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Abstract

We are in a historical period for humanity in which the energy transition plays a fundamental role in future perspective. The aim is to decrease climate change and air pollution by reducing our dependence on fossil fuels. As well known, the main solution is the integration of renewable sources in the countries energy mix but is also known the weak point of RES that is the intermittence in energy supplying due to natural conditions. For these reasons, the storage of energy comes to help with playing a very big role in power systems. In order to integrate more RES in the countries' energy mix maintaining stability and reliability of energy supply, the EES (electrical energy storage) is crucial indeed.

Many kinds of storage technologies, going from mechanical to electrical, chemical, electrochemical and thermal are established but among these, lithium-ion batteries nowadays are the most promising in terms of high efficiency, power densities, and others favorable characteristics making them most useful for power system applications.

In particular, their present and future application regard grid distribution and above all the automotive field in which, coupled with electric or hybrid engines, play the important role for the propulsion of the vehicle. Being the engine technology very developed and advanced today, the improvement of lithium-ion batteries represents the key in the development of the vehicle itself, especially with price-performance ratio, safety and lifetime, the main cell characteristic which must be optimized and enhanced in order to reach a level able to satisfy the demand of power and energy.

This work forms the first task of FCA project in which Politecnico di Torino is involved: its first part focuses its attention on the development of a electrochemical-thermal model; this model accurately predicts the behavior of the battery for a wide range of current rates and therefore aims to project and build a battery pack voted to hybrid or full-electric drive.

The battery model is based on a pseudo-2D (P2D) physics of a nickel-manganese-cobalt (NMC-cathode) lithium-ion battery able to estimate discharging conditions for a wide range of current rates and so leading to predict electrochemical and not least thermal behavior. The latter in fact, affect lifetime and ageing characteristics of the battery, being one of the most important actors in the role of degradation; so

the work also looks into the heat generation of the cell to understand the reversible heat, highlighting also the important role of the graphite anode electrode.

The following tasks of the project (not covered by this work) are strictly dependent by the first; the ageing campaign: battery performances drop with time, so in order to investigate the cell lifetime, long-term accelerated tests are used to quantify it. From these comes out that the ageing behavior changes with referring to Calendar or Cycle ageing. In general in the first situation, low temperatures and low state of charge (SOC) lead to low degradation in the cell. With the Cycle ageing, low temperatures and high current rates operating conditions affect negatively the performance of batteries. Then the third task in which the model is used to evaluate the real possibility to substitute the graphite anode with metallic lithium and predict the aging effect on the cell. Finally last part is about Artificial Intelligence approaches: Different AI approaches will be tested to extract ageing information from experimental/detailed model data.

Given that, the purpose of the project is the integration in a hybrid/electric vehicle, but lithium-ion battery are also very flexible for a huge number of applications considering their cost depends on the local electric market condition.

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Chapter 1

Introduction

Nowadays, the automotive sector propulsion is dominated by the consumption of gasoline or diesel fuel internal combustion engines. A growing number of hybrid or full-electric vehicles are being introduced in the automotive market but they still represent the very smallest part of the total. Another important category is the plug-in electric vehicles, most of them represented by the sharing market of electric scooters or e-bike already been used; they get energy from the electric grid by means of connecting through an electric plug, usually charging during night. Obviously the automotive market includes this category in its products considering also the plug-in hybrid.

Hybrid vehicles combine the ICE (internal combustion engine) propulsion with electric engine, which can act also like a generator to recover energy during the braking phase; in this way, the amount of fuel used will be lower than traditional propulsion. Full-electric vehicles, as the name suggests, do not have ICE and are driven by one or more electric motor. Figure **??** clearly explains these differences.

1.1 Battery storage

The electric energy generated during driving or provided by the grid must be stored in order to cover discrete distances. There are several ways to store it but, in the automotive field, the most established is by means of electrochemical energy that is battery storage. Characteristics of it change with the category: e.g. hybrids have relatively small capacity because the amount of energy that needs is limited. Thus these batteries must operate at high rates. For this purpose

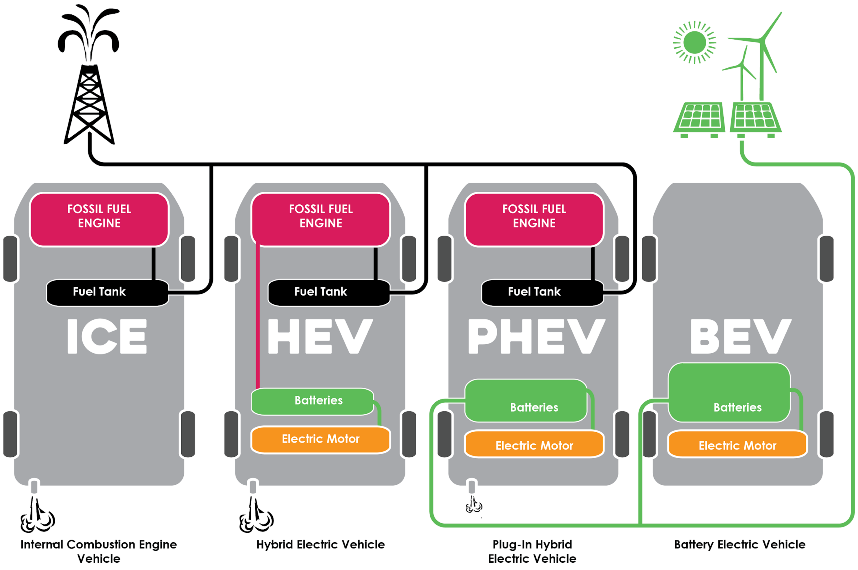

Figure 1.1: vehicle types

Metal hydrate/nickel batteries are now used, but the attention is moving toward lithium-ion battery because, with the same weight, are able to store more energy and operate at higher power.

The full-electric and hybrid plug-in vehicles are different in function of the utility range they must fulfill. They must store a very large amount of energy, meaning they require very heavy and large batteries. As consequence, in order to minimize these last parameters, batteries must be optimized in terms of energy stored or power provided to the vehicle.

Up to now the highest energy possible to storage for batteries is not adequate to satisfy the long-term moving needs of the society, but with the new taxation limiting emission by developed countries, the tendency to have EVs increases and leads to improve battery performance. In fact nowadays, a full-electric vehicle battery can reach energy going from 40-45 kWh (330 km WLTP autonomy) to 77 kWh (550 km WLTP autonomy)[1], depending on the manufacturer.

Essentially battery consists of the positive electrode, the negative electrode and the electrolyte. The energy can be stored if a difference of the electric potential between the electrodes exists and is maintained. Unlike some other storage technologies (CAES, PHES), they are modular and their position is independent with respect to the location of the plant, thus battery is a very flexible storage technology. Also, they are very fast in responding time and don't have mechanical parts moving. The cost of batteries is one of the most important factors obviously, especially for the growing lithium-ion battery market. In terms of market maturity, in fact, they receive much more attention than e.g. super-capacitors or SMES (superconducting magnetic energy storage), with a large amount of research and development interest at the present time.

1.2 Primary vs secondary batteries

Generally, the cathode and anode of a cell are composed of two metals or compounds with different chemical potentials and separated with a porous insulator. The electrolyte instead is constituted by conducting fluid such as salt and water and is used to transfer ions from one metal to the other during the reaction. The Anode is the compound which lose electrons and the Cathode is the compounds which accepts electrons; thus the flow of electrons from the anode to the cathode through the external connection is what we use to run our electronic devices. When the reactions producing this flow of electrons is not reversible, the battery is defined Primary; therefore the battery dies when one of the two reactant is consumed.

Examples of primary battery is zinc-carbon; e.g. it can be bought at the supermarket. This disposable model is inefficient and is not commercially viable, so the challenge was to find a way to reuse battery: rechargeable or secondary batteries came out.

The Lead-acid battery, the earliest type of rechargeable battery, was invented in 1859 [2] and is still used in most of vehicle as system to start-up the internal combustion engine. Nowadays batteries are produced with various size ranges, from large Megawatt able to store energy from solar or substations plant in order to guarantee a stable supply, down to tiny batteries like those used in electronic watches

Another example of rechargeable battery is the nickel-cadmium battery (NiCd) developed for the first time in 1899 and then in 1989 nickel-metal hydrogen batteries (NiMH) came out [2]. These batteries offer the possibility to be reused but they suffer the overcharging and overheating during charging phase, with the process typically needs all the night. Therefore larger applications with higher safety became a more significant need.

1.3 Lithium-ion batteries technology

An American physicist Professor, John Goodenough, invented in 1980 the lithium battery in which the lithium (Li) could migrate through the battery from one electrode to the other as a Li+ ion [2].The benefits of lithium were immediately evident: since is the lightest metal element in the periodic table and it has one of the largest electrochemical potentials, the use of lithium produces some of the highest possible voltages in the most compact and lightest volumes.

Nowadays, this technology is used in most of laptops, mobile phones indeed and in general used in portable electric tools, e-bikes, etc. Recent statistics have reported that the use of this kind of batteries in electric vehicles (EVs) will soon exceed the use for personal electronic devices[3].

The growing use and popularity of LIBs (lithium-ion batteries) is due to characteristics making them more suitable and at the same time versatility than lead-acid battery used up to now for vehicles. With respect to the second in fact, they have higher energy storable, efficiencies, and power densities. This last characteristic is much higher than flow batteries like e.g. Vanadium red-ox. The benefits include also its much more reduced space occupied and the easy-to-install way than other battery types.

LIBs recalls a series of subspecies of lithium-ion batteries differing each other in the cathode chemical composition: there are lithium nickel manganese cobalt (NMC), lithium iron phosphate (LFP), lithium manganese oxide (LMO), lithium nickel cobalt aluminum (NCA), etc.

	Voltages[V]	**Specific energy[Wh/kg]**	**Charge[C]**	**Discharge[C]**	**Cycle life**	**thermal runaway[°C]**	**cost[$/KWh]**
LCO	3.60 nom	150-200	0.7-1	1	500-1000	150	-
LMO	3.70 nom	100-150	0.7-1	1	300-700	250	-
NMC	3.60,3.70 nom	150-220	0.7-1	1;2 possible	1000-2000	210	420
LFP	3.20,3.30 nom	90-120	1	1;25 possible	2000 and higher	270	580
NCA	3.60 nom	200-260	0.7	1 typical	500	150	350
LTO	2.40 nom	50-80	1 typical	10 possible	3000-7000	-(one of the safest)	1005

Table 1.1: Different LIBs battery types

As it's possible to see in Table 1.1, different chemistries can have different performance and so different costs[4]. E.g. the LTO type reach the highest cycle life but its specific energy and its cost doesn't make it the best compromise. By comparison, in fact, NMC represents the best in terms of nominal voltage, has the second-highest specific energy density, a very good cycle life, not the best in terms of thermal characteristic but a good compromise in costs. Therefore, among these the subject of focus of this work are lithium-NMC batteries.

Nowadays people who are buying a car, make wrinkle their noses when they think about an electric or hybrid vehicle due to its cost; in an electric vehicle, the entire battery pack still constitute on an average 48% of the total cost(!), while operating and maintenance costs are low[3]. Therefore an ordinary customer is not encouraged to buy a new electric car due to initial capital and replacement costs. But the R&D and the works through the principle of the economic scale are in the direction of reducing costs of production and thanks to supply chain improvements and the large scale production, the lithium-ion prices are falling rapidly down. These improvements are also accompanied by the new discovery and development in the materials field which permits the use of more affordable cell components and chemistry. But there are other features relative to this battery type to improve; safety, as just mentioned, represents an important issue: the overheating causes the thermal runaways in the battery or worse fires and explosions; these kinds of batteries in fact make some goods such as laptops or pad dangerous on airplanes.

Then lithium-NMC Battery lifetime, despite nowadays lithium-ion technology as reached important values thanks mainly to materials research (reported in Table 1.1), are still not enough to cover long distances in the automotive field. Also, rapid loss in performance and unexpected failures must be reduced in order to communicate correctly with the grid.

1.4 Developing to Validation of the model path

The problems mentioned above can't be treated separately, this because enhancing only one of these three areas, for example Safety, by improving materials or cooling system, will lead to an increasing in battery life but also will raise the capital costs of the battery pack. So the understanding and prediction of the battery limits are needed.

1. The necessity of behavior prediction in different conditions of load is satisfied by the Modelling process; with the lifetime battery advancing, performances become worse and overheating is a consequence, therefore the understanding of the behavior over its lifetime is mandatory. The modelization of the battery is performed by using the Pseudo 2D model (P2D). After the implementation of the mathematical description regarding electrochemical and thermal coupled

behavior, the parametrization of the physics-based model for lithium-NMC battery follows;

2. To obtain this new generation of lithium-NMC, values and parameters from existing market and mature lithium-ion batteries must be extracted thanks to the experimental approach. It constitutes an important part of this work because the data achieved are needed for the modelization process.
3. Finally, the model and experiment's informations are summed up in order to validate the lithium-ion battery.

Chapter 2

Modeling

2.1 Overview

Lithium-ion batteries (LIBs) are becoming the most important storage devices in many sectors like communications, RES (renewable energy sources), and above all transportations. However, the highest energy storage possible for LIBs is insufficient for the vehicle autonomy needs. With the issue of carbon dioxide emissions, the popularity of EVs is increasing especially in developed countries. To satisfy this increasing energy demand, the refining of cycling stability, the enhancing of voltage window, the larger energy density cathode and higher capacity anode researching are mandatory. On the other hand, the advancement will led to more affordable battery types than today's, which is crucial in the developing market, taking to the diffusion of emissionless transportation. The attention toward Lithium became realty in the 70s when the first primary lithium cell was commercialized for example with lithium-sulphur dioxide (LI/SO_2). This interest is due to the lightest characteristics, the lowest reduction potential and the highest energy density with respect to other metals in electrochemical field.

A more intensive commercialization of lithium based battery were seen in the 80s with the discovery of the fast ion conduction of lithium in an electrochemically conducting lattice containing transition metal atoms. With this technology were firstly used rechargeable batteries like lithium-titanium sulphide (Li/TiS_2), and lithium-molybdenum sulphide (Li/MoS_2). Later, due to short circuits problems caused by tendency to form powder depositions in these kind of battery, the use of lithium as intercalation material to form the anode instead of metallic lithium was firstly adopted and than, in the 1981, was firstly used graphyte as intercalation material in an organic solvent. The possibility to use metal oxides like Ni, Mn, Co was discovered in the same period by Goodenough. As mentioned before, is considered the father of lithium-ion battery because was the first to patent $LiCoO_2$ as an intercalation cathode material.

As a result of this studies were discovered three classes of oxide cathodes:

1. Cathode class I - Layered Oxides;
2. Cathode class II - Spinel Oxides;
3. Cathode class III - Polyanion Oxides;

The classes varies from each others according to their chemical structure[5].

Thanks to Goodenough studies the first lithium-ion battery was launched in the market by Sony in 1991, based on graphite anode and a $LiCoO_2$ cathode.

2.2 How does lithium-ion battery works?

The lithium-ion cell of interest is composed, as shown in Figure 2.1, by negative electrode collector (Cu), negative electrode (Li_xC_6), separator, positive electrode (tipically Li_yCoO_4), and the positive electrode collector (Al). These two electrodes are insulated the porous separator, a polymer membrane (typically polyethylene), which permits only the migration of lithium ions but not of electrons and the electrolyte permeates the two electrodes. The electrons shuttle between the two collectors by a external conductive connection. The moving of ions and electrons depends on the charging or discharging state of the cell.

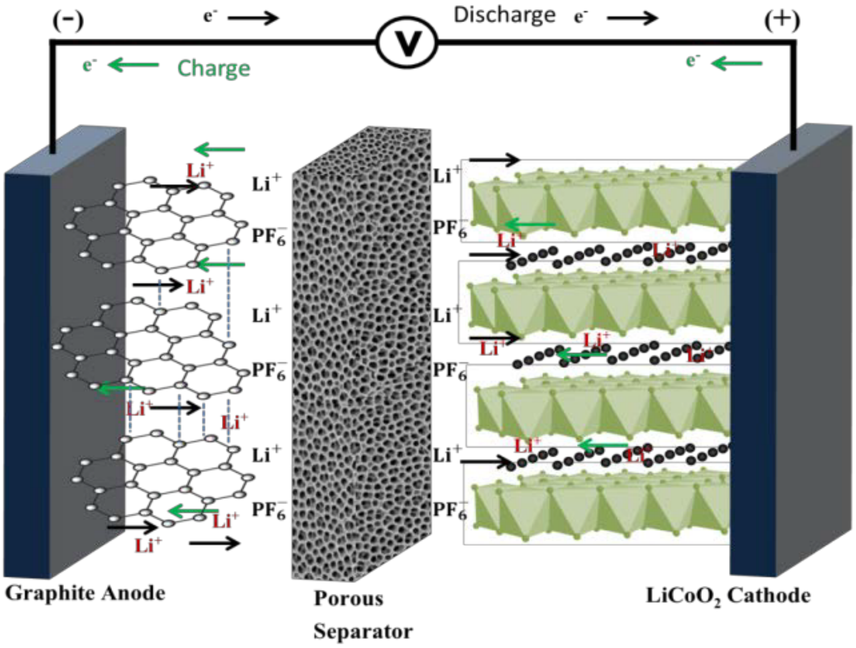

Figure 2.1: Schematic representation of a Li-ion cell: Li+ ions shuttle through the electrolyte and goes into the anode with electrons arriving at it through the external circuit.

Usually is called Anode where the oxidation occur, and cathode is the electrode where reduction take place during discharging, but during charging the names are switched. So for simplicity, Negative and Positive electrode terminology is used in this work.

When cell discharges, the lithium ions migrate from negative electrode toward positive electrode through the porous membrane. So lithium ions insert into solid particles of the positive electrode and de-insert from solid particles of the negative electrode. This enable the electrochemical reaction and so the electricity is produced by means of shuttling of the electrons generated by the reaction. Lithium ion diffusion in the solid phase and the electrolyte depletion in the positive electrode are two common limiting mechanisms of cell discharge. Also negative electrode is chosen in such a way that it permits the insertion at a higher voltage than the deposition of lithium, preventing the problem of deposition itself.

The reaction at the anode is:

$$\mathbf{Li_xC_6} \underset{charge}{\overset{discharge}{\rightleftharpoons}} \mathbf{Li_{x-y}C_6 + yLi^+ + ye^-}$$

The lithium ions that intercalate into positive electrode are the same amount of ions extracted from the graphite during discharging.

The reaction at the positive electrode is:

$$\mathbf{Li_{z-y}Mp + yLi^+ + ye^-} \underset{charge}{\overset{discharge}{\rightleftharpoons}} \mathbf{Li_zMp}$$

Where Mp is a generic material for the positive electrode.

The electrolyte, that allow the shuttling of the ions, can be alkyl carbonate such as ethylene carbonate (EC), dymethyl carbonate (DMC), etc. but the most used is the salt lithium hexafluorophosphate ($LiPF_6$) with also the presence of alkyl carbonate in a certain ratio.

2.3 NMC chemistry of elements

In LIBs many elements are used starting from lithium, graphite, aluminium, cobalt manganese, nickel, copper, carbon, titanium, silicon etc. These elements can be extracted from mines or from brine. The rapidly increasing of LIBs in automotive application, has been affect the production of raw materials like lithium, cobalt, manganese and nickel. Up to now lithium was used most for industrial purposes instead of batteries, but with the technology progress done during these last years, batteries became the major application for this element, accounting in the 39% of global Li market [6]. Cobalt is a more problematic element than lithium. Despite it permits increased energy density and structural stability, it also has some negative aspects like toxicity, high price and limited production. In fact more than 50% of cobalt mineral reserves are concentrated in Congo and Zambia, and for geo-political reason its supply is not so easy.

As explained in the previous chapter, the LIBs include a series of battery chemistries with different assemblages of anode and cathode materials. To each combinations corresponds positive and negative aspects of performance, safety, cost etc. Nowadays the most LIB kind used for consumer electronics is the lithium cobalt oxide (LCO). Its chemistry conformation is not so much suitable for vehicles application because of its safety risks, given by structural instability, and the high cost of cobalt and its availability difficulties. For these reasons spinel LMO, NCA, NMC and LFP importance is rising in this field because of their more stable crystal structure[6], but also they are composed by more cheaper elements. This family of LIBs can be compared on a technical way considering the following five aspects:

1. Energy density;
2. Power density;
3. Safety;
4. Cost;
5. Lifetime;

Up to now many car makers such as Tesla, BMW, VolksWagen, Chevrolet, Nissan and others have adopted these different kinds of LIBs, as consequence of laws imposed in order to mitigating oil consumption and reducing GHG emissions.

Among these LIBs types, the work focuses its attention on layered lithium nickel manganese cobalt oxide (NMC, precisely LiNixMnyCozO2). It is one of the most promising classes of positive electrode materials, in facts $\mathrm{LiNi_{1/3}MN_{1/3}Co_{1/3}O_2}$ (in other words NMC111) is already used for automotive applications. As reported in bibliography[7], in order to reach a driving range of 300 miles, which is a fairly satisfying distance, the nowadays LIBs needs a specific energy at least equal to 750 Wh/kg on a cathode active material level. Therefore arise the necessity to improve the positive electrode materials.

Ni-rich NMCs, meaning there is much more content of Ni than Mn and Co content, have significantly higher specific capacities. Studies on NMC811($\mathrm{LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2}$)and NMC622($\mathrm{LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2}$)[7][11] reports a reversible capacities of 175-190 mAh/g_{nmc}, much better if compared with 160

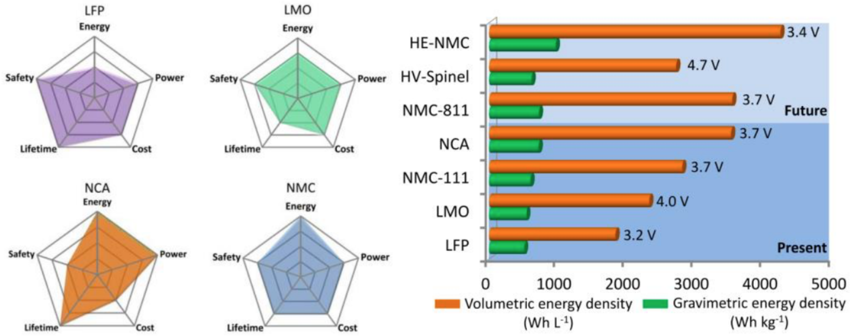

Figure 2.2: left: performance characteristics of four current battery chemistries for Evs. right: Volumetric energy densities and gravimetric energy densities of various electrode materials; possible to see the high advantages of Ni-rich cathode (NMC-811 as example).

mAh/g$_{nmc}$ of NMC111,and permits to get close to the 750 Wh/kg specific energy needs. But if on one hand there is a significant increase of specific energy, on the other hand the higher surface reactivity of Ni-rich positive electrode determine the formation of impurities due to reactions with carbon dioxide and water. The use of Ni-rich NMC cathode is also justified by the lower cobalt content with respect to NMC111. Co is still utilized in LIBs because replace adequately pure $LiNiO_2$ behavior with good electrochemical performances guaranteeing the overcoming of $LiNiO_2$ shortcomings like cycling and thermal stability. Ni-rich cathode still represent the best options for near-term advancements, with Co playing a necessary role in practical application.

2.3.1 Geometry and Format

Electrochemical cell is the smallest base element composing a battery; In facts, batteries can be adaptable to different devices by varying the cell number and the geometry.

The geometry of a battery is defined by dimensions: length, width and thickness of different layers. The packaging instead, refers to the total packaging of differents cells; it can be cylindrical, button, pouch and prismatic.

The battery geometry and packaging is designed with respect to a compromise of performance and space available. These two characteristics affect current, potentials and thermal distributions inside the cell indeed and so their performance, safety and lifetime. For example using the same materials but varying the length or thickness of the battery can led to higher capacity or higher power. Therefore they also dictate the overall pack energy density, power density and cost. The choice, sizing and economics is also determinant for the implementation of cooling system for battery packs.

Figure 2.3.3: different cell format type

2.4 Modeling

The aim of modellize a lithium-ion battery is to understand and forecast its behavior, therefore it permits a good design anable a scale up all parameters concerned the battery.

In model development is usually to start with simple model and gradually add more details until the results are sufficiently accurate for the model purpose itself. In the literature various type of models for this kind of batteries exists:

1. Empirical: this kind of model is the most simple and presents a very modest accuracy, therefore it has low computational costs. They can be linear, exponential or other functions commonly implemented, and their combinations are used to compare experimental data directly to get parameters. Usually empirical model is used to perform battery management systems due to its simplicity that permits fast computations. For example in [8] the lifetime of cell is obtained by splitting the analysis in calendar and cycle aging. More than 60 cells are tested at different conditions. Then test curve (e.g. capacity measured data curve) is fitted with different exponential functions and the one with the best similar shape to test curve is finally chosen. Is possible to realize that their prediction capability, especially when extrapolating from the usual operating conditions, is poor.

2. SPM: the Single Particle Model include kinetics and diffusion phenomena in the electrode and in the electrolyte; these are implemented thanks to partial differential equations (PDE). As the name suggests, each electrode can be seen as a single particle with a surface equal to the electrode area. Finite Element Analysis (FEA) is performed. This model is able to simulate thin electrode and low current conditions, but has shortcomings at high current conditions.

3. P2D: this model is more accurate than the previous with the higher computational costs compromise. Also pseudo two dimensional model include diffusion in electrolyte and in the solid electrode but the insertion/extraction kinetics is described by using Butler-Volmer equations which led to higher accurate results.

4. MD/KMC: Kinetic Monte Carlo is the most accurate method. Is based on physics prediction such as mobility of lithium ions, thermodynamic properties

of material etc. but this model can be used to predict only a particular aspect of the process taking place in a very small fraction of time.

In this work a P2D modeling is implemented. This physics based approach is employed using the first principles-based lithium-ion battery model developed by Newman, Doyle and Fuller [9] and implemented in COMSOL Multiphysics®. This model consists in a series of a set of a partial differential equations (PDEs) solved with the finite element method or the finite volume method. It has been chosen this model type due to its good compromise between accuracy and computational effort cost with the advantage of flexibility of the model because stress-strain and thermal behavior can be coupled with it.

The P2D model is constituted by two dimensions: the 1D along the cell thickness model, to which is added the other 1D that modelize the particles of the active materials. In particular, the first modellize charge and mass transport in porous electrodes and in the electrolyte at the interface where there are electrochemical reactions. The second models the one-dimensional diffusion transport in the particle. Finally thanks to the conservation law of species these two dimensions are coupled. Schematic representation is reported in Figure 2.4.1.

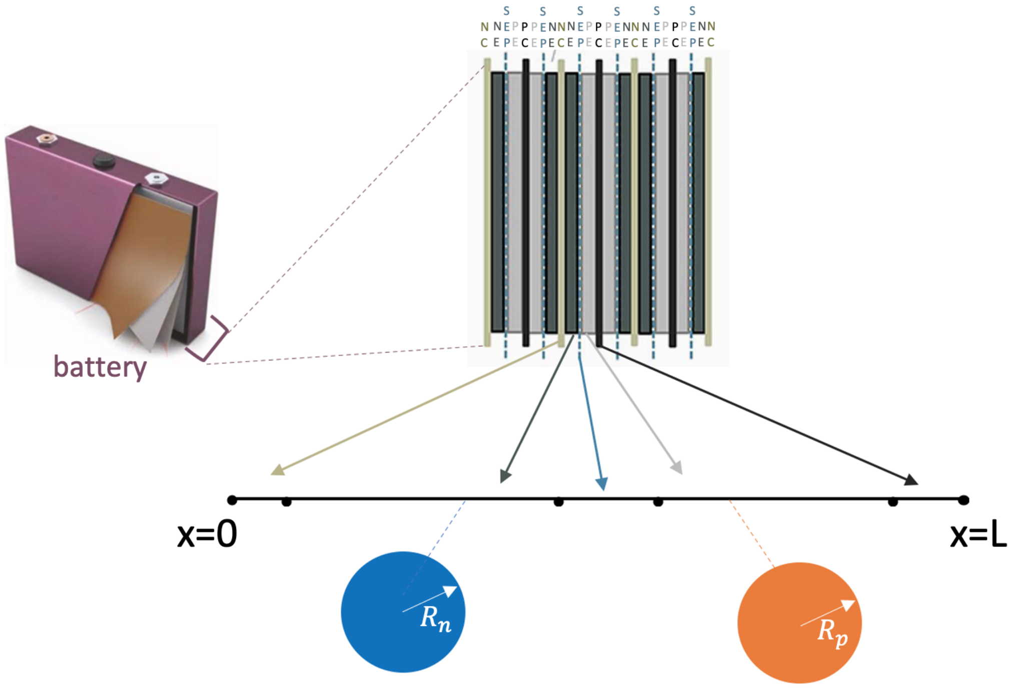

Figure 2.4.1: P2D model schematic

2.5 Equations

The P2D modelling equations for lithium-ion cell are based on Law of conservation of mass and charge and Ohm's law combined with theory of kinetics and diffusion[2].

As said the electrode used in lithium-ion cell are porous and consists in two phases: solid phase, that is the electrode actually, and the solution phase, the electrolyte. Electrochemical reactions occur at the interface of these phases and so two Butler-Volmer kinetics equations describing the rate of these reactions are needed:

One for electrode phase,

$$\nabla i_s = -a_v \cdot i_0 \cdot \left[exp\left(\frac{\alpha_a \cdot F \cdot \eta}{R \cdot T}\right)\right] - \left[exp\left(\frac{-\alpha_c \cdot F \cdot \eta}{R \cdot T}\right)\right] \tag{2.1}$$

and another for electrolyte phase,

$$\nabla i_l = a_v \cdot i_0 \cdot \left[exp\left(\frac{\alpha_a \cdot F \cdot \eta}{R \cdot T}\right)\right] - \left[exp\left(\frac{-\alpha_c \cdot F \cdot \eta}{R \cdot T}\right)\right] \tag{2.2}$$

with

- i_s is the current density in the solid $(A \cdot m^{-2})$
- i_l is the current density in the liquid $(A \cdot m^{-2})$
- T is the temperature (K)
- α is the dimensionless charge transfer coefficient
- η is the surface over-potential (V)
- R is the gas constant equal to 8.314 $(J \cdot K^{-1} \cdot mol^{-1})$
- F is the Faraday constant approximately equal to 96 485 $(C \cdot mol^{-1})$

where the exchange current density is:

$$i_0 = F \cdot k_c^{\alpha_a} \cdot k_a^{\alpha_c} \cdot (c_{s,max} - c_s)^{\alpha_a} \cdot c_s^{\alpha_c} \cdot \left(\frac{c_l}{c_{l,ref}}\right)^{\alpha_a} \tag{2.3}$$

with:

- k is the rate constant of electrochemical reaction ($m \cdot s^{-1}$)
- $c_{s,max}$ is the maximum concentration of lithium in the solid particle ($mol \cdot m^{-3}$)
- c_s is the lithium instantaneous concentration in the solid particle ($mol \cdot m^{-3}$)
- c_l is the lithium instantaneous concentration in the solid particle ($mol \cdot m^{-3}$)
- $c_{l,ref}$ is the reference concentration of lithium in the solution ($mol \cdot m^{-3}$)
- ($c_{s,max} - c_s$) is the concentration of unoccupied sites in the inserctions of electrode porous material

If c_s is 0 or equal to $c_{s,max}$, the exchange current density becomes 0. The cathodic and anodic transfer coefficients (α_c and α_a respectively) decide the preference of the applied potential at the cathodic and anodic directions of the overall reaction.

a_v is the specific inter-facial area of each electrode:

$$a_v = \frac{(3 \cdot \epsilon_s)}{r_p} \tag{2.4}$$

with

- ϵ_s volume fraction of the solid active material
- r_p is the particle radius (m)

Another important equation takes into account of the deviation of the actual potential difference between the solid solution from the equilibrium potential of the solid with respect to reference lithium electrode

$$\eta = \phi_s - \phi_l - E_{eq} \tag{2.5}$$

and it has been defined as surface overpotential, with:

- ϕ_s solid surface potential (V)
- ϕ_l solution potential (V)
- E_{eq} equilibrium potential of the electrode material (V)

The reaction at interface is driven by a flux of electrons and ions in the site where reaction take place; therefore Ohm's law is able to describe the conduction of electrons in the solid phase:

$$i_s = -\sigma_s \cdot \nabla \phi_s \tag{2.6}$$

with σ_s that is the solid phase conductivity $(S \cdot m^{-1})$.

Concerning processes in the electrolyte phase the theory of concentrated solution use the following expression in which the current density can be calculated as:

$$i_l = -\sigma_l \cdot \nabla \phi_l + \frac{2 \cdot \sigma_l \cdot R \cdot T}{F} \cdot \left(1 + \frac{\partial ln\, f_\pm}{\partial ln\, c_l}\right) \cdot (1 - t_+) \cdot \nabla ln\, c_l \tag{2.7}$$

with:

- δ_l conductivity of the solution $(S \cdot m^{-1})$
- $f_\pm$ coefficient of mean molar activity
- t_+ Ion transport number also called Transfered number (total electrical current carried in an electrolyte by a given ionic species)

As it's possible to see, the equation just mentioned is similar to the Ohm's law corrected with an additional term on the right that takes into account of the concentration differences in the solution phase. In facts,there are additionally the coefficient of mean molar activity and the ion transport number. These two parameters are important because the first provides the voltage polarization resulting from the concentration gradient and the second takes into account of concentration gradients that form under load conditions.

Knowing i_l is possible to perform a mass balance in the electrolyte phase:

$$(2.8)\epsilon_l \cdot \frac{\partial c_l}{\partial t} = \nabla(D_l \cdot \nabla c_l) - \nabla \left(\frac{i_l \cdot t_+}{F}\right) + \frac{\nabla i_l}{F} \tag{2.8}$$

with:

- ϵ_l volume fraction of solution phase
- D_l diffusivity in the electrolyte $(m^2 \cdot s^{-1})$

The first therm on the right takes into account the contribution of diffusion, the others terms consider the contribution of the migration. The contribution of convection instead can be assumed equal to zero in the battery because the velocity of solvent is not significant. These terms determine a change of concentration of lithium in the electrolyte.

The effects of tortuosity affects the diffusivity and conductivity with Brugmann coefficient. Also the film resistance R_{film} must be taken into account thanks to the equations becoming:

$$\eta = \phi_s - \phi_l - E_{eq} - R_{film} \cdot i \tag{2.9}$$

R_{film} led to the formation of SEI (solid electrolyte interphase) and this layer as a very important influence, both in negative and in positive way, for the performance and also for safety and lifetime of the battery itself .

Lithium transportation through the active material particle (which constitute the material of the electrode) occurs thanks to the diffusion mechanism; this is described by the Fick's second law:

$$\frac{\partial c_s}{\partial t} = \nabla(-D_s \cdot \nabla c_s) \tag{2.10}$$

In which:

- D_s diffusion coefficient in the solid particle $(m^2 \cdot s^{-1})$

Finally boundary conditions must defined in the solid particle:

$$\frac{\partial c_s}{\partial r} = 0|_{r=0} \tag{2.11}$$

$$-D_s \cdot \left.\frac{\partial c_s}{\partial r}\right|_{r=r_p} = -\frac{\nabla i_s}{F \cdot a_v} \tag{2.12}$$

Boundary conditions are important because guarantee that mass balance calculations are coupled to reaction rate connecting the two 1D ensembles of the P2D model. No interaction between particles has been assumed which is justified by much larger space between particles compared to the length scale inside of it.

2.6 Including thermal equations

The heat generated during insertion, extraction and transport of lithium during charge/discharge phases inevitably led to irreversible degradation processes inside the cells. It's possible to distinguish two kind of heat[10]:

1. Irreversible heat: caused by limitations in physical processes like ohmic heat generation, polarized heat generation and side reactions phenomena leading to loss of performance and battery life not recoverable.
2. Reversible heat: due to changes in the crystal order following the electro-chemical reactions.

It is possible to compute the total heat generated as sum of Irreversible and Reversible heat:

$$Q = Q_{irr} + Q_{rev} \tag{2.13}$$

where the irreversible heat is:

$$Q_{irr} = i_l \cdot \nabla\phi_l + i_s \cdot \nabla\phi_s + (\nabla i_l) \cdot \eta \tag{2.14}$$

in which the first two terms represent ohmic losses in the solid and electrolyte phases, intead the last represent the polarization heat.

Reversible heat is:

$$Q_{rev} = (\nabla i_l) \cdot T \cdot \frac{dE_{eq}}{dT} \tag{2.15}$$

From a thermal point of view in a cell is possible to distinguish an active region where the heat is generated, composed by electrodes and electrolyte, and a inactive region in which heat can be conducted, including the separator, the case material and the rests of components. Also cell performance is strongly influenced by environment following unconstant behavior. Studies [10] shows that performances are more sensitive to change of temperature when cell exchange heat, by means of conduction, convention and radiation, at low environment temperatures and also the self-heating of NCM lithium-ion battery can decrease the polarization and increase discharge capacity.

Therefore there is an expression that sums up all these phenomena considering also environment:

$$\rho \cdot C_p \cdot \frac{\partial T}{\partial t} = Q + \nabla(k_T \cdot \nabla T) - \nabla(h \cdot (T - T_a)) - \nabla(\sigma_T \cdot \epsilon_T \cdot (T^4 - T_a^4)) \qquad (2.16)$$

with:

- ρ density $(kg \cdot m^{-3})$
- C_p specific heat capacity $(J \cdot kg^{-1} \cdot K^{-1})$
- K_T thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$
- h heat transfer coefficient $(W \cdot m^{-2} \cdot K^{-1})$
- σ_T Stefan Boltzmann constant equal to $5.67x10^{-8}(W \cdot m^{-2} \cdot K^{-4})$
- ϵ_T is the emissivity
- T_a is the ambient Temperature (K)

The thermal model must be developed because heat generation represent a crucial aspect for two reasons:

1. From battery safety point of view, the implementation of a model to take into account thermal behaviour is necessary to permits the cell operating in a optimum temperature operating range.
2. There is a strong dependence of some physical and chemical parameters on temperatures such as thermodynamic factor, ionic conductivity of electrolyte, diffusivity of the electrodes and the electrolyte and the reaction rate constants.

Chapter 3

From experimental to parameters

3.1 Overview

In this work are reported several techniques for parameterization of a commercial cell P2D model. Various experimental methods are employed to determine information on the geometry, chemistry and electrode microstructure. In particular the focus is on determine electrode and cell thermodynamic, kinetic and transport properties. The accuracy of the experimental parameters is investigated by comparing simulations performed thanks to the elaboration of the P2D electrochemical coupled with 3D thermal model, developed using COMSOL Multiphysics® battery patch modelling software. As just said, P2D electrochemical modeling approach is used due its flexibility, reliability and accuracy of prediction applicable in many operating conditions instead it is more complicated physical laws based and intensive computational costs. The commercial materials under examination are provided by CRF (centro ricerche Fiat) and analysed through experimental testing in order to acquire the parameters needed for the modelisation. Geometrical properties of the electrodes which compose the cell are obtained from direct measurement, instead physical and electrochemical properties needs a process of teardown and rebuilding of full coin cell or half cell (with metallic lithium as reference); half cells are important for the evaluation of separate electrode material properties.

3.2 Geometrical Parameters

To build the cell in Comsol geometrical parameters are needed. As previously reported, the model is characterized by two different geometries:

1. 1D geometry: needed for the evaluation of the electrochemical characteristics of lithium-ion cell (P2D model).

Parameter	Value	Unit
Negative current collector thickness	0.0143	mm
Negative electrode thickness	0.0691	mm
Separator thickness	0.0250	mm
Positive electrode thickness	0.0600	mm
Positive current collector thickness	0.0180	mm

Table 3.2.1: values useful for the P2D model in Comsol®

2. 3D geometry: needed for the study of the thermal properties and the heat transfer inside the cell itself. The geometry required is a coin cell geometry.

Parameter	Value	Unit
Negative current collector diameter	18	mm
Negative electrode diameter	18	mm
Separator diameter	20	mm
Positive electrode diameter	15	mm
Positive current collector diameter	15	mm

Table 3.2.2: values useful for the 3D themral model in Comsol®

This thickness measurements are obtained by the stacks of cathode and anode materials provided by FCA. One stack is composed by multiple layers of electrode/collector in this way: the two faces of a collector foil are covered by electrode material(graphite or NMC 622). The procedure starts with measuring the thickness of these material as supplied; then, as it shown in Figure 3.2.1, one of the two faces covered by electrode(graphite in this picture) is scratched out to get the only one layer of electrode(graphite) and only one layer of collector(copper); therefore their thickness is measured. Finally thickness of the only electrode layer is obtained by average differences. Measurements are reported in Table 3.2.1.

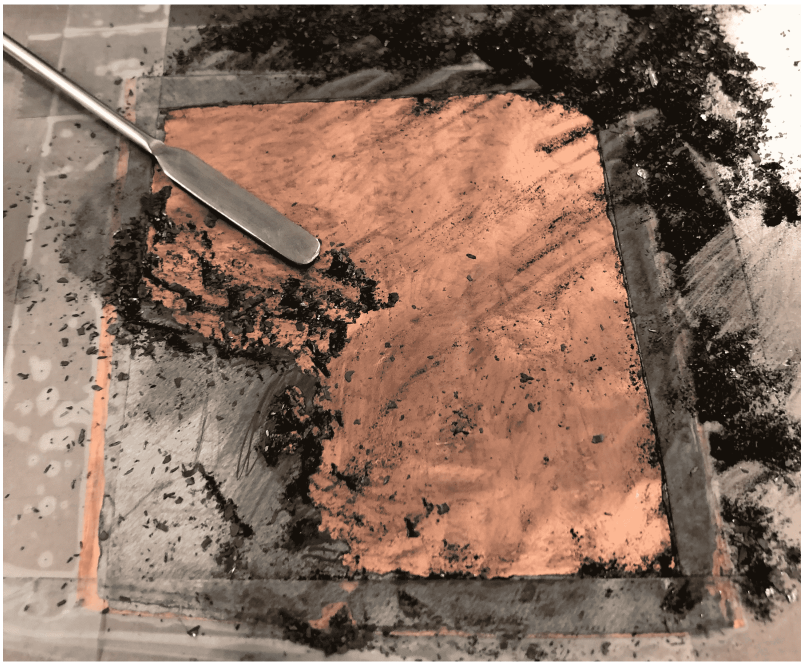

Figure 3.2.1: In picture the scratch out procedure to obtain layer of copper and graphite as anode.

3.3 NMC 622 Electrode Properties

For the building of the model, the electrode parameters represent the key data. As anticipated the electrode materials involved in the cell structure is NMC 622 for cathode.

Electrode properties can be divided in two categories consistent with the two kind of models: electrochemical ones and thermal ones.

3.4 Electrochemical

Particle radius: It's the average distance between particle center and particle surface, and it is an important parameter for Fick's equation application. The

NMC 622 material has been analyzed thanks to FESEM technique. It is an electric microscopic method which allows the topographical characterization of flat surfaces. In this way it has been obtained the particle radius of the NMC 622 with a value of $6.9 \cdot 10^{-6} m$.

Volumetric fraction: The electrode in the model is composed by solid phase and liquid phase(electrolyte). To determine this parameter a coin cell composed by graphite as anode, NMC622 as cathode and LiPF6 EC:DEC 1M 1:1 with celgard separator(Figure 3.4.1) is cycled in the Arbin (Arbin Instruments®) cycler; 5 cycles with C-rate at C/10 are performed up to cut-off voltage of 2.5 V. It as been assumed that, at the end of discharge, lithium concentration is maximum ($x = 1$). Therefore test data obtained are input in the following equation:

$$c_{s,max} \cdot \epsilon_s \cdot d \cdot \Delta x \cdot F = i \cdot t \tag{3.1}$$

- $c_{s,max}$ maximum permissible concentration of lithium in the electrode.
- ϵ_s volume fraction of the solid phase.
- d electrode thickness.
- F Faraday constant.
- i current density.
- t time duration of charge/discharge.

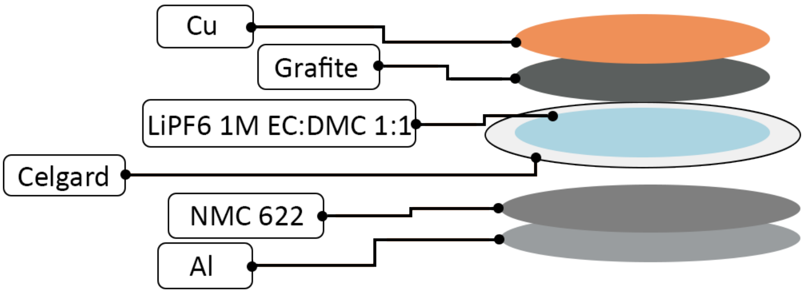

Figure 3.4.1: The structure of a tested coin cell.

A value of 0.445 it has been found.

Diffusion coefficient in electrode:In order to obtain it, a GITT (Galvanostatic intermittent titration technique) test must be performed using the Arbin cycler; this procedure consists of a sequence of discharge pulse followed by a relaxation time repeated until the battery is fully discharged. First of all a coin cell composed with cathode in NMC622 and metallic lithium as anode has been cycled with charge/discharge procedure 3-times at C/10 current rate (3 "formation cycles"). Than charged again at C/10 and so GITT is started: the coin cell is repeatedly discharged with current pulse of C/20 current rates for 15 min followed each time by a period of relaxation 45 min long. During this discharging pulse phase, the potential quickly decrease proportionally to IR where R is the sum of the uncompensated resistance and the charge transfer resistance. Then the potential starts decreasing slowly, due to the galvanostatic discharge pulse, instead during the following relaxation time the potential suddenly increases proportionally to IR; Therefore the potential keeps to slowly increase again up to equilibrium ($\frac{dE}{dt} = 0$) at the OCV [12].Assuming that the diffusion in each NMC particle is a 1D diffusion process, and neglecting the double-layer charging process, the charge-transfer process, and the phase transformation[13], the D_s can be calculated by Fick's law through the following equation

5cm file=arbin.png,width=4cm

$$D_s = \frac{4}{\pi}\left(\frac{IV_m}{z_A FS}\right)^2 \left[\frac{\left(\frac{dE}{d\phi}\right)}{\left(\frac{dE}{d\sqrt{t}}\right)}\right]^2 \tag{3.2}$$

Where:

- I=current applied [A].
- V_m=molar volume of electrode [$\frac{cm^3}{mol}$].
- Z_A=charge number.
- F=Faraday constant [96485 $\frac{C}{mol}$].
- S=electrode/electrolyte contact area [cm^3].
- $\frac{dE}{d\sigma}$=slope of tritation curve at each titration step.
- $\frac{dE}{dt}$=potential variation over time pulse.

It is possible to simplify the expression because sufficient small currents are applied; by doing so $\frac{dE}{dt}$ can be considered linear and therefore also the tritation curve can be also considered linear over the composition range; the expression becomes:

$$D_s = \frac{4}{\pi\tau}\left(\frac{n_m V_m}{S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \tag{3.3}$$

Where:

- τ=duration of current pulse [s].
- ΔE_s= steady-state voltage difference between previous step and the current one measured both at equilibrium $\left(\frac{dE}{dt} = 0\right)$.
- ΔE_t= potential drop due to galvanostatic discharge pulse(not considering IR drop).

The voltage difference and the potential drop are well explained in figure 3.4.2. Considering also the equivalent particle radius R_s which compensate the variance of particle radius due to the Gaussian distribution, the expression becomes the following:

$$D_s = \frac{4}{\pi\tau}\left(\frac{R_s}{3}\right)^2 \left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \tag{3.4}$$

in which:

$$R_s = \frac{3\bar{V}}{\bar{S}} \tag{3.5}$$

It has been found that GITT can be accurate only for $0.2 < \sigma < 0.5$; in this interval the value of the activation energy useful to obtain the D_0 is equal to 457 meV. Therefore it is possible to obtain it, considering that is temperature dependent following an Arrhenius expression:

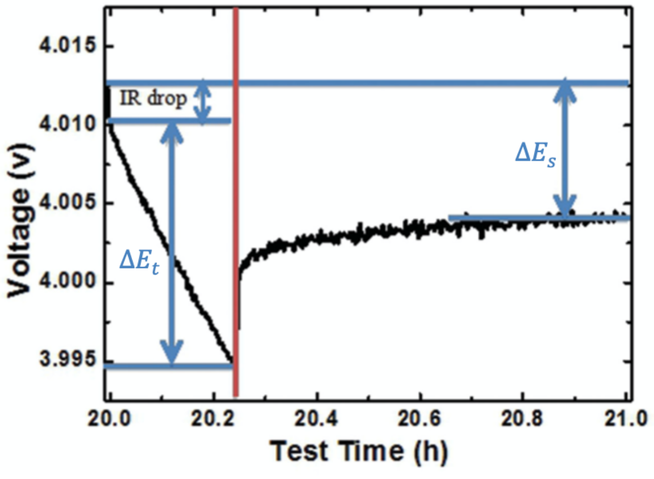

Figure 3.4.2: Voltage response of a discharge pulse in the GITT experiment. The red line divides the figure into two parts. The left part stands for the discharge pulse, while the right part stands for the rest step [13].

$$D_s = D_0 \cdot e^{-\frac{Ea}{kT_{ref}}} \tag{3.6}$$

Where T_{ref} is the temperature at which GITT test has been performed and k is the Boltzmann constant ($8.617 \cdot 10^{-5}[\frac{eV}{K}]$). Finally knowing D_0 and using the following expression it has been obtained the Diffusion coefficient curve dependent from temperature reported in figure 3.4.3:

$$D_s = D_0 \cdot e^{\frac{Ean}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)} \tag{3.7}$$

Maximum concentration of solid phase in the electrode:This value is useful in order to calculate the reaction rate constant. From [14] it has been found a value of 0.059493 $[mol/cm^3]$ for positive electrode.

Activation energy of the reaction: This parameter is present in the expression of the reaction rate. It has been found in literature [15] a value of 58 [kJ/mol].

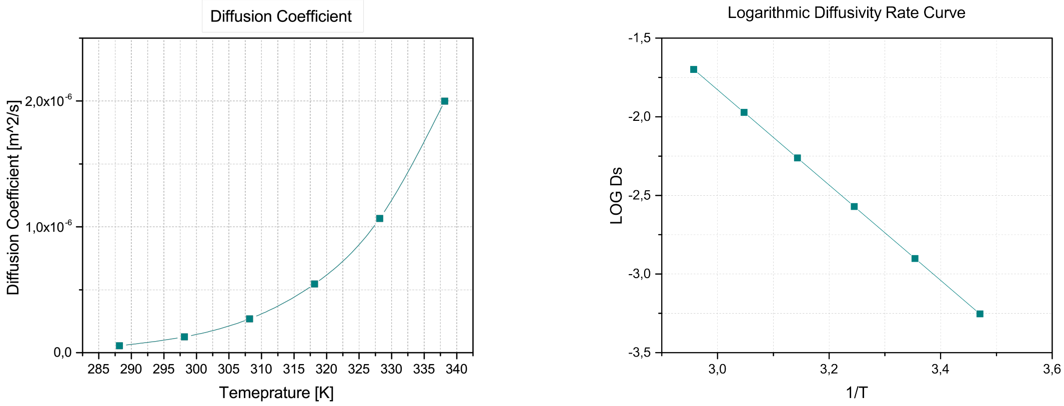

Figure 3.4.3: Diffusion curve with respect to temperature

Initial concentration: through discharge/charge tests with low C-rate and following CC-CV procedure is possible to obtain this parameter. The initial concentration can be obtained by fitting with the experimental curve basing on two assumption:

- it can be assumed that at the end of the charging procedure the concentration of lithium in the positive electrode is x=0. So, since the positive electrode doesn't vary its potential for a wide range of x while the negative shows the characteristic curve of graphite,at very low C rate the effect of polarization and ohmic resistance are low.
- Another assumption is that with this C-rate level the voltage curve is approximately equal to the difference between the positive electrode equilibrium potential curve and the negative electrode equilibrium potential curve.

with these assumptions the initial x can be determined comparing graphically the equilibrium electrode potential curves with the discharge curve.

Reaction rate constant: This value represent an important parameter for the function of the reaction rate constant with Temperature dependence. The temperature dependence is taking into account using the Arrhenius equation:

$$k_n = k_{p,0} \cdot exp\left[\frac{Ea_p}{R} \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \tag{3.8}$$

Where Ea_n is the Activation Energy.

k_0 strictly depends by the exchange current density at room temperature value as reported in the following equation:

$$k_0 = \frac{2j_0}{{c_s}^{max} \cdot \sqrt{c_e}} \tag{3.9}$$

In which:

- j_0=exchange current density A/m^2
- ${c_s}^{max}$=maximum electrode concentration mol/m^3
- c_e=electrolyte concentration mol/m^3

Since in Comsol is possible to directly enter current density, the aim of experimental procedure is to find it. The exchange current density define the rates of electron transfer as the ion migration from electrode and electrolyte and vice versa. It is the current measured at zero overpotential and with the absence of any net charge transfer. This value is obtained by charge transfer resistance (R_{ct}) measurement with EIS (Electrochemical Impedance Spectroscopy)[16].

This measurement must be referred to NMC and graphite separately; therefore half-cells (coin cell geometry) have been built (fig.[3.4.4]).

NMC half-cell:

- Anode: Lithium.
- Separator: Celgard 2500 porous material with electrolyzer LiPF6 1M EC:DEC 1:1 filled.
- Cathode: NMC 622 electrode with aluminum collector.

Graphite half-cell:

- Anode: Lithium.
- Separator: Celgard 2325 porous material with electrolyzer LiPF6 1M EC:DEC 1:1 filled.
- Cathode: graphite electrode with copper collector.

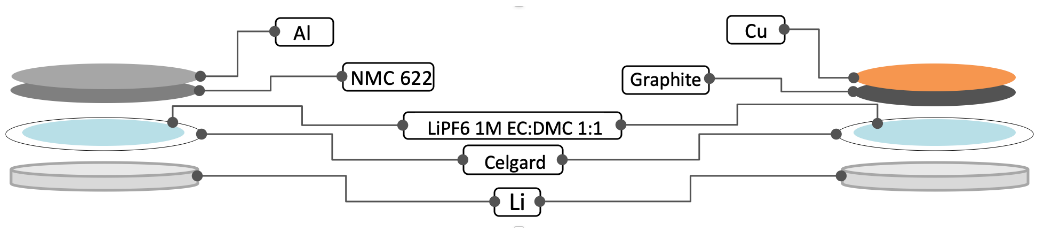

Figure 3.4.4: The structure of lithium and graphite half-cells.

Before EIS, a lithiation and delithiation of the two cathode in the half-cells is needed by means of formation cycles in the Arbin cycler. Therefore EIS measurement is performed in potentiostatic mode with a voltage amplitude of 10 mV, in the frequency range of 10 mHz to 500 kHZ. The electrode condition must be 50% SOC. After that, the exchange current density can be determined by:

$$R_{ct} = \frac{RT}{j_0 SF} \tag{3.10}$$

Where S is the electrode/electrolyte surface area.
By doing so the exchange current density is finally obtained.

Equilibrium electrode potential: The electrode potential at the equilibrium varies with respect to the particular material in exam. Particles would have identical Li-content if they would have the same equilibrium potential indeed, but electrode materials have different chemistries, so they are lithiated and delithiated in different way depending on that equilibrium potential curves which characterize them. This value can be measured as the potential at low current rate but it could not be a final parameter since can differ basing on this low current value or if the measurement is done in charge or discharge condition. For these reasons to find graphite equilibrium electrode potential the equation form [3] is used.

$$\begin{aligned}\mathrm{E}_{eq} &= 0.2033 + 0.6613 \cdot exp(-68.63 \cdot x) + 0.02674 \cdot \tanh\left(-\tfrac{x-0.1814}{0.03031}\right) \\ &- 0.006943 \cdot \tanh\left(-\tfrac{x-0.4895}{0.0854}\right) - 0.00925 \cdot \tanh\left(-\tfrac{x-0.0317}{0.053}\right) \\ &- 0.075\tanh\left(-\tfrac{x-0.5692}{0.875}\right) \end{aligned} \tag{3.11}$$

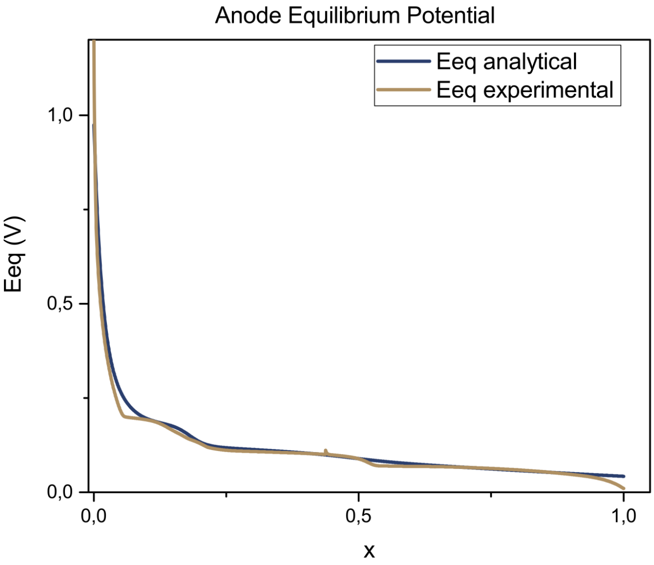

Figure 3.4.5: Equilibrium potential of the Anode: analytical and experimental curve compare.

Where x is the ratio between Discharge capacity (mAh/g) and maximum lithium concentration in the electrode(mAh/g). Simulations results are strictly affected by this curve shape, so it is important to compare it with experimental data obtained with respect to the lithium reference electrode. For this reason experimental measurement must be referred to NMC and graphite separately in half cells with lithium electrode as anode; so, similarly to exchange current density procedure, the half-cells (coin cell geometry) have been built and cycled at a sufficiently low current rate, that is C/25, as found in literature [17]; as explained, an ideal measurement should be done under open-circuit condition, in order to optimally take into account of each active material contribution, but the quasi-equilibrium potential condition (C/25 galvanostatic discharge curve) is slow enough for the experimental (potential-capacity) curve to approximate well the equilibrium potential of the electrode in exam.

electric conductivity: Graphite has high electric conductivity meaning that the conductivity for the negative electrode is not a limiting factor. Usually a value of $100 S \cdot m^{-1}$ is chosen as reported in many references[3]. For positive electrode 0.1 $[S/cm]$ value from [14] has been used.

3.5 Thermal

Heat Capacity: it has been difficult to obtain this NMC 622 value by looking for it in the scientific literature, therefore a Differential Scanning Calorimetry (DSC) test must be performed. The DSC, a thermal analysis technique, is used to measure the temperature and heat flux associated with the transitions that occur in a sample. The basic principle of this technique is to obtain information about the material by heating or cooling it in a controlled manner. In particular, the DSC is based on the measurement of the difference in heat flow between the sample under examination and a reference one while the two are bound to a variable temperature defined by a pre-established program.

Knowing that heat capacity Cp is defined as the partial derivative of enthalpy with respect to temperature, to obtain this quantity, three DSC traces must be compared: the thermogram of a reference, the sample under examination and the empty sample holder. Therefore knowing the scanning speed (T/t) and the volume of the areas subtended by the thermograms (corresponding to the heat flow q/t) in the zone between two chosen temperatures (generally over a range of 100 $°C$) is possible to find the heat given divided by the temperature increase, i.e. the value of Cp, characteristic of the material.The Cp can be obtained from:

$$C_p = \frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} \tag{3.12}$$

The samples has been equilibrated at $40°C$ with an isothermal step of 2 min followed by a heating to $350°C$ with a rate of 5 K/min in high-pressure capsules. For DSC measurements the cells has been charged at 4.3 V in coin-type cells but disassembled in an argon filled glove box.

Thermal conductivity: for this parameter the value of a material close in characteristic, the NMC811, has been taken as a reference, assuming a negligible difference compared to NMC 622 since it was not possible to find a technique for testing. 1.58 $[W/(kg \cdot K)]$ is the value found for NMC811 and implemented in the model.

After having described and reported the methods for the calculation of the electtrochemical and thermal parameters referred to the NMC622 cathode, following the summary tables which show the parameters of the negative electrode, of the copper and aluminum collectors and of the electrolyte / separator already present in the Comsol® libraries.

3.6 Negative Electrode: Graphite

Parameter	**Value**	**Unit**
Particle radius	$4.5 \cdot 10^{-6}$	m
Electrical conductivity	100	S/m
Volumetric fraction	0.6	-
Diffusion coefficient	Equation defined by Comsol®	m^2/s
Equilibrium potential	Equation defined by Comsol®	V
Reference concentration	31507	mol/m^3
Maximum electrode state-of-charge	0.98	-
Minimum electrode state-of-charge	0	-
Thermal conductivity	4.21	$W/(m \cdot K)$
heat capacity at constant pressure	881	$J/(kg \cdot K)$
Density	2270	kg/m^3

Table 3.6.1: Negative electrode parameters

3.7 Negative collector: Copper

Copper parameters are reported:

Parameter	**Value**	**Unit**
Electrical conductivity	$5.998 \cdot e^7$	S/m
Relative permeability	1	-
Relative permittivity	1	-
Thermal conductivity	400	$W/(m \cdot K)$
heat capacity at constant pressure	385	$J/(kg \cdot K)$
Density	8960	kg/m^3

Table 3.7.1: Negative collector parameters

3.8 Positive collector: Aluminum

Aluminum parameters are reported:

Parameter	**Value**	**Unit**
Electrical conductivity	$3.774 \cdot e^7$	S/m
Relative permeability	1	-
Relative permittivity	1	-
Thermal conductivity	238	$W/(m \cdot K)$
heat capacity at constant pressure	900	$J/(kg \cdot K)$
Density	2700	kg/m^3

Table 3.8.1: Positive collector parameters

3.9 Electrolyte: LiPF6 EC:DEC 1:1 1M

Electrolyte parameters are reported:

Parameter	Value	Unit
Negative Electrolyte volumetric fraction	0.32	-
Positive Electrolyte volumetric fraction	0.445	-
Diffusion coefficient	Equation defined by Comsol®	m^2/s
Electrolyte conductivity	Equation defined by Comsol®	S/m
Transport number	Equation defined by Comsol®	-
Activity dependence	Equation defined by Comsol®	-
Electrolyte salt concentration	1000	mol/m^3

Table 3.9.1: Electrolyte parameters

3.10 Cell Thermal Parameters

Lumped thermal parameters obtained in the previous paragraphs must be resumed for the composite cell since these properties depends on the dimensions and on layers of material used.

Thermal conductivity: Thermal conductivity is an anisotropic property, therefore his value depends on the cell layers stacking described by two equations in function of the layer direction:

$$K_{\parallel} = \frac{L_{NC} \cdot K_{NC} + L_{NE} \cdot K_{NE} + L_S \cdot K_S + L_{PE} \cdot K_{PE} + L_{PC} \cdot K_{PC}}{L_{tot}} \tag{3.13}$$

$$\frac{L_{tot}}{K_{\perp}} = \frac{L_{NC}}{K_{NC}} + \frac{L_{NE}}{K_{NE}} + \frac{L_S}{K_S} + \frac{L_{PE}}{K_{PE}} + \frac{L_{PC}}{K_{PC}} \tag{3.13}$$

Where:

- NC=negative current collector.
- NE=negative electrode.

- S=separator.
- PE=positive electrode.
- PC=positive current collector.

density: the density is calculated as a volume average of the different cell layers through the following equation:

$$\overline{\rho} = \frac{\sum_i \rho_i \cdot L_i}{L_{tot}} \tag{3.14}$$

Heat capacity: for heat capacity also an equation based on volume average is used:

$$\overline{C} = \frac{\sum_i C_i \cdot L_i}{L_{tot}} \tag{3.15}$$

Chapter 4

Validation

To verify if the model correctly meets the purpose of the project, it is necessary to compare the data obtained from it with the experimental ones. The validation process is tackled using methods and properties extracted from experimental procedures and from literature as explained in the previous chapter.
The electrochemical validation process of the batteries, therefore, consists in comparing discharge curves experimentally obtained through cyclers with those obtained by the model at different C-rates. Since as reference geometry is used a Coin Cell kind, with reduced surfaces and materials, a relatively low-medium C-rates have been used for the purpose. A temperature analysis has been reported also, necessary to evaluate the behavior of cell during the discharge phase.

4.1 Discharge results

As anticipated, for the electrochemical validation low C-rates have been used: C/10, C/5, 1C. In figures 4.1.1 graphic comparisons between Experimental and model curve has been reported. At C/10 and also c/5 rates the model voltages are very close to the one of the tested cell throughout the full discharge;

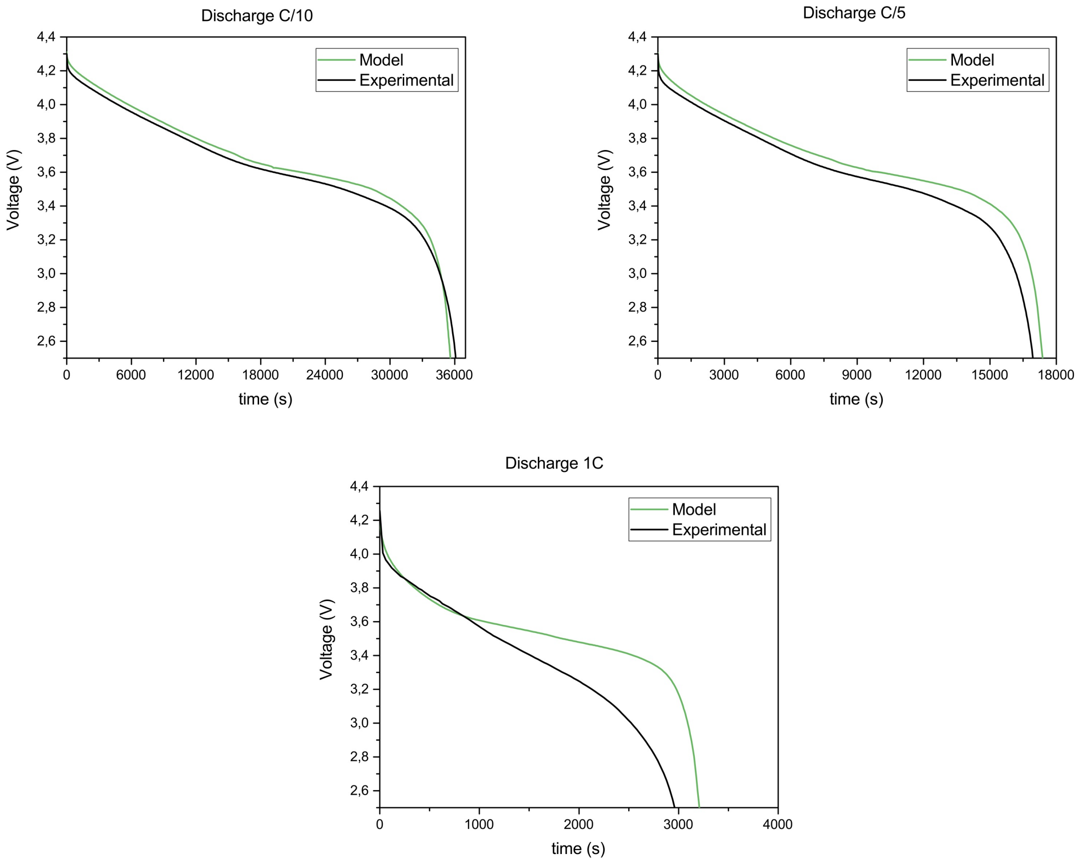

Figure 4.1.1: modeled discharge curve C/10, C/5, 1C: differences increase between the experimental and modeled curve with the C-rate rising

During Modeling it has been observed the strongly influence of the negative electrode on the flat potential plateau, in particular graphite active material effect the extension of it. This is due to lithium de-intercalation process within the graphene planes of the graphite[3]; therefore the more active graphite material (graphene planes) is present, the more time is spent in the intercalation process. This behaviour makes the plateau flat for all the modelled c-rates but it tends to be more sloped with the increasing of current rate.
The deviation between the curves becomes greater at 1C current rates probably because the experimental cell, before being cycled at 1C, faced several cycles at C/10 and C/5 and the heat generated previously led to an increase in temperatures; therefore properties with Arrhenius type dependence on temperature cause a change toward degradation in the discharge behaviour process which is not observable in

the model since it is calculated "as a fresh cell", so at 1C-rate from the beginning.

4.2 Thermal results

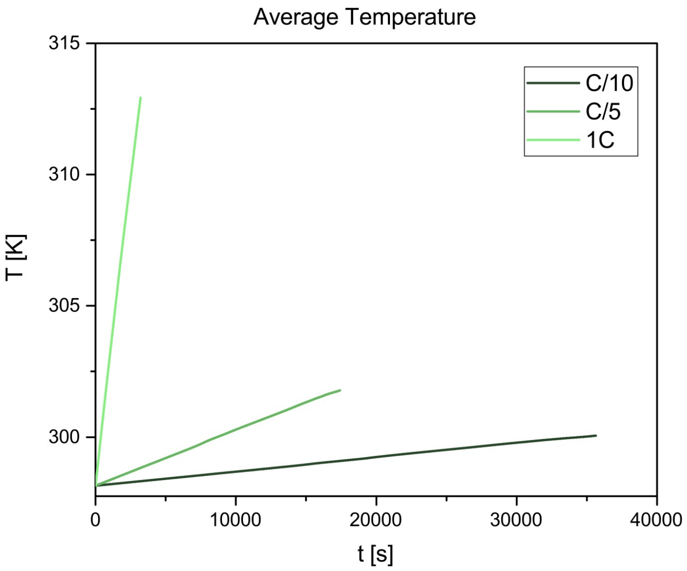

Figure 4.2.1: Temperature variation during discharge: obtained for C/10, C/5, 1C.

It hasn't been possible to conduct a thermal validation campaign but a temperatures study have also been implemented in the results. In figure 4.2.1 the temperature with respect to C/10, C/5 and 1C cycle time is reported. In general, there is an increase of temperature with time: this due to the irreversible heat flow rates in particular ohmic losses, charge transfer, and ionic diffusion during discharge process[18]. As expected, it's possible to observe that the higher is the current rate, the higher are temperature slope of curve. In particular the 1C rate led to an increase of temperature to very high values despite the small size and active material of a coin cell; this because the control volume on which thermal calculations are made by the model is isolated from the environment; consequently there is no heat dissipation towards the outside and therefore this leads to a very sloped temperature curve.

Temperature distribution in the 3D model of the cell has been reported in figure 4.2.2; it's possible to observe the areas with the highest temperature; these areas

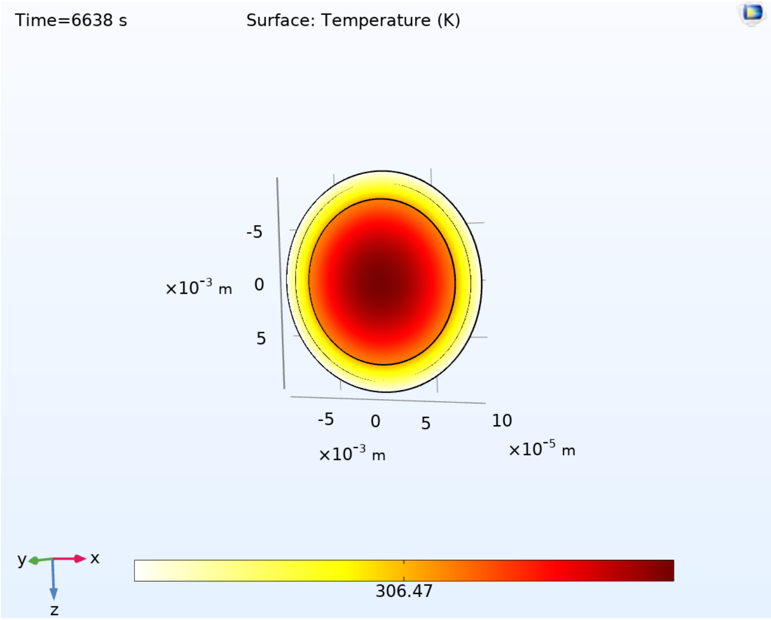

Figure 4.2.2: Temperature distribution in the 3D model.

coincide with the two cathodes and collectors (smaller diameters) where the active material is present; the lower temperature areas are present on the separator (bigger diameter); according to the model it does not generate heat, but is affected by the heat generated by the adjacent components.

Chapter 5

conclusion

After a general analysis of the uses and applications of lithium-ion batteries, a detailed description of the mathematical / physical model has been reported with the description of all the equations and parameters involved. Therefore, a careful search of the parameters referred to the commercial NMC 622 cathode material has been done through scientific literature or experimental tests described in all their phases and finally the model was obtained using the Comsol multiphysics calculation software. This model predicts quite accurately the electrochemical and thermal behavior of the coin cell with commercial NMC 622 cathode and graphite anode for a wide range of operating conditions, in particular the discharge conditions at C/10, C/5 and 1C were analyzed. The effect of electrode or separator thickness, electrode loading, etc. on the electrochemical and thermal performance of the cell can be studied using the developed model; therefore this parameterized model is valid for cells with NMC cathodes but some parameterization techniques used in this work can also be applied for the development of other types of lithium-ion batteries, and thanks to this it is possible to understand in more detail the behavior of many other types of cells. The volume fraction, the equilibrium potential as well as the diffusion coefficient or the current density referred to the active materials that forms the anode and cathode have a great influence on the duration and shape of the modeled discharge curve; the temperatures of the coin cell obtained at high C-rates instead differ from what could be the real values as this model simulates operations in an isolated environment. However, the model developed in this way, offering the possibility of modulation towards larger scale applications, is very useful as a starting point for the study of an entire battery composed of several cells, and if implemented with the aging study is able to offer an in-depth analysis of the behavior of the battery itself.

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fig 2.3.3

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fig 2.4.1

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fig. 3.4.2

"Optimized Temperature Effect of Li-Ion Diffusion with Layer Distance in Li(NixMnyCoz)O2 Cathode Materials for High Performance Li-Ion Battery"