e_{Di3}$	$e_{Di4}$	$e_{Di5}$
$e_{D0j}$	36598	512,967	6,07961	0,0645374	0,000671832	$7,11759*10^{-6}$
$e_{D1j}$	-110570	7502, 86	2,63769	-1,76407	-0,0540983	-0,00126972
$e_{D2j}$	633875	-77249, 2	-267,715	10,6131	0,378776	0,00924288
$e_{D3j}$	$-1,54735*10^{6}$	224042	975,691	-24,52714	-0,950928	-0,0236342
$e_{D4j}$	$1,71786 * 10^{6}$	-262673	-1268, 34	24,8516	1,02273	0,0257285
$e_{D5j}$	-708374	108849	559,604	-9,23056	-0,398603	-0,0101199

Table 5.8:  $e_{Dij}$  values with m = 5 approximation

•  $R_{Cohm}$  :

$$R_{Cohm}(SoC, SoH, T, n) = \sum_{i=0}^{m} \sum_{j=0}^{m} a_{Cij}(SoH, n) * SoC^{i} * T^{j}$$
(5.8)

The result obtained for SoH = 1, number of cells n = 2 and with an approximation of the series for m = 3 are represented in figure 5.7, while the  $a_{Cij}$  values are reported in table 5.9 in matrix form. Figure 5.7 shows how the internal resistance on the charge branch depends on State of Charge and Temperature. An higher internal resistance means more losses and so a lower efficiency of the charge process. On the contrary of what happens on the discharge branch,  $R_{Cohm}$  is lower when battery is empty and increases as the battery is charged and the State of Charge increases. The curve slope becomes greater near to the end of charge condition, when battery begins to refuse more charge. It has also a strong dependence on temperature, in fact  $R_{Cohm}$  as  $R_{Dohm}$  increases as temperature decreases, which means that battery does not operate well at very low temperatures.



Fig. 5.7:  $R_{Cohm}$  trend in function of SoC and T

	$a_{Ci0}$	$a_{Ci1}$	$a_{Ci2}$	$a_{Ci3}$
$a_{C0j}$	0,272707	-0,0205057	0,000715032	$-7,76072*10^{-6}$
$a_{C1j}$	0,436848	-0,0261882	0,000270794	$6,45144*10^{-7}$
$a_{C2j}$	-1,44723	0,0950962	-0,00191819	0,0000171165
$a_{C3j}$	1,46349	-0,0806444	0,00148249	-0,0000121915

Table 5.9:  $a_{Cij}$  values with m = 3 approximation

•  $R_{Cct}$  :

$$R_{Cct}(SoC, SoH, T, n) = \sum_{i=0}^{m} \sum_{j=0}^{m} b_{Cij}(SoH, n) * SoC^{i} * T^{j}$$
(5.9)

The result obtained for SoH = 1, number of cells n = 2 and with an approximation of the series for m = 5 are represented in figure 5.8, while the  $b_{Cij}$  values are reported in table 5.10 in matrix form. Figure 5.8 shows how the charge transfer resistance on the charge branch depends on State of Charge and Temperature.  $R_{Cct}$  represents losses due to the electrochemical reaction in charge process, its minimum values are in the range of SoC between 20 - 40%, than it increases as the battery is charged and the State of Charge increases. As for the  $R_{Cohm}$ , it is higher at low temperatures.



Fig. 5.8:  $R_{Cct}$  trend in function of SoC and T

	$b_{Ci0}$	$b_{Ci1}$	$b_{Ci2}$	$b_{Ci3}$	$b_{Ci4}$	$b_{Ci5}$
$b_{C0j}$	-0,0365131	-0,00861595	-0,0000339472	$1,01219 * 10^{-6}$	$3,78123 * 10^{-8}$	$9,32244 * 10^{-10}$
$b_{C1j}$	2,22505	0,0732772	0,00015034	-0,0000125565	$-4,11423*10^{-7}$	$-9,83093 * 10^{-9}$
$b_{C2j}$	-15,084	-0,247015	0,0000989277	0,0000596802	$1,78308 * 10^{-6}$	$4,15448 * 10^{-8}$
$b_{C3j}$	41,4708	0,387235	-0,00155072	-0,000134514	$-3,74046*10^{-6}$	$-8,52769 * 10^{-8}$
$b_{C4j}$	50, 6429	-0,272375	0,00272902	0,000143498	$3,76713 * 10^{-6}$	$8,42756 * 10^{-8}$
$b_{C5j}$	22,975	0,0582886	-0,00149058	-0,0000581007	$-1,44597*10^{-6}$	$-3,17433*10^{-8}$

Table 5.10:  $b_{Cij}$  values with m = 5 approximation

•  $C_{Cdl}$  :

$$C_{Cdl}(SoC, SoH, T, n) = \begin{cases} \sum_{i=0}^{m} \sum_{j=0}^{m} c_{1Cij}(SoH, n) * SoC^{i} * T^{j} & SoC \leq 0, 48\\ \sum_{i=0}^{m} \sum_{j=0}^{m} c_{2Cij}(SoH, n) * SoC^{i} * T^{j} & 0, 48 < SoC < 0, 68 \\ \sum_{i=0}^{m} \sum_{i=0}^{m} c_{3Cij}(SoH, n) * SoC^{i} * T^{j} & SoC \geq 0, 68 \end{cases}$$
(5.10)

For  $C_{Cdl}$  because of the discontinuous trend between the known points the best fit result was found by cutting the function in three parts determined by three different ranges of SoC. The result obtained for SoH = 1, number of cells n = 2and with an approximation of the series for m = 5 are represented in figure 5.9, while the  $c_{1Cij}$ ,  $c_{2Cij}$  and  $c_{3Cij}$  values are reported in tables 5.11, 5.12, 5.13 in matrix form. Figure 5.9 shows how the double layer capacitance on the charge branch depends on State of Charge and Temperature. Together with  $R_{Cct}$  models the dynamics due to the chemical reaction during charge processes. Its maximum values are at high temperatures.



(a)  $C_{Cdl}$  trend with  $SoC \leq 0.48$ .



(b)  $C_{Cdl}$  trend with 0.48 < SoC < 0.68.





Fig. 5.9:  $C_{Cdl}$  trend in function of SoC and T

	$c_{1Ci0}$	$c_{1Ci1}$	$c_{1Ci2}$	$c_{1Ci3}$	$c_{1Ci4}$	$c_{1Ci5}$
$c_{1C0j}$	-9497, 2	163, 123	1,49176	0,00666481	-0,000113487	$-4,76703 * 10^{-6}$
$c_{1C1j}$	54790, 5	518, 415	0,48341	-0,115132	-0,003602	-0,0000850106
$c_{1C2j}$	49423,8	-1422,87	-8,2149	0,10386	0,00491929	0,000126962
$c_{1C3j}$	-122291	-6252,08	-31,7731	0,617433	0,0256491	0,000646572
$c_{1C4j}$	-312643	-5800,77	-31,4518	0,534209	0,0231057	0,000586991
$c_{1C5j}$	345178	33791, 6	212, 236	-2,33308	-0,117525	-0,00306454

Table 5.11:  $c_{1Cij}$  values with m = 5 approximation

	$c_{2Ci0}$	$c_{2Ci1}$	$c_{2Ci2}$	$c_{2Ci3}$	$c_{2Ci4}$	$c_{2Ci5}$
$c_{2C0j}$	19469, 2	212,828	3,97232	0,0722813	0,00135292	0,0000260385
$c_{2C1j}$	-5299, 13	-225, 241	-3,49231	-0,0537715	-0,000891191	-0,0000158967
$c_{2C2j}$	-37541, 6	-752, 107	-12,6371	-0,20908	-0,00366018	-0,0000676577
$c_{2C3j}$	-52934, 8	-884,429	-15,1772	-0,254483	-0,00449234	-0,0000834487
$c_{2C4j}$	-5260, 98	306,773	5,01932	0,0799913	0,00135658	0,0000245512
$c_{2C5j}$	181194	4379, 39	75,2988	1,25039	0,0218515	0,000403094

Table 5.12:  $c_{2Cij}$  values with m = 5 approximation

	$c_{3Ci0}$	$c_{3Ci1}$	$c_{3Ci2}$	$c_{3Ci3}$	$c_{3Ci4}$	$c_{3Ci5}$
$c_{3C0j}$	65600, 5	2049, 42	42,3026	0,835059	0	0
$c_{3C1j}$	-67240, 8	-2225,93	-51,5719	-1,08272	0	0
$c_{3C2j}$	-102834	-2949, 15	-64,5605	-1,32131	0	0
$c_{3C3j}$	105082	3503, 18	79,6896	1,66538	0	0
$c_{3C4j}$	0	0	0	0	0	0
$c_{3C5j}$	0	0	0	0	0	0

Table 5.13:  $c_{3Cij}$  values with m = 5 approximation

•  $R_{Cdiff}$  :

$$R_{Cdiff}(SoC, SoH, T, n) = \sum_{i=0}^{m} \sum_{j=0}^{m} d_{Cij}(SoH, n) * SoC^{i} * T^{j}$$
(5.11)

The result obtained for SoH = 1, number of cells n = 2 and with an approximation of the series for m = 5 are represented in figure 5.10, while the  $d_{Cij}$  values are reported in table 5.14 in matrix form. Figure 5.10 shows how the diffusion resistance on the charge branch depends on State of Charge and Temperature.  $R_{Cdiff}$  represents losses due to carriers diffusion in charge process, its minimum values are in the range of SoC between 20 - 40%, than it increases as the battery is charged and the State of Charge increases. As for the  $R_{Cohm}$  and  $R_{Cct}$ , it is higher at low temperatures.



Fig. 5.10:  $R_{Cdiff}$  trend in function of SoC and T

	$d_{Ci0}$	$d_{Ci1}$	$d_{Ci2}$	$d_{Ci3}$	$d_{Ci4}$	$d_{Ci5}$
$d_{C0j}$	-0,0172712	-0,00876787	-0,0000371537	$9,48631*10^{-7}$	$3,65602 * 10^{-8}$	$9,07458 * 10^{-10}$
$d_{C1j}$	1,99509	0,0738082	0,000184697	-0,0000116144	$-3,90087 * 10^{-7}$	$-9,37993 * 10^{-9}$
$d_{C2j}$	-14,0152	-0,244295	-0,0000420153	0,0000547046	$1,66193 * 10^{-6}$	$3,89082 * 10^{-8}$
$d_{C3j}$	39,0515	0,372032	-0,00127205	-0,00012254	$-3,43649*10^{-}6$	$-7,85569 * 10^{-8}$
$d_{C4j}$	-47,9707	-0,249245	0,00246055	0,000130188	$3,42086 * 10^{-6}$	$7,65532 * 10^{-8}$
$d_{C5j}$	21,821	0,0472395	-0,00138758	-0,000052564	$-1,3002*10^{-6}$	$-2,84789 * 10^{-8}$

Table 5.14:  $d_{Cij}$  values with m = 5 approximation

•  $C_{Cdiff}$  :

$$C_{Cdiff}(SoC, SoH, T, n) = \begin{cases} \sum_{i=0}^{m} \sum_{j=0}^{m} e_{1Cij}(SoH, n) * SoC^{i} * T^{j} & SoC \leq 0, 48\\ \sum_{i=0}^{m} \sum_{j=0}^{m} e_{2Cij}(SoH, n) * SoC^{i} * T^{j} & 0, 48 < SoC < 0, 58 \end{cases}$$
(5.12)  
$$\sum_{i=0}^{m} \sum_{j=0}^{m} e_{3Cij}(SoH, n) * SoC^{i} * T^{j} & SoC \geq 0, 58 \end{cases}$$

For  $C_{Cdiff}$  because of the discontinuous trend between the known points the best fit result was found by cutting the function in three parts determined by three different ranges of SoC. The result obtained for SoH = 1, number of cells n = 2and with an approximation of the series for m = 5 are represented in figure 5.11, while the  $e_{1Cij}$ ,  $e_{2Cij}$  and  $e_{3Cij}$  values are reported in tables 5.15, 5.16, 5.17 in matrix form. Figure 5.11 shows how the diffusion capacitance on the charge branch depends on State of Charge and Temperature. Together with  $R_{Cdiff}$  models the dynamics due to carriers diffusion during charge processes, which is slower than that due to the chemical reaction.



(c)  $C_{Cdiff}$  trend with  $SoC \ge 0.58$ .

Fig. 5.11:  $C_{Cdiff}$  trend in function of SoC and T

	$e_{1Ci0}$	$e_{1Ci1}$	$e_{1Ci2}$	$e_{1Ci3}$	$e_{1Ci4}$	$e_{1Ci5}$
$e_{1C0j}$	134757	-6279, 47	-41,3068	0,249317	0,0163104	0,00044015
$e_{1C1j}$	272119	10424,2	49,1263	-1,072	-0,0430456	-0,00107768
$e_{1C2j}$	-897468	30596, 2	260, 317	0,417059	-0,0430622	-0,00138135
$e_{1C3j}$	$-3,20214 * 10^{6}$	20337, 1	320, 241	4,89142	0,0800331	0,00141312
$e_{1C4j}$	$-2,08612 * 10^{6}$	-55779	-329,847	4,26067	0,201396	0,00519716
$e_{1C5j}$	$1,79686 * 10^7$	-215108	-2616, 29	-25,7936	-0,217348	-0,0012745

Table 5.15:  $e_{1Cij}$  values with m = 5 approximation

	$e_{2Ci0}$	$e_{2Ci1}$	$e_{2Ci2}$	$e_{2Ci3}$	$e_{2Ci4}$	$e_{2Ci5}$
$e_{2C0j}$	-11022, 9	1206, 78	5,74393	-0,116782	-0,00476018	-0,000119525
$e_{2C1j}$	4038, 87	1291, 43	7,19308	-0,0960046	-0,00444561	-0,000114286
$e_{2C2j}$	44381	292, 216	3,22832	0,0279582	0,0001607	$-8,4928*10^{-7}$
$e_{2C3j}$	129097	-3628, 61	-18,0484	0,361366	0,014871	0,000374166
$e_{2C4j}$	283729	-14316, 5	-83,9338	1,07017	0,0507021	0,00130879
$e_{2C5j}$	537757	-39466, 6	-253, 158	2,39385	0,127877	0,0033636

Table 5.16:  $e_{2Cij}$  values with m = 5 approximation

	$e_{3Ci0}$	$e_{3Ci1}$	$e_{3Ci2}$	$e_{3Ci3}$	$e_{3Ci4}$	$e_{3Ci5}$
$e_{3C0j}$	644932	25411, 6	659, 683	14, 5	0,300963	0,00611609
$e_{3C1j}$	$-3,06742 * 10^{6}$	-123926	-2949, 41	-62,4294	-1,27329	-0,025658
$e_{3C2j}$	$4,22727 * 10^{6}$	155066	3453, 55	70,8127	1,42207	0,0284381
$e_{3C3j}$	$1,60099 * 10^{6}$	68270, 5	1641, 28	34,941	0,714917	0,0144305
$e_{3C4j}$	$-7,30855 * 10^{6}$	-236278	-5206, 19	-106,262	-2, 12969	-0,042549
$e_{3C5j}$	$4,00019 * 10^{6}$	109434	2388, 86	48,5361	0,970573	0,0193696

Table 5.17:  $e_{3Cij}$  values with m = 5 approximation

The 3D functions seen above were calculated with the polynomial fitting technique between known points of the software Wolfram Mathematica. Known points are at the target temperatures of  $0^{\circ}C$ ,  $25^{\circ}C$ ,  $50^{\circ}C$  with  $\Delta SoC$  intervals of 0.1. In figure 5.12 are showed, as an example, portions of the fitting curves in 2D for the parameters  $V_{oc}$ ,  $R_{Dohm}$  and  $R_{Cohm}$  where the red dots are the experimentally found points.



(c)  $R_{Cohm}$  at  $50^{\circ}C$ .

Fig. 5.12: Portions of the fitting curves in 2D for the parameters  $V_{oc}$ ,  $R_{Dohm}$  and  $R_{Cohm}$ 

#### 5.2 Temperature effects on battery life

To analyze temperature effects on battery life, it was necessary to analyze battery ageing in the different operating conditions of ambient temperature. As said in 2.1.2 ageing is measured as a loss of capacity during time. At the end of the test operations it was observed that the battery set which has been tested at  $50^{\circ}C$  has lost much more capacity then the batteries tested at  $0^{\circ}C$  and  $25^{\circ}C$ . Capacity is measured with the *Coulomb Counting technique* during the parametric tests described in section 4.3. For each unit under test, table 5.18 reports the available capacity after 30 discharge and charge cycles (as described in section 4.3) and the *SoH* calculated with the equation 2.4.

	StartingCapacity[Ah]	FinalCapacity[Ah]	SoH[%]
$0^{\circ}C$	2, 22	2, 13	96
$25^{\circ}C$	2, 22	2,175	98
$50^{\circ}C$	2, 22	2,05	93

Table 5.18: Residual Capacity and SoH after 30 discharge and charge cycles

Further analysis come from the characterization of the model, as described in previous section: by characterizing the model and taking the parameters values cycle by cycle, it is possible to obtain a curve which represents the dynamics of the parameters in function of the number of cycles and temperature. The parameter of interest for the evaluation of battery ageing is the internal resistance  $R_{Dohm}$  on the discharge branch and  $R_{Cohm}$  on the charge branch. From literature, an increment of the internal resistance in the same operating conditions and at the same State of Charge can be directly related to a reduction of the battery's State of Health. In figure 5.13 is represented the  $R_{Dohm}$  at SoC = 0, 9 curve in function of number of cycles and temperature. The curve is obtained with a polynomial fitting technique between the known points, which are the red dots in figure. Figure 5.14 instead shows the Partial derivative  $\partial R_{Dohm}/\partial n$  and it gives an important information on how fast is the variation of  $R_{Dohm}$  in the various operating conditions.

As can be seen, in all operating conditions partial derivative has a negative trend in the first 3-5 cycles, so internal resistance decreases in the first cycles and then settles around its final value. This means that a new battery needs some training cycles in order to reach its maximum performances, then internal resistance increases as battery ages. The curve obtained interpolating experimental data highlights that in the first 30cycles internal resistance does not vary too much at low and mid temperatures.  $R_{Dohm}$  has its maximum values at  $0^{\circ}C$  and it is inversely proportional to temperature, in fact the minimum internal resistance is at  $50^{\circ}C$ . On the other hand if in the range of temperatures  $0-30^{\circ}C$  internal resistance does not vary too much in the first 30 cycles, this is not true at higher temperatures, and the higher is temperature



Fig. 5.13:  $R_{Dohm}$  evolution in function of the number of cycles and T at SoC = 0.9



Fig. 5.14: Partial derivative  $\partial R_{Dohm}/\partial n$  of the function of figure 5.13

the faster internal resistance increases in time. An high internal resistance means high losses and then a low energy efficiency of the discharge and charge processes, moreover it reaches earlier the end of discharge/end of charge condition, with the consequence of a capacity reduction. For that reason  $LiFePO_4$  batteries are not well suited to work at low temperatures. At first glance it would seem that the battery works better around  $50^{\circ}C$  and in general at high temperatures, since internal resistance is lower. However it is a temporary condition in fact after few cycles internal resistance begins to increase, with the consequence of an irreversible loss of capacity and loss of efficiency in discharge and charge processes. High temperatures are very harmful for battery life: figure 5.14 shows that the higher is ambient temperature where battery operates, the faster internal resistance increases and then battery ages.

By analyzing the curves in figures 5.13 and 5.14 we come to the conclusion that: in order to obtain the best performances over time from the examined typology of batteries, they should never operate out of a certain range of temperatures, which is between  $20^{\circ}C$  and  $30^{\circ}C$ , with a best trade off between instantaneous performances and lifetime extension around  $27^{\circ}C$ .

## 5.3 Validation of the model

For the validation of the model, additional discharge/charge tests have been performed at the intermediate target ambient temperatures of  $12^{\circ}C$  and  $38^{\circ}C$  on new batteries. It was therefore compared the trend of the voltage at the battery terminals provided by the model with the one measured. A measure of the model accuracy is given by the evaluation of relative error, whose medium value is below 1% and peak value never exceeds 7%. In figure 5.15 is reported the comparison between  $V_{batt}$  provided by the model and  $V_{batt}$  measured, and the relative error for a discharge process at a temperature of  $12^{\circ}C$  and an initial SoC of 50%. In this condition, medium error is below 1% and peak error near the fast transients is 6, 9%. Figure 5.16 shows the same quantities for a charge process at a temperature of  $12^{\circ}C$  and an initial SoC of 27%. In this condition, medium error is below 1% and peak error near the fast transients is 1, 35%.

Figure 5.17 shows the comparison between  $V_{batt}$  provided by the model and  $V_{batt}$  measured, and the relative error for a discharge process at a temperature of  $38^{\circ}C$  and an initial SoC of 80%. In this condition, medium error is below 1% and peak error near the fast transients is 2,6%. Figure 5.18 shows the same quantities for a charge process at a temperature of  $38^{\circ}C$  and an initial SoC of 56%. In this condition, medium error is below 1% and peak error near the fast transients is 0,7%.



(a)  $V_{batt}$  provided by the model and  $V_{batt}$  measured.



(b) Relative error.

Fig. 5.15: Discharge: Model's  $V_{batt}$  and  $V_{batt}$  measured for  $T = 12^{\circ}C$ , SoC = 0, 5



(a)  $V_{batt}$  provided by the model and  $V_{batt}$  measured.



(b) Relative error.

Fig. 5.16: Charge: Model's  $V_{batt}$  and  $V_{batt}$  measured for  $T = 12^{\circ}C$ , SoC = 0, 27



(a)  $V_{batt}$  provided by the model and  $V_{batt}$  measured.



(b) Relative error.

Fig. 5.17: Discharge: Model's  $V_{batt}$  and  $V_{batt}$  measured for  $T = 38^{\circ}C$ , SoC = 0, 8



(a)  $V_{batt}$  provided by the model and  $V_{batt}$  measured.



(b) Relative error.

Fig. 5.18: Charge: Model's  $V_{batt}$  and  $V_{batt}$  measured for  $T = 38^{\circ}C$ , SoC = 0, 56
#### 5.4 Limits and opportunities of the model

The main limit of the model discussed is that near to the end of charge and the end of discharge conditions it does not work well: the relative error increases exponentially, because the model does not represent well the higher order phenomena which are not negligible in these operating conditions. This limit can also become an opportunity for the model, in fact by analyzing the voltage deviation between the model and the measurement at the battery terminals, it is possible to find the moment when some higher order phenomena (such gassing) become relevant; these phenomena have always a negative effect on energy efficiency and on battery ageing. These informations can be used in order to create new effective control systems to optimize charge/discharge processes, in order to improve energy efficiency and battery life. Furthermore it is possible, if the operative conditions are known, to estimate in runtime SoC and SoH by comparing the circuital parameters measured with a look up table. This can be essential in Battery Management Systems and Energy Storage Management Systems in order to have smart systems which can adapt charge and discharge processes depending on the battery's internal state, in order to improve energy efficiency and battery life.

In fact as future developments, it would be possible to project a control algorithm of an Energy Storage Management System which can compare in real time measurement data with data provided by the model. The system should implement a closed loop control on the discharge/charge currents in order to minimize the deviation between model and measurement. Doing that, it would be possible to measure the benefits of the technology applied in terms of energy efficiency and lifetime extension in a wide range of operating conditions.

## Conclusions

In conclusion the research activities made and discussed in this Ph.D. Thesis consist in the study and definition of innovative methodologies and technologies for the estimation of State of Charge and State of Health of energy storage systems. The first activity was a preliminary study of the state of the art, which led to the definition of an innovative, dynamic circuital model which allows to accurately represent the functioning of a battery (in charge and discharge) in function of its state of charge (SoC), state of health (SoH) and temperature (T). Characterization of the model was made through tests in laboratory on three different sets of  $LiFePO_4$  batteries at the ambient temperature setpoints of  $0^{\circ}C$ ,  $25^{\circ}C$  and  $50^{\circ}C$  set in climatic chamber. In order to perform these tests a key activity was the project, configuration and implementation of an automatic platform (SCADA System) for the execution of constant current discharge profiles, standard charge profiles and pulsed discharge and charge profiles. Once the tests were completed, the data obtained were analyzed in the frequency domain to obtain the parameters of the capacitance - resistance model of the battery. So, with non linear interpolation techniques between known points, it was found a relation for each parameter, that highlights its dependence on: temperature, state of charge, state of health and number of cells. Moreover an ideal room temperature range was identified for the type of batteries under examination, in order to improve their performances over time in terms of energy efficiency and extension of useful life. The model was finally validated by performing tests on new batteries at the intermediate ambient temperature conditions of  $12^{\circ}C$  and  $38^{\circ}C$ , and comparing the data provided by the model with the data obtained from the measurements. The medium relative error between measurements and model is below 1% while maximum peak error near transients is below 7%. This model lets to determine, if operating conditions are known, battery's internal state and its evolution in run-time through the measurement of the parameters of the model. So it is well suited for the usage in smart battery management systems in order to optimize charge and discharge processes in terms of energy efficiency and lifetime extension.

# Appendix A - Instrumentation used

In the tables below, are reported the main characteristics (which are of interest for the operations performed in this Ph.D. thesis) of the instrumentation used. If you want to have further details, please consult the instrumentation datasheets and manuals.

# A.1 Power Supply Ametek SGI 15/801

	Power Requirements	
Nominal Voltage	380/400 VAC 10% 3 phases $+G,47/63 Hz$	
Power Factor	> 0,72	
Operating specifications		
Voltage range	0-15V	
Current range	0 - 801A	
Power	12kW	
RMS Ripple Noise		
(20Hz - 300kHz)	20mV	
p-p Ripple Noise		
(20Hz - 20MHz)	50mV	
Output Voltage rise time	$10ms~({\rm from}~10\%$ to $90\%$ of the output voltage change - resistive load, typical)	
Output Voltage fall time	50ms (no load condition), $10ms$ (under load)	
	(from 90% to 10% of the output voltage change - resistive load, typical)	
DC Current Slew Rate	45A/ms typical - resistive load	
Load Transient response	$1ms$ to recover $\pm 0,75\%$ of full-scale of steadystate output for a 50% load change	
Sensing		
Terminals are provided to se	nse output voltage at point of load. Line drop $1V$ of rated voltage per line	
for $10 - 20V$ models.(Greater line drop is allowed, but output regulation specifications no longer apply).		
Remote Digital Interface		
Voltage accuracy	$\pm 0,1\%$ of full scale	
Current accuracy	$\pm 0,4\%$ of full scale	
Current and Voltage resolution	$\pm 0,002\%$ of full scale	
Physical		
Dimensions	48, 3cm (W) X 71, $35cm$ (D) X 13, $3cm$ (H)	
Weight	50kg	

Table A.1: Ametek SGI 15/801 - data sheet specifications

### A.2 Programmable Electronic Load Amrel PLA 10K-60-1500

Power Requirements		
Nominal Voltage	95/240VAC , $48/62Hz$	
Operating specifications		
Voltage range	0 - 60V	
Current range	0 - 1500	
Power	10kW	
Vmin at Imax	1% of nominal voltage	
Resistance range	0.0013 - 100Ω	
Transient Time Range	0, 5 - 51, 19ms	
Operating Temperature	$5^{\circ}C - 40^{\circ}C$	
Derating for higher temperatures	$(-)1,67\% RatedPower/^{\circ}C$	
Sensing		
1V Maximum voltage drop compensation		
Remote	Digital Interface	
CV Accuracy*2	$0,05\% \pm (0,1\% * Vmax)V$	
CV Resolution	1/16000 of Rated Voltage	
CP Accuracy*2	$1,00\% \pm (P * 0.5\%)W$	
CP Resolution	1/16000 of Rated Power	
CC Accuracy*2	$0,05\% \pm (I*0,1\%)A$	
CC Resolution	1/16000 of Rated Current	
CR Resolution	1/16000 of Rated Resistance	
Physical		
Dimensions	48,26cm~(W)~X~65,35cm~(D)~X~34,62cm~(H)	
Weight	80kg	

Table A.2: Amrel PLA 10K-60-1500 - datasheet specifications

### A.3 Power analyzer Yokogawa WT1800

Range		
Basic power accuracy $(50/60Hz)$	0,1% of reading $+0,05%$ of range	
Power frequency range	DC, $0.1Hz - 1MHz$	
Input elements	6	
Sampling Frequency	2MS/s	
Voltage range	1,5/3/6/10/15/30/60/100/150/300/600/1000[V]	
Current range (direct input)	10m/20m/50m/100m/200m/500m/1/2/5[A] or, $1/2/5/10/20/50[A]$	
Current range (external sensor input)	50m/100m/250m/500/1/2.5/5/10[V]	
Guaranteed accuracy range		
for voltage and current	1% to 110%	
Data updating interval	50m/100m/250m/500m/1/2/5/10/20[s]	
N	leasurement Parameters	
Main measurements	Voltage, current, active power, reactive power, apparent power,	
	power factor, phase angle, peak voltage, peak current, crest factor	
Voltage RMS/MEAN measurement	YES	
Average active power	YES	
Active power integration (WP)	YES	
Apparent power integration (WS)	YES	
Reactive power integration (WQ)	YES	
Efficiency	YES	
User Defined Functions	20 functions	
Physical		
Dimensions	42,6cm (W) X $45,9cm$ (D) X $17,7cm$ (H)	
Weight	15kg	

Table A.3: Yokogawa WT1800 - datasheet specifications

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### A.4 Data Acquisition Switch Agilent 34970A

Power Requirements		
Nominal Voltage	100V/120V/220V/240V10%, $48/62Hz$	
General Informations		
Modules	$34901\mathrm{A},\ 34902\mathrm{A},\ 34908\mathrm{A},\ 34903\mathrm{A},\ 34904\mathrm{A},\ 34905\mathrm{A},\ 34906\mathrm{A},\ 34907\mathrm{A}$	
Measurements	DC Voltage, AC Voltage, Resistance (2-wire and 4-wire)	
	Frequency and Period, DC Current, AC Current, Temperature	
Operating environment Full accuracy	for 0 to $55^{\circ}C$	
Accuracy	for Temperature measurements	
Thermocouple		
Type-B	$1,2^{\circ}C$	
Type E	$1^{\circ}C$	
Type J	$1^{\circ}C$	
Туре К	$1^{\circ}C$	
Type N	$1^{\circ}C$	
Type R	$1,2^{\circ}C$	
Type S	$1,2^{\circ}C$	
Type T	1°C	
RTD		
$R_0$ from $49\Omega$ to $2.1k\Omega$	$0,06^{\circ}C$	
Thermistor		
$2.2k\Omega, 5k\Omega, 10k\Omega$	$0,08^\circ C$	
Operating Characteristics		
Thermocouple		
res.0, $1^{\circ}C$ (10plc)	6 (5)	
res.0, $1^{\circ}C$ $(1plc)$	52 (47)	
res. $(0, 02plc)$	280	
Physical		
Dimensions	25, 4cm (W) X 37, 4cm (D) X 10, 36cm (H)	
Weight	3,6kg	

Table A.4: Agilent 34970A - data sheet specifications

### A.5 NI CompactDAQ 9178 and acquisition module NI9233

#### A.5.1 NI CompactDAQ 9178

Power Requirements		
Input Voltage Range	9 to $30V$	
Maximum Required Input Power	15W	
Power consumption from USB	$500 \mu A$ max. at 4,10 to 5,25V	
	Bus Interface	
USB Specifications	USB 2.0 Hi-Speed	
High-performance data streams	7	
Data stream types available	Analog input, analog output, digital input, digital output, counter/timer input, counter/timer output, NI-XNET	
Analog Input		
Input FIFO Size	127S per slot	
Maximum sample rate	Determined by the C Series I/O modules	
Timing accuracy	50ppm of sample rate	
Timing resolution	12.5ns	
Number of channels supported	Determined by the C Series I/O modules	
Physical		
Dimensions	25, 4cm (W) X 8, 81cm (D) X 5, 89cm (H)	
Weight	878g	

Table A.5: NI CDAQ 9178 - datasheet specifications

#### A.5.2 Analog Input module NI9233

Input Characteristics		
Number of channels	4 analog input channels	
ADC resolution	24bits	
Type of ADC	Delta-Sigma (with analog prefiltering)	
Sampling mode	Simultaneous	
Internal master timebase $(f_M)$	$12,8MHz\pm100ppm$	
Data rate range $(f_s)$ internal master timebase	min: $2, 0kS/s$	
	max: $50, 0kS/s$	
Data rate range $(f_s)$ external master timebase	min: $2, 0kS/s$	
	max: $51, 3kS/s$	
Input range	$\pm 5V$	
Accuracy	Typical: $\pm 0, 1dB$	
	$\max:\pm 0, 6dB$	

Table A.6: Acquisition module NI9233 - datasheet specifications

#### A.6 Current transducer LEM CT 10-T

Electrical Data	
Primary nominal r.m.s. current	10A
Primary current, measuring range	$0 - \pm 15A$
Analog output voltage	5V
Conversion ratio	10A/5V
Supply voltage ( $\pm 5\%$ )	$\pm 15VDC$
Current consumption	$90 + V_{OUT}/R_L mA$
Accuracy - Dynamic performance data	
Overall accuracy	$\pm 0,1\%$
Offset voltage	max: $\pm 0, 6mV$
Physical	
Dimensions	13,2cm~(W)~X~6,1cm~(D)~X~6,65cm~(H)
Weight	670g

Table A.7: LEM CT 10-T - datasheet specifications

	General informations $400V + 100'$ (50 $U - (2 + V + T)$	
Supply voltage	$400V \pm 10\% / 30H z / 3ph + N + 1$	
Power	7.2kW (average: 4.3kW)	
Acoustic Noise	59 <i>dB</i>	
	renormances	
Temperature range	$-40^{\circ}C - +180^{\circ}C$	
Relative unidity range	between 10% and 98% in the temperature range: $+5^{\circ}C - +95^{\circ}C$	
Temperature accuracy	±0,3°C	
Relative Umidity accuracy	±3%	
Temperature variation rate		
from $-40^{\circ}C$ to $+180^{\circ}ircC$	5°C/min	
Temperature variation rate		
trom $180^{\circ}C$ to $-40^{\circ}ircC$	$-3,5^{\circ}C/min$	
Physical		
External Dimensions	91,9cm (W) X 155,5cm (D) X 163,8cm (H)	
Internal Dimensions	60, 1cm (W) X 54, 5cm (D) X 69, 2cm (H)	
Volume	2261	
Weight	680 kg	

### A.7 Climatic Chamber Angelantoni Discovery DY 250

Table A.8: Climatic Chamber Angelantoni Discovery DY 250

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