Characterization of electrodes for lithium-ion batteries through electrochemical impedance spectroscopy and mass spectrometry

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Characterization of Electrodes for Lithium-Ion Batteries through Electrochemical Impedance Spectroscopy and Mass Spectrometry

ABHANDLUNG
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# Index

Motivation of the PhD Work .................................................................................................................. 1

## 1 Introduction .......................................................................................................................... 3

1.1 Lithium-ion Batteries .............................................................................................................. 4

1.2 Active Materials for the Negative Electrode of the Lithium-Ion Batteries ... 7

1.3 Active Materials for the Positive Electrode of the Lithium-Ion Batteries ... 10

1.4 Electrolytes for Lithium-Ion Batteries ............................................................................. 13

## 2 Theoretical Background .................................................................................................. 17

2.1 Electrochemistry .................................................................................................................. 17

2.2 Mass Spectrometry ............................................................................................................ 22

2.3 Differential Electrochemical Mass Spectrometry (DEMS) ........................................... 25

2.4 Electrochemical Impedance Spectroscopy ........................................................................ 30

## 3 Development of the Mathematical Models .................................................................. 41

3.1 Model of the Intercalation Process .................................................................................... 41

3.2 Models of the Porous Electrode ...................................................................................... 48

3.3 Models of the Transport in Pores .................................................................................... 56

3.4 Mathematical Simulations .............................................................................................. 61

## 4 Experimental Setup ....................................................................................................... 65

4.1 Preparation of the Electrodes ............................................................................................ 65

4.2 Synthesis of the Electro-Active Materials ...................................................................... 66

4.3 Standard Electrochemical Experiments .......................................................................... 66

4.4 Differential Electrochemical Mass Spectrometry (DEMS) ........................................... 67

4.5 Electrochemical Impedance Spectroscopy (EIS) .......................................................... 72

4.6 Multiple-Working-Electrode Cell (MWE) ...................................................................... 73

## 5 Study of the Negative Electrodes .................................................................................. 75

5.1 Introduction .......................................................................................................................... 75

5.2 Standard Electrochemical Measurements ...................................................................... 78

5.3 EIS measurements ............................................................................................................. 83
Abstract

The high specific energy and power available from lithium-ion batteries and the possibility to charge / discharge them many times are the reasons of their key importance in electronic portable devices, and future development of hybrid and fully electric vehicles. Graphite and LiCoO$_2$ are used as electro-active materials in standard commercially available lithium-ion batteries. Despite their utilization, the current active materials have some severe disadvantages. They are expensive, have slow kinetics of reaction for high-power applications, cannot deliver the total charge stored inside, and LiCoO$_2$ is carcinogenic.

Many challenges rise from the effort to increase the specific energy and power, and also to increase the cycle life of the battery. A greater understanding of the Li$^+$ exchange mechanism will facilitate the development of new active materials with higher performances. The motivation for this Ph.D. work was deepening the insight on the mechanisms of the overall intercalation processes by using the electrochemical impedance spectroscopy technique (EIS) and correlating the electro-catalytic properties of the active materials with their structure by using the differential electrochemical mass spectrometry technique (DEMS).

Differential Electrochemical Mass Spectrometry permits a qualitative and quantitative analysis of the electrochemically developed volatile compounds. It was used to determine the interactions between the active materials and the electrolyte. These interactions are followed by degradation of the active material, with loss of the electro-catalytic properties, or passivation of the surface of the active material, which kinetically blocks further interactions. Both these processes commonly involve gaseous products, which can be detected by a mass spectrometer. A new cell and a new experimental setup were built to provide an increased sensitivity of the experimental data. The new cell has given the possibility to implement a third electrode as reference electrode for the electrochemical measurements. The new experimental setup, based on two controlled argon fluxes, has reduced the influence of the background intensity on the data quality. An analytical tool to process the experimental results was developed, to subtract the background intensity from the mass signals. The DEMS
study on graphite particles has shown the development of CO$_2$ at 1 V (Li/Li$^+$) in the first reductive half-cycle. The development of CO$_2$ was indirectly suggested but never experimentally proved before. It was possible thanks to the increased sensitivity of the DEMS setup and the sophisticated subtraction of the background intensity from the mass signals. The DEMS study on Li$_{1+x}$(Mn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$)$_{1-x}$O$_2$ compounds, possible substitutes of LiCoO$_2$, has proved the development of oxygen in the first cycle at potentials above 4.5 V (Li/Li$^+$) for the compound with $x = 0.1$, while no oxygen was detected for the compound with $x = 0$. The quantitative analysis of the DEMS data for the compound with $x = 0.1$ has confirmed that the irreversible specific charge observed during the galvanostatic cycling experiments for the $x = 0.1$ compound in the first cycle is due to the oxygen loss.

Electrochemical Impedance Spectroscopy is an electrochemical tool which helps in the detection of the kinetic limitations in the system under investigation. It can reach high time resolution ($10^{-6}$ s) and is particularly suitable to the study of reaction mechanisms (effects of the surface energetic), current density distribution (effects of electrode geometry), and transport of mass (diffusion and migration in the bulk). Several physico-chemical models describing surface and bulk processes was developed and the correlation between EIS data and kinetic properties of the system were obtained. A new electrochemical cell was designed, to bring the experimental setup nearer to the mathematical description of the models. An analytical tool to fit the experimental data with different models was successfully developed and used. It was found out that the only plausible electrochemical process describing the EIS data before the formation of the SEI for several types of graphite particles is an adsorption through surface states. It was also observed that the limitations due to the pore structure in electrodes based on graphite are dependent on the size of the particles; in particular, the smaller the graphite particle, the higher is the resistance of the pores.

Beside the original PhD goals, a new cell for the study of the current density distribution was developed and tested on electrodes based on graphite particles. The new cell is called multiple-working-electrode (MWE) cell. Using the MWE cell, it was observed that the layer of graphite nearer to the counter electrode has a higher value of the irreversible specific charge with respect to the farer layers. A hypothesis for explaining this behavior of the graphite electrodes was formulated.
Riassunto

L’elevata energia specifica e potenza disponibile nelle batterie a litio-ione e la possibilità di caricarle / scaricarle centinaia di volte sono la ragione della loro importanza nei dispositivi elettronici portatili e per il futuro sviluppo di veicoli elettrici e/o ibridi. La grafite e LiCoO₂ sono i materiali elettro-attivi più usati nelle batterie a litio-ione disponibili nel mercato. Nonostante il loro utilizzo, gli attuali materiali elettro-attivi presentano gravi svantaggi: sono costosi; la cinetica di elettrodo è lenta per applicazioni di potenza; non possono rilasciare tutta la carica che immagazzinanano; LiCoO₂ è cancerogeno.

Molte sfide nascono dal tentativo di aumentare l’energia e la potenza specifica delle batterie a litio-ione e di aumentare il loro numero di cicli di vita. Una comprensione migliore del meccanismo di scambio di Li⁺ faciliterà lo sviluppo di nuovi materiali attivi con prestazioni più elevate. La motivazione di questo lavoro di dottorato è stata l’approfondimento della conoscenza del meccanismo di reazione del processo di intercalazione utilizzando la tecnica di spettroscopia di impedenza elettrochimica (EIS) e correlare le proprietà elettro-catalitiche dei materiali attivi con la loro struttura utilizzando la tecnica di spettrometria differenziale di massa elettrochimica (DEMS).

La spettrometria differenziale di massa elettrochimica permette un’analisi qualitativa e quantitativa dei composti volatili sviluppati elettrochimicamente. È stata usata per determinare le interazioni fra il materiale attivo e l’elettrolita. Queste interazioni si manifestano come degradazione del materiale attivo, con perdita delle proprietà elettro-catalitiche, o la passivazione della superficie del materiale attivo, che blocca cineticamente ulteriori interazioni. Entrambi questi processi coinvolgono normalmente prodotti gassosi, che possono essere osservati con uno spettrometro di massa. Una nuova cella e un nuovo apparato sperimentale sono stati costruiti per incrementare la risoluzione dei dati sperimentali. La nuova cella ha dato la possibilità di includere un terzo elettrodo come elettrodo di riferimento per le misure elettrochimiche. Il nuovo apparato sperimentale, basato su due flussi controllati di argon, ha ridotto l’influenza dell’intensità del background sulla qualità dei dati. È stato
sviluppato uno strumento analitico per la sottrazione dell’intensità del background dai segnali di massa. Gli studi fatti con il DEMS su particelle di grafite hanno mostrato lo sviluppo di CO₂ a 1 V (Li/Li⁺) nel primo mezzo ciclo riduttivo. Lo sviluppo di CO₂ era stato suggerito indirettamente ma mai provato sperimentalmente prima. Questo è stato possibile grazie all’aumentata risoluzione dell’apparato DEMS e alla sottrazione dell’intensità del background dai segnali di massa. Gli studi fatti col DEMS sui composti Li₁₊ₓ(Mn₁/₃Ni₁/₃Co₁/₃)₁₋ₓO₂, possibili sostituti di LiCoO₂, hanno dimostrato lo sviluppo di ossigeno nel primo ciclo a potenziali superiori a 4.5 V (Li/Li⁺) per il composto con x = 0.1, mentre l’ossigeno non è stato osservato per il composto con x = 0. L’analisi quantitativa dei dati DEMS per il composto con x = 0.1 ha confermato che la carica specifica irreversibile osservata durante gli esperimenti galvanostatici per il composto con x = 0.1 nel primo ciclo è dovuta al rilascio di ossigeno dalla struttura del materiale attivo.

La spettroscopia di impedenza elettrochimica è uno strumento elettrochimico, che aiuta nella determinazione dei limiti cinetici del sistema sotto osservazione. Può raggiungere una risoluzione temporale molto elevata (10⁻⁶ s) ed è particolarmente indicato per lo studio dei meccanismi di reazione (effetto dell’energetica di superficie), della distribuzione di densità di corrente (effetto della geometria dell’elettrodo) e del trasporto di massa (diffusione e migrazione). Vari modelli fisico-chimici, che descrivono i processi di superficie e di bulk, sono stati sviluppati e le correlazioni fra i dati di EIS e le proprietà cinetiche del sistema sono state ottenute. Una nuova cella elettrochimica è stata sviluppata, per avvicinare l’apparato sperimentale alla descrizione matematica dei modelli fisico-chimici. Uno strumento analitico per fittare i dati sperimentali con diversi modelli è stato sviluppato con successo e usato. Si è osservato che l’unico processo elettrochimico plausibile per descrivere i dati di EIS per vari tipi di grafite prima della formazione del SEI è un adsorbimento tramite stati superficiali. È stato anche osservato che le limitazioni dovute alla struttura dei pori negli elettrodi a base di grafite sono dovute alle dimensioni delle particelle; più piccole sono le particelle, maggiore è la resistenza nei pori.

Accanto agli obiettivi del dottorato, una nuova cella per lo studio della distribuzione delle densità di corrente è stata sviluppata e testata su elettrodi a base di grafite. La nuova cella è stata chiamata cella a elettrodi di lavoro multipli (MWE). Utilizzando la cella MWE, si è osservato che lo strato di grafite più vicino al contro elettrodo ha una carica specifica
irreversibile più elevata degli strati più lontani dal contro elettrodo. È stata formulata un’ipotesi per spiegare questo comportamento degli elettrodi di grafite.
Den Unbedenklichen, die niemals zweifeln
Begegnen die Bedenklichen, die niemals handeln.
Sie zweifeln nicht, um zur Entscheidung zu kommen, sondern
Um der Entscheidung auszuweichen. Köpfe
Benützen sie nur zum Schütteln. Mit besorgter Miene
Warnen sie die Insassen sinkender Schiffe vor dem Wasser.
Unter der Axt des Mörders
Fragen sie sich, ob er nicht auch ein Mensch ist.
Mit der gemurmelten Bemerkung
Daß die Sache noch nicht durchforscht ist, steigen sie ins Bett.
Ihre Tätigkeit besteht in Schwanken.
Ihr Lieblingswort ist: nicht spruchreif.

Freilich, wenn ihr den Zweifel lobt
So lobt nicht
Das Zweifeln, das ein Verzweifeln ist!

Was hilft zweifeln können dem
Der sich nicht entschließen kann!
Falsch mag handeln
Der sich mit zu wenig Gründen begnügt
Aber untätig bleibt in der Gefahr
Der zu viele braucht.

Du, der du ein Führer bist, vergiß nicht
Daß du es bist, weil du an Führern gezweifelt hast!
So gestatte den Geführten
Zu zweifeln!

(Bertolt Brecht, Lob des Zweifels)

Science alone of all the subjects contains within itself the lesson of the danger of belief in the infallibility of the greatest teachers in the preceding generation ... Learn from science that you must doubt the experts. As a matter of fact, I can also define science another way: Science is the belief in the ignorance of experts.

(Richard Feynman, The Pleasure of Finding Things Out: The Best Short Works of Richard Feynman)
Motivation of the PhD Work

The high specific energy and power available from lithium-ion batteries and the possibility to charge / discharge them hundreds of times are the reasons of their key importance in electronic portable devices and future development of hybrid and fully electric vehicles. Carbons (both graphitized and amorphous) and lithium metal oxides (mainly LiCoO$_2$) are used as electro-active materials in standard commercially available lithium-ion batteries. Despite their utilization, the current active materials have some severe drawbacks. They are expensive, have slow kinetics of reaction for high-power applications, cannot deliver the total charge chemically stored inside, and LiCoO$_2$ is carcinogenic.

Many challenges rise from the effort to increase the specific energy and power, and also to increase the cycle life of the battery, as required from the automotive market. The many interactions between different properties of the electro-active material, related to both bulk and surface, and interaction with the electrolyte, make this challenge an interdisciplinary effort. A greater understanding of the Li$^+$ exchange mechanism will facilitate the development of new active materials with higher performances. The motivation for this Ph.D. work was deepening the insight on the mechanisms of the overall intercalation processes by using the electrochemical impedance spectroscopy technique (EIS) and correlating the electro-catalytic properties of the active materials with their structure by using the differential electrochemical mass spectrometry technique (DEMS).

Differential Electrochemical Mass Spectrometry permits a qualitative and quantitative analysis of the electrochemically developed volatile compounds. It was used to determine the interactions between the active materials and the electrolyte. These interactions are followed by degradation of the active material, with loss of the electro-catalytic properties, or passivation of the surface of the active material, which kinetically blocks further interactions. Both processes commonly involve gaseous products, which can be detected by a mass spectrometer. The passive
film coating the particles is very important for the cycle life of the battery. The aim of the PhD work was to build a new experimental setup, a new electrochemical cell, and to develop an analytical tool for the analysis of the experimental data. The new setup has to provide an increased resolution of the experimental data, by reducing the influence of the background line on the data quality. The new electrochemical cell has to implement a third electrode as reference electrode for the electrochemical measurements. The analytical treatment of the experimental data is necessary to achieve high resolution of the gases developed in the cell; it purifies the data from the background line.

Electrochemical Impedance Spectroscopy is an electrochemical tool which helps in the detection of the kinetic limitations in the system under investigation. It can reach high time resolution ($10^{-6}$ s) and is particularly suitable to the study of reaction mechanisms (effect on the surface energetic), current density distributions (effect of electrode geometry), and transport of mass (diffusion and migration in the bulk). Even if this method is very popular in electrochemistry, it is often misused. A rigorous mathematical treatment of the experimental data is necessary to extract creditable kinetic parameters. The aim of the PhD work was to develop several physico-chemical models describing surface and bulk processes, and to build a new electrochemical cell. The physico-chemical models have to provide the correlation between impedance data and kinetic properties of the system. An analytical tool to fit the experimental data with different models is necessary to extract the kinetic properties of the system from the experimental data. The new electrochemical cell has to adapt the experimental setup to the mathematical description of the models.
1 Introduction

The technology of lithium-ion batteries is a main topic in the energy conversion field thanks to the very interesting characteristics of this power source. A well designed lithium-ion battery can reach high energy and power density, and can be recharged many times. The research in the field of lithium-ion battery is focused on the development of systems with even higher power and energy density and longer cycle life; the goal of the research is to use the lithium-ion batteries as power source of hybrid or fully electric vehicles. For this purpose, in the last years an intensive effort was spent in developing new materials for positive (oxides [1-3], phosphates [4]) and negative electrodes (different graphite types, alloys [5], and carbon based compounds), separators, electrolytes (ionic liquids, polymeric electrolytes, and inorganic solids). Because of this strong push in material science direction, the electrochemical aspects of this challenge and the intrinsic limitations of the system were sometime disregarded. Lithium-ion batteries are complex systems; both bulk and surface properties of the materials are important for the final performance of the system.

Surface plays a very important role in the cycle life of a battery; the material has to be stable in the battery electrolyte for the whole potential range used during the battery cycle, and vice versa. This condition is quite always reached thanks to the formation of a protective layer at the surface of the electrode [6-10]. The surface layer, called solid electrolyte interphase (SEI), can be an oxidation/reduction product, in which case it consumes part of the charge of the battery, or a chemical product, formed by contacting the particles with the electrolyte [11-13]. The SEI influences the kinetic behavior of the electrode, the irreversible charge consumed during cycling, and the cycle life. Investigation of SEI formation, its stability and its influence on the kinetic behavior of the electrode are all aspects of primary importance in enhancing the performances of lithium-ion batteries.

Moreover, the design of the electrochemical cell has a not negligible importance in the performances of this power source, due to the low specific conductivity of the electrolyte (~0.01 S·cm⁻¹ [14]). From an electrochemical point of view, it is clear that a high power
battery will never work homogeneously, because even small differences in the distance, thickness, and density of the electrodes can cause big kinetic limitations. As can be seen from this short overview, the challenge to increase the performances of lithium-ion batteries covers many scientific fields, which are interconnected and influence each other.

1.1 Lithium-Ion Batteries

The electrochemical systems for the storage of energy can be classified in three main types: electrochemical capacitors; batteries; fuel cells. These power sources are composed of two electrodes in contact with an electrolyte. To increase the contact surface area between electrode and electrolyte, porous electrodes are used instead of solid ones. The increase of the surface area has the advantage to decrease the kinetic limitations generated by the current flow. In electrochemical capacitors the energy is stored in the double layer formed at the interface electrode/electrolyte. The increase of the contact surface area electrode/ electrolyte increases the amount of charge stored. The charging process of the double layer is very fast ($10^{-8}$ s), the electrodes should provide only passage of electrons. These systems have high specific power but low specific energy. In batteries, a part of the electrode, the so called active mass, participate to a reaction with the components of the electrolyte, the charge is stored in the bulk of the active mass or is accumulated in a precipitated compound. Compared to the electrochemical capacitors, the increase in the specific energy is accompanied by a decrease of the specific power, because of the slower faradaic reaction needed to store the charge (between $10^{-2}$ and $10^{-4}$ s). In fuel cells the electrodes provide electrons for the faradaic reaction; the reactant of the faradaic reaction is a fuel, which is stored in a tank outside the electrochemical system and is transported to the electrodes of the fuel cell in gaseous phase. Fuel cells are systems with low specific power, but high specific energy [15].

Batteries can be divided in primary and secondary batteries. The former can be used only once and than have to be discarded. The latter can be recharged after discharge and are also named accumulators or rechargeable batteries. The possibility to recharge a battery is strictly connected with the reversibility of the electrochemical process and with the safety of the battery. For battery systems it is important to have a large temperature range of operation. Standard applications need a temperature range between 0 and 40 °C, while automotive or military applications need operational temperatures between -40 and 85 °C. Self-discharge is the loss of performance when a battery is not in use. Self-discharge phenomena have to be
maintained as slow as possible. In an ideal battery, the discharge has to occur at constant potential, so that a constant power is delivered during the time; this requirement implies that active materials having two phases during the discharge are preferred. High specific energy is achieved by using electrodes which can deliver an high amount of specific charge at an high voltage. High specific power is granted by fast electrochemical reaction, high specific conductivity of the electrolyte, high electronic conductivity of the electrodes and current collectors.

![Ragone chart of the main secondary battery systems](image)

**Figure 1.1:** Ragone chart of the main secondary battery systems (Adapted from M. Broussely, in PSI Tagessymposium, Villigen, Switzerland, 2005).

The combined properties to have the most negative equilibrium potential in the electrochemical scale and a very low atomic mass make lithium a very interesting element in the field of the energy storage. The advantage of storage systems based on lithium is clear from a Ragone chart (see figure 1.1). (Safety problems are due to the high reactivity of metallic lithium. Nonacqueous and aprotic solvents have to be used in the electrolyte). Batteries based on the lithium technology can be divided in two classes: lithium batteries and lithium-ion batteries. In the former metallic lithium is used as negative electrode, while in the latter lithium ions are exchanged between compounds which contain lithium atoms. In
primary lithium batteries developed in the 70’s, the active material of the positive electrode is a sulfide (MoS$_2$, FeS$_2$), an oxide (MnO$_2$), or a fluorinated carbon (CF$_x$) [16-19]. Depending on the positive electrode, such batteries can reach voltage up to circa 3 V, therefore high specific energy, have slow self-discharge processes, can be used at low temperature [16-18,20]. Nonacqueous and aprotic solvents have to be used in the electrolyte to avoid the complete dissolution of the metallic lithium. To enhance the safety of the lithium battery, the metallic lithium had to be substituted with less reactive compounds.

Figure 1.2: Schematic description of a lithium-ion cell based on electrochemical intercalation process (discharge). Anode is composed by graphite, while cathode is a layered oxide. Lithium ions are removed from the graphene layers and simultaneously are accommodated in the layered oxide [21].

At the end of 70’s the first lithium-ion batteries are born. They were based on the electrochemical process of insertion. The negative and positive electrodes were substituted with host materials which can accommodate (release) lithium ions in (from) the structure. In the case of two dimensional structures, this process is called intercalation (see figure 1.2). The intercalation is an intrinsically reversible process. For this reason lithium-ion batteries are commonly rechargeable. It is possible to distinguish between single phase systems and two-phase systems. The former do not change structure during Li$^+$ insertion and accommodate the
Li-ions through changes in the lattice parameters. The equilibrium potential of these compounds depends on the amount of Li\textsuperscript{+} intercalated into the structure. The equilibrium potential of two phase systems is independent from the amount of Li\textsuperscript{+} intercalated; the structure arrangement is related to the lithium content. The most common active materials used in lithium-ion batteries are graphite and LiCoO\textsubscript{2}.

There are other electrochemical processes which can be used as working principle in lithium-ion batteries. Lithium can electrochemically alloy with numerous metals. Many known Li alloys can be used as active materials for the negative electrode; the equilibrium potential of such alloys in Li\textsuperscript{+} electrolytes is generally between 1.0 and 0.3 V (Li/Li\textsuperscript{+}). Lithium alloys are normally quite brittle, because of their ionic character, and the alloying causes large volume expansion. Combination of these two effects results in the cracking of the electrode after few cycles.

Theoretically, it could be possible to combine an intercalation compound at the positive electrode with metallic lithium at the negative electrode. The problem in a practical application is related to the surface stability of the metallic lithium. The electrolyte solvents are not thermodynamically stable in contact with metallic lithium; they form an SEI at the interface which protects the solvent molecules from further reduction. When fresh metallic lithium is deposited at the negative electrode, it often forms a needle-like and brittle surface (dendrites) [22-25], and the following non homogeneous dissolution of lithium will create isolated lithium particles (loss of specific capacity), which eventually can short-circuit the battery. It was found that the formation of the dendrites depends strongly on the electrolyte salt used; in particular LiAsF\textsubscript{6} minimizes this phenomenon, but should not be used in commercial cells because of the toxicity of As.

1.2 Active Materials for the Negative Electrode of the Lithium-Ion Batteries

The negative electrode in lithium-ion batteries substitutes metallic lithium. As explained before, this is necessary because metallic lithium has not a stable surface during charge / discharge and the risk of a shot-circuit can arise. To obtain high specific energy, the active material has to store high amount of charge and to have a more cathodic equilibrium potential for the Li exchange. Some limits on the latter properties are set by the stability window of the electrolyte (see paragraph 1.4) and the deposition potential of metallic lithium (electroplating).
on the electrode, which could result in the formation of dendrites. To avoid electroplating of lithium, the equilibrium potential has to be higher than 60 mV (Li/Li$^+$). It is possible to classify the active materials for the negative electrode of the lithium-ion batteries are classified in intercalation compounds and lithium alloys [26].

The most common active material for negative electrodes in lithium-ion batteries is graphite. It is a layered compound formed by graphene sheets; in between these sheets the lithium ions can intercalate. It forms four different compounds by intercalation of Li$^+$ at low potential, namely, Li$_x$C$_6$ (see Table 1.1). The theoretical maximum specific charge, obtained at $y = 1$, is equal to 372 mAh g$^{-1}$. Intercalation of lithium in graphite is highly ordered; there is one intercalated layer each $1/y$ layers (stage formation) [27]. This order is repeated in the whole crystallite. For this reason, lithium-graphite compounds have different structures, and so different phases. Before the formation of the $y = 1/3$ phase, there is the so called diluted phase. For $0 = y < 1/6$, a single solid phase appears; the intercalation of lithium ions is disordered. Intercalation potentials of the different phases are between 0.22 and 0.1 V (Li/Li$^+$) [28]. These characteristics make graphite a good compound for negative electrode in high voltage batteries. The nature and surface of graphite influence strongly the cycle life of the battery [6-10]. In the potential range of Li$^+$ intercalation in graphite, most of the electrolytes are thermodynamically unstable. The formation of a stable passivation film at the surface of graphite particle is necessary. This passivation film, the so called Solid Electrolyte Interphase (SEI), has to be electronically isolating and to allow the passage of Li$^+$. It is composed by organic (polymeric) and inorganic lithium salts, formed during the reduction of the electrolyte [11-13]. The nature and the properties of the SEI are correlated with the surface groups in graphite, as well as with the electrolyte solvents and solutes.

Many metals have shown the possibility to form alloys with lithium at low potential. These alloys show very high specific charge (even higher than graphite); therefore they are suitable substitutes of metallic lithium in lithium batteries. The theoretical maximum specific charge of Si and Sn are circa 4000 and 1000 mAh g$^{-1}$, respectively [5]. The equilibrium potential of such alloys in electrolytes containing Li$^+$ ranges between 1.0 and 0.3 V (Li/Li$^+$) [26,29-31]. Being the equilibrium potential of the lithium alloys more anodic than the equilibrium potential of the lithium-graphite, the charge loss in alloys due to the reduction of the solvents in the electrolyte is smaller with respect to graphite. The normally short cycle life,
due to embrittlement and large volume expansion of the particles during alloying, makes these materials not competitive with graphite negative electrodes [5,29,32,33]. Trials to improve the cycle life of lithium alloys were done by applying shallow charging and/or using matrix compounds mixed with the active material [34-36]. The matrix should work as an expansion absorber, to limit the stress in the active material. In both cases the result is an improvement of the cycle life, but decrease of the specific charge. The cycle life of the lithium alloys were also improved by electrochemically reducing compounds based on the alloying metal. During the first cycle, the real active material has to be formed by reduction of the compounds. SnO and SnₓFeᵧ are two examples of this class of compounds [37-41]. In both cases a high amount of irreversible specific charge was obtained in the first cycle, due to the electrochemical formation of Sn from the starting compounds.

TiO$_2$ and titanates are included in the list of negative intercalation electrodes for lithium-ion batteries, even if it is possible to use them as positive ones. The equilibrium potential of titanium oxide is 1.8 V (Li/Li$^+$), while lithium titanate has an equilibrium potential of 1.5 V (Li/Li$^+$) [42,43]. Lithium-ion batteries using such negative electrodes show low voltage (~2 V) with respect to standard batteries (~3.7 V). The maximum theoretical capacity of TiO$_2$ is around 170 mAh g$^{-1}$. These characteristics make TiO$_2$ aimed for low energy lithium-ion batteries. Both titanium compounds form two phase systems during Li$^+$ intercalation, thus showing a very well defined equilibrium potential [44]. The advantage of using such electrodes is related to the more anodic equilibrium potential of the intercalated compound. In this potential region the reduction of the electrolyte is not thermodynamically favored and also lithium electroplating is impossible, allowing the usage of much higher current density (high power and fast charge). This is not the case of negative electrodes based on graphite particles, for which the equilibrium potential of the richer Li compound is around 0.1 V (Li/Li$^+$).

In table 1.1 the main characteristics of the most common active materials for the negative electrode of lithium-ion batteries are given.
Reduced form | Oxidized form | $E_{eq} (\text{Li/Li}^+ \text{)}$ / $V$ | $Q_{max}$ / mAh g$^{-1}$
---|---|---|---
**Negative electrode active materials**
Li | Li$^{+}$(c) | 0 | 3861
Graphite based compounds
LiC$_6$ | Graphite | 0.1 | 372
Li$_{1/2}$C$_6$ | Graphite | 0.13 | 186
Li$_{1/3}$C$_6$ | Graphite | 0.22 | 124
Alloys
LiAl | Al | 0.35 | 993
Li$_{22}$Sn$_5$ | Sn | 0.42 - 0.66 | 994
Li$_5$Sb | Sb | 0.9 | 660
Li$_{21}$Si$_5$ | Si | 0.3 | 4000
Titanates
Li$_k$TiO$_2$ | TiO$_2$ | 1.8 | 170
Li$_{4+x}$Ti$_5$O$_{12}$ | Li$_4$Ti$_5$O$_{12}$ | 1.5 | 160

Table 1.1: Main characteristics of negative electrode active materials for lithium-ion batteries, including metallic lithium. $E_{eq}$ is the equilibrium potential and $Q_{max}$ is the maximum theoretical specific charge. (a) The electrochemical activity can be observed in a range of potentials. (b) The specific charge is relative to the weight of the pristine active material. (c) Li$^+$ is in solution. (Source ref. [26,43,45])

1.3 Active Materials for the Positive Electrode of the Lithium-Ion Batteries

In general, the active materials for positive electrodes are compounds based on transition metals which can release lithium ions from the structure by oxidation of the transition metal cations [19]. To obtain high rate capability and high reversibility, it is important that during intercalation the structure of the active material remains unaltered. Most of the active materials for the positive electrode of the lithium-ion batteries have a layered structure, with transitional metal ions ordered in a layer (slab) and lithium ions in the following layer (interslab). The disorder of the structure can be quantified from the amount of transition metals which are in the interslab. Li$^+$ can diffuse rapidly in the structure only if the material is highly ordered [19,46]. Moreover, to obtain high enough specific energy density, it is necessary that at least one Li$^+$ per transition metal can be removed from (accommodated in) the structure. Also the electronic conductivity of the compounds is important. If it is too low, some conductive additives (mainly carbonaceous) have to be mixed in the electrode composition, thus lowering the specific energy. In this case, the reaction can occur only in the regions where the three phases (conductive additives, active material and electrolyte) meet together.
The compounds which show electrochemical activity to lithium intercalation were known before 1970 (layered dichalcogenides and trichalcogenides). Between them, TiS$_2$ was particularly appealing for lithium-ion intercalation [18,47]. $\text{Li}_x\text{TiS}_2$ shows a single structure in the whole range of composition $0 = x = 1$ [48]. The disorder influences strongly the diffusion of lithium ions; even a small amount of Ti in the interslab reduces drastically the diffusion coefficient [46]. The equilibrium potential is around 2 V and the discharge/charge curve is sloppy. These characteristics make the compound uninteresting for high energy applications or when the delivery of constant power is required.

Vanadium oxide, V$_2$O$_5$, was one of the first layered oxides studied [48-51]. It has a complex intercalation behavior, involving several phases in relationship with the lithium content. After the first full charge, the lithiated compound shows a sloppy behavior during galvanostatic cycling. This effect makes V$_2$O$_5$ uninteresting for practical applications. Other vanadium oxide compounds were studied, such as V$_6$O$_{13}$ [52], which can intercalate up to 1 Li per V, and LiV$_3$O$_8$ [53,54], which structure can be swelled to accommodate more lithium ions.

LiCoO$_2$ was the first active material for positive electrode commercialized in large scale [55]. The LiCoO$_2$ has a layered structure. The complete removal of the lithium ions from the interslab results structural changes. The oxygen layers rearrange in a hexagonal close packed cell [56]. CoO$_2$ is then electrochemically inactive with respect to Li$^+$ intercalation. Removal of more than 50% of lithium results in an increase of the amount of the irreversible specific charge, without benefit for the reversible specific charge. For this reason, the maximum practical specific charge results circa 135 mAh g$^{-1}$. LiCoO$_2$ is not the ideal material; it has several and severe disadvantages, related to the safety of the battery, pollution, healthcare, and cost of the cobalt.

LiNiO$_2$ has the same structure of the cobalt equivalent, with the advantage of the lower cost of Ni with respect to Co. Studies on this compound suggest an excess of nickel in the structure, localized in the interslab [19]. This disorder causes a reduction of the diffusion coefficient and consequently of the power capability [19]. Moreover, the de-intercalated compound seems to be unstable and therefore dangerous in contact with organic liquids. Many modifications were tried, by substituting part of the nickel with Co or Al [57-59]. The effect of these additives is to reduce the disorder in the interslab and increase the stability of the structure at low lithium content, respectively, thus bettering the reversibility and the life
cycle. Both nickel and cobalt compounds are so called first-generation cathodes for lithium-ion batteries.

Second-generation cathodes include modifications of the LiNiO₂, spinel cathodes LiMn₂O₄, layered LiMnO₂, and its modifications. The LiMn₂O₄ spinel compound has three equilibrium potentials for lithium ion intercalation, two are at 4.0 and 4.1 V (Li/Li⁺), one is at circa 3.0 V (Li/Li⁺). Often only the lithium intercalation at 4.0 and 4.1 V (Li/Li⁺) is used, so that the cell is constructed in the discharged state [60-62]. The average oxidation state of the manganese is critical to obtain effective cycle life. When the oxidation state of the manganese is 3.58 or higher, like in the Li₁₊ₓMn₂₋ₓO₄ compounds, the dissolution of the manganese is minimized and the spinel compound has a longer cycle life [62]. LiMnO₂ has a layered structure; it is a low cost compound, and environmental friendly. It is synthesized by ion exchange process starting from NaMnO₂ [63,64]. In de-intercalated state, the structure is not stable and change to spinel [65]. To stabilize the structure, Ni and/or Co are used as substitutes of Mn [66]. Good results are obtained with the compound LiNi₁/₂Mn₁/₂O₂, which has also a higher thermal stability with respect to LiCoO₂. The substitution of Mn with Co, Ni or Fe has beneficial effects on the electronic conductivity of the compound [19].

The layered oxide class Li(NiₓMnₓCo₁₋ₓ)O₂, the so called NMC compounds, is the third generation of active materials for the positive electrode of lithium-ion batteries [1-3]. The most studied compounds are the ones with z = y. In particular the z = y = 1/3 compound was extensively studied. As general rule, manganese and cobalt are present in the structure as Mn⁺⁴ and Co⁺³ respectively, while nickel is observed as a mixing of Ni⁺² and Ni⁺³. XPS studies have confirmed that, when y = z, nickel ions are in divalent state [67]. The presence of cobalt ions decreases the disorder in the interslab. The y = z compounds show good thermal stability [68-70]. These compounds can reach high specific charge density (circa 170 mAh g⁻¹) and long cycle life. The overlithiated form of the NMC, with general formula Li₁₊ₓ(NiₓMnₓCo₁₋ₓ)O₂, does exist.

LiFePO₄ is the first positive material which is low cost, environmentally benign, and can be charged reversibly up to 1 Li per Fe [4]. The compound is an olivine electrochemically active to Li⁺ intercalation. During de-intercalation, it forms a two phase system; LiFePO₄ is in equilibrium with FePO₄. The equilibrium potential of such a system in an electrolyte containing Li⁺ is equal to 3.4 V (Li/Li⁺). The theoretical specific charge of the LiFePO₄
compound is equal to 170 mAh g$^{-1}$. The low electronic conductivity of such compounds ($10^{-9}$ S/cm) does not permit to use them “as they are” in positive electrodes [71]. They have to be mixed with carbonaceous compounds. Alternatively, doping with some parts per million of Nb increases the conductivity by 8 order of magnitude [72]. Carbon coating was also used to enhance the electronic transport [73].

In table 1.2 the main characteristics of the most common active materials for the positive electrode of lithium-ion batteries are given.

<table>
<thead>
<tr>
<th>Reduced form</th>
<th>Oxidized form</th>
<th>$E_{eq} \ (\text{Li}/\text{Li}^+)$ / V (a)</th>
<th>$Q_{max}$ / mAh g$^{-1}$ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive electrode active materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Layered compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiTiS$_2$</td>
<td>TiS$_2$</td>
<td>1.5 - 2.4</td>
<td>239</td>
</tr>
<tr>
<td>Li$_3$V$_2$O$_5$</td>
<td>V$_2$O$_5$</td>
<td>2 - 3.5</td>
<td>442</td>
</tr>
<tr>
<td>LiCoO$_2$</td>
<td>Li$_4$CoO$_2$</td>
<td>3.5 - 4.2</td>
<td>274</td>
</tr>
<tr>
<td>LiNiO$_2$</td>
<td>Li$_4$NiO$_2$</td>
<td>3.5 - 4.2</td>
<td>274</td>
</tr>
<tr>
<td>LiMnO$_2$</td>
<td>Li$_4$MnO$_2$</td>
<td>3.5 - 4.2</td>
<td>285</td>
</tr>
<tr>
<td>Li(NiMnCo)O$_2$</td>
<td>Li$_4$(NiMnCo)O$_2$</td>
<td>3 - 4.5$^\text{(c)}$</td>
<td>274$^\text{(c)}$</td>
</tr>
<tr>
<td>Spinels and Olivines</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiMnO$_4$</td>
<td>Li$_4$MnO$_4$</td>
<td>3 - 4</td>
<td>213</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>FePO$_4$</td>
<td>3.4</td>
<td>170</td>
</tr>
</tbody>
</table>

Table 1.2: Main characteristics of positive electrode active materials for lithium-ion batteries. $E_{eq}$ is the equilibrium potential and $Q_{max}$ is the maximum theoretical specific charge. (a) The electrochemical activity can be observed in a range of potentials. (b) The specific charge is relative to the weight of the pristine active material and all lithium ions removed. (c) The mixed oxides can show very different behavior depending on the exact composition. (Source ref. [19])

1.4 Electrolytes for Lithium-Ion Batteries

The function of the electrolyte in electrochemical systems is to provide ionic connection between the electrodes, avoiding electronic charge flow. Normally the electrolyte is composed by one or more liquid solvents and one or more salts which dissociate and provide the ions. In lithium and lithium-ion batteries the solvents used are nonaqueous and aprotic. The electrolyte has to be compatible with both positive and negative electrode, current collectors, and separator. The electrolyte has also to be stable in contact with the strong oxidizing / reducing surface of the electrodes (chemically / electrochemically inert). This condition is often reached by the formation of a passivation layer on the surface of the electrode (kinetic protection). The passivation layer, the SEI, depends on the presence and nature of additives.
and impurities, solvents and solutes. Solutes have also to be mostly dissociated in the solvent, and to have a large range of temperature stability. Other important factors which determine the choice of an electrolyte are the cost, safety, health, and environmental compatibility. The exact formulation of the electrolyte is very important for the cycle life of the battery [74].

From the electrochemical point of view, the ionic conductivity is the most important property, because it is directly connected with the specific power of the cell. The specific conductivity of a binary electrolyte (electrolyte composed of a single salt) is connected with both mobility and number of the ions in the solvent. The latter is strictly connected with the dissociation constant of the salt. The Stokes-Einstein relation connects the mobility of the ion and the viscosity of the solvent [21]:

$$\mu_i = \frac{1}{6\pi \eta r_i}$$

where $\mu_i$ is the ionic mobility, $\eta$ is the viscosity of the solvent, and $r_i$ is the ionic radius (inclusive of the solvation shell). Solvents with low viscosity are necessary in the formulation of the electrolyte. Moreover, the cations in the electrolyte ($\text{Li}^{+}$) participate in the electrochemical reaction at both electrodes and no support electrolyte is present in lithium-ion batteries. The contribution of the lithium ions to the total conductivity becomes very important. It is given by its transport number:

$$t_{\text{Li}^{+}} = \frac{\mu_{\text{Li}^{+}}}{\mu_{\text{Li}^{+}} + \mu_{A^-}}$$

where $t$ is the transport number, and $A^-$ is the corresponding anion of the lithium salt. A transport number near to 1 is much desired, because it would eliminate partially or completely the limitations connected with the diffusion of lithium-ions in the electrolyte. Unfortunately, the measured transference numbers for $\text{Li}^{+}$ in standard nonaqueous electrolytes used in lithium-ion batteries range from 0.2 to 0.4, due to the bigger solvation shell of $\text{Li}^{+}$ with respect to the one of $A^-$ [75,76].

The formulation of the electrolyte most used in commercially available lithium-ion batteries is a combination of linear and cyclic carbonates as solvents, with presence of passivating additives, and LiPF$_6$ as electrolyte solute. The high dielectric constant of ethylene carbonate (EC) and its low viscosity (with respect to other cyclic carbonates), makes it a good candidate as electrolyte solvent [21]. At room temperature it is solid (see table 1.3). The most
used linear carbonate is dimethyl carbonate (DMC). The mixture of DMC and EC is liquid in a large range of compositions. LiPF$_6$ is chosen as solute because it has a good balance between conductivity, safety and hazard for health. A 1M LiPF$_6$ solution of EC:DMC 1:1 (wt.) has a conductivity of 10.7 mS cm$^{-1}$ (see table 1.4), and it is usable in the temperature range between -20 and 50 °C. The conductivity is quite high for a nonaqueous electrolyte, but is still too low to avoid non-homogeneous usage of thick electrodes when high power is required.

Apart LiPF$_6$, other solutes are often used in laboratory to investigate the effect of the anion on the battery cycle life, on the reduction and oxidation products generated during the formation of the SEI, and on the temperature stability. LiClO$_4$ can create SEI films with enhanced ionic conductivity, because of its relatively low reactivity with moisture [77]. LiPF$_6$ reacts with moisture traces and the hydrolysis gives HF, which forms then LiF in the SEI, a poor ionic conductor [78]. Unfortunately, by high current or high temperature, the ClO$_4^-$ is not stable [79]. LiAsF$_6$ has the same advantage as the perchlorate, and also prevents the formation of dendrites in metallic lithium electrodes, making this electrolyte interesting for lithium batteries [80]. But the toxicity of As makes this salt not usable in commercial batteries. LiBF$_4$ has the inconvenience of a low conductivity, due to the low dissociation constant [75].

Polymer electrolytes and ionic liquids are believed to be the electrolytes for the next generation of lithium-ion batteries [21]. Solid polymer electrolytes are not interesting for the industry, because of the very low conductivity (< 1 mS cm$^{-1}$) [81], and they show no practical advantage with respect to the liquid ones. Also the application of ionic liquid electrolytes in lithium-ion batteries seems to remain a long term goal [21]. Gel polymer electrolyte entered in the market in 2000 (known as Li-polymer). They mainly consist of a rubber-like matrix swollen in a liquid electrolyte. The liquid electrolytes used are the same described previously. The ionic conductivity of this class of electrolytes is around 4 mS cm$^{-1}$ [82]. Depending on the composition of the matrix, they can show good mechanical strength, good electrolyte/active material contact, good flexibility, and processability. Especially this last point is very important in the choice of the polymeric matrix, because the electrochemical performance is strictly dependent on the liquid electrolyte, as the thermal and potential stability windows.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_m / ^\circ C$</th>
<th>$T_b / ^\circ C$</th>
<th>$\eta / \text{cP}^{(a)}$</th>
<th>$\varepsilon^{(a)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cyclic Carbonates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>36.4</td>
<td>248</td>
<td>1.9$^{(b)}$</td>
<td>89.8</td>
</tr>
<tr>
<td>PC</td>
<td>-48.8</td>
<td>242</td>
<td>2.5</td>
<td>64.9</td>
</tr>
<tr>
<td><strong>Linear Carbonates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMC</td>
<td>4.6</td>
<td>91</td>
<td>0.59</td>
<td>3.1</td>
</tr>
<tr>
<td>DEC</td>
<td>-74.3</td>
<td>126</td>
<td>0.75</td>
<td>2.8</td>
</tr>
<tr>
<td>EMC</td>
<td>-53</td>
<td>110</td>
<td>0.65</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 1.3: Main characteristics of the commonest solvent used in lithium-ion batteries. $T_m$ is the melting temperature; $T_b$ is the boiling temperature; $\eta$ is the viscosity of the solvent; $\varepsilon$ is the relative dielectric constant. (a) Measured at 25 °C. (b) Measured at 40 °C. (Source ref. [21])

<table>
<thead>
<tr>
<th>Solute</th>
<th>$T_{\text{dec}} / ^\circ C$</th>
<th>$\sigma / \text{mS cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBF$_4$</td>
<td>$&gt; 100$</td>
<td>PC 3.4</td>
</tr>
<tr>
<td>LiPF$_6$</td>
<td>~ 80</td>
<td>5.8</td>
</tr>
<tr>
<td>LiAsF$_6$</td>
<td>$&gt; 100$</td>
<td>5.7</td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>$&gt; 100$</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Table 1.4: Main characteristics of the commonest solutes investigated in lithium-ion cells. $T_{\text{dec}}$ is the temperature of decomposition; $\sigma$ is the specific conductivity of the solute in the indicated solvents. (Source ref. [21])
2 Theoretical Background

The following paragraphs introduce the theoretical background of electrochemistry, mass spectrometry, and the techniques used during the PhD work. For further information on these themes, the textbooks cited at the end of the thesis are advised [83-86].

2.1 Electrochemistry

Electrochemistry concerns reduction/oxidation reactions (located at two different positions of the system) and/or accumulation of charged particles (ions and/or electrons). The simplest electrochemical system (also called electrochemical cell) is composed by two electron-conductive phases, the electrodes, separated by an ion-conductive phase, the electrolyte. The electrode at which the reduction occurs is called cathode. The electrode at which the oxidation occurs is called anode. Commonly, electrodes are solids or liquids which exchange electrons with the reactants and electrolytes are liquid solutions composed by a solvent and a dissolved ionic solute. Complex electrochemical systems can be constituted by other electron- and/or ion-conductive phases between electrode and electrolyte.

By contacting two phases, there is an exchange of the common species between them. This exchange proceeds until the chemical potentials of the common species in the two phases, \( \mu_i^\alpha \) and \( \mu_i^\beta \), are equal (equilibrium condition). In the case of charged species, the equilibrium condition is given by the equality of the electrochemical potentials, \( \mu_i^\alpha \) and \( \mu_i^\beta \) (see reference [83], chapter 3). The electrochemical potentials are dependent on the concentration of the species in the phase and the electric state of the phase. An electric potential difference between the two phases in contact is established because of the exchange of charged particles and orientation of the dipoles (see figure 2.1).

The charged particles are located near the boundary of the two phases: the interface. They form a high electric field between the two phases even if a small exchange occurs. This region of transition between the two phases in contact is called double layer, because it is formed at both sides of the boundary. The charge stored on one side is equal in value and
opposite in sign with respect to the charge stored on the other side. If one of the two phases is a liquid, there is a minimum distance that the solvated ions can reach, due to their solvation shell. This region of minimum distance, indicated with \( d_H \), is the so called Helmholtz plane. The region external to the Helmholtz plane is called the outer Helmholtz layer. The ions can be located at distances below \( d_H \). This region is called the inner Helmholtz layer. To enter into the inner Helmholtz layer, the ions have to lose partially or totally the solvation shell (see reference [83], chapter 4). Their physico-chemical condition is different with respect to their condition in the bulk of the electrolyte. The plane where the ions are adsorbed is called inner Helmholtz plane, indicated with \( d_i \) (see figure 2.1).

![Figure 2.1](image)

**Figure 2.1:** a) Representation of an electrochemical cell, with two solid electrodes and a liquid electrolyte separating them. b) Representation of the interface electrode / electrolyte; \( d_H \) is the Helmholtz plane and \( d_i \) is the inner Helmholtz plane. (Adapted from reference [83] figure 4.1)

The electrochemical reactions are classified in outer- and inner-sphere reactions, depending on the position of the ions which participate in the reaction. This classification is very important for the study of kinetics, because the two classes of reaction behave very differently. The outer-sphere reactions involve ions located in the outer Helmholtz layer. These are typically redox reactions, in which the ions change their valence state but still remain in the same phase, such as

\[
Fe^{3+}(\varepsilon) + e^-(\sigma) \rightarrow Fe^{2+}(\varepsilon)
\]

where \( \varepsilon \) is indicating the electrolyte phase and \( \sigma \) the electrode phase. In such reaction, the electrons have to tunnel through the inner Helmholtz layer. Because the tunnel probability
decreases with increasing distance, the reaction takes place mainly near the Helmholtz plane. Such reactions are normally fast and weakly influenced by the electrode material.

Inner-sphere reactions involve ions that are located in the inner Helmholtz plane. The reaction occurs with the change of the physico-chemical conditions and phase of the ions. Typical of this class of reaction is the electrochemical adsorption of a species, e.g., $H^+$,

$$H^+_{(e)} + e_{(g)} \xleftrightarrow{r} H^*_{(i)}$$

where $i$ is indicating the inner Helmholtz layer. Because the adsorption process is specific for the nature and the crystallographic structure of the solid phase, such reactions are strongly influenced by the choice of the electrode; the kinetic parameters can change several orders of magnitude. In this case one speaks about the electro-catalytic properties of the electrode. In general the inner-sphere reactions are slower than the outer-sphere reactions. Electrochemical insertion, intercalation and alloying are all processes involving inner-sphere mechanisms.

In an electrochemical system it is possible to control one more parameter with respect to the standard chemical systems: the potential difference between the two electrodes. The potential difference between the electrodes is generated by the equilibrium processes between each electrode and the electrolyte. By changing the potential difference with respect to the equilibrium value, electric current flows through the system. The current intensity is given by the number of electrons produced at the anode and consumed at the cathode, which means it is related to the rate of reaction. It is also possible to impose the current intensity, in which case the potential difference in the cell will change to adapt to the current flow. Independently from the experimental setup, it is only possible to impose one parameter between current intensity and potential difference; the other will be set consequently.

The commonly used experimental setups to study electrochemical systems are cyclic voltammetry and galvanostatic cycling. In cyclic voltammetry the potential difference is changed continuously with a fixed slope, called sweep rate. The sweep rate is changed in sign once a maximum or a minimum potential difference is reached. During such experiments, the current intensity is registered as function of the potential and, in general, the shape depends on the sweep rate. In galvanostatic cycling experiments the current intensity is imposed and constant. The potential will be registered as function of the total charge passed through the system. In general the shape of this curve is a function of the current intensity. Also in this
experiment, the current intensity is changed in sign once a maximum or a minimum potential difference is reached. The shape of such curves is related to the reaction mechanism, transport of the reactants from the bulk of the phase to the interface, and transport of the product in the opposite direction.

An electrochemical cell can implement other auxiliary electrodes. The simplest case is the use of a third electrode as a reference electrode. It is necessary when a reference potential is needed to study only one electrode, also called working electrode (see figure 2.2). The counter electrode is the electrode not connected to the reference electrode. The reference electrode has to maintain the same potential even if some current is flowing through it (ideally non-polarizable electrode). In a three electrode cell, the potential difference between working and reference electrode is registered or controlled, while the current flows mainly between working and counter electrode. By moving the reference electrode with respect to the working one, the potential distribution along the electrolyte could be measured, both in equilibrium and during current flow. In equilibrium condition, the bulk of the electrolyte is at constant potential, while in the electrolyte nearer to the electrodes there is a potential distribution, due to the accumulation of charged particles (see figure 2.2).

![Diagram of an electrochemical cell](image)

**Figure 2.2:** a) Representation of an electrochemical cell, containing working, counter and reference electrode. The potential difference between the working and the reference electrode is registered or controlled. The current flows between working and counter electrode. b) Representation of the potential distribution at the interface electrode / electrolyte. Electrolyte is considered to have $\phi = 0$. (Adapted from reference [83], figure 4.1)
Let us suppose the working electrode to be in an equilibrium condition (zero current) at a potential $E_{eq}$, to let some current flow through the interface electrode/electrolyte, the potential of the electrode has to change to a value $E$. The difference $E - E_{eq}$ is called overpotential, $\eta$. The overpotential represents the loss due to the current flow (non-equilibrium condition). There are different types of overpotentials. They can be divided in four different classes. The ohmic overpotential, or ohmic potential drop, is generated by the current flow in the bulk of the electrolyte, in the current collectors, in the solid electrode, and in the cables connected to the electrochemical cell, which have a finite value of the specific conductivity (ionic or electronic). It follows the Ohm law

$$\eta_{ohm} = \frac{I}{G_{el}}$$

where $G_{el}$ is the conductivity of the electrolyte and $I$ is the current intensity. The charge transfer overpotential, $\eta_{ct}$, is located at the interface electrode/electrolyte and is due to the kinetics of the electrochemical reaction. The relationship between the current density, $i$, and the charge transfer overpotential is given by the Butler-Volmer equation

$$i = i_0 \left[ \exp \left( \frac{\alpha nRT}{\eta_{ct}} \right) - \exp \left( \frac{(1-\alpha)nRT}{\eta_{ct}} \right) \right]$$

where $i_0$ is the exchange current density, $\alpha$ is the charge transfer coefficient (or symmetry coefficient), $n$ is the number of electrons involved in the step, $R$ is the gas universal constant, and $T$ is the absolute temperature. The mass transfer overpotential, $\eta_{m}$, is due to the consumption of the reactants at the surface of the electrode. Depleting the solution from the reactants will slow down the reaction rate and to maintain the same current density a higher potential will be necessary. The fourth class of overpotentials contains special cases, such as the deposition overpotential, generated during the electroplating of a metal and due to the fact that the deposition site of the metallic atom and the discharge site of the metallic ion are not the same (see reference [83], chapter 5).

The working principle of lithium-ion batteries involves inner-sphere mechanism, because the lithium has to pass from the electrolyte solution to the host material; the charge transfer overpotential influences the performance of the cell. Transport of lithium from one electrode to the other is also limiting the reaction rate, and high concentration gradient is generated during the charge and discharge; it is an intrinsic limitation due to the nature and
composition of the electrolyte. Finally, the electrolyte used in the lithium-ion batteries has a relatively low specific conductivity, about 0.01 S cm$^{-1}$. All the common classes of overpotentials are determining the performance of the battery.

Figure 2.3: Potential distribution in the different parts of the electrochemical cell at equilibrium conditions (---) and under current flow (?). a) Ohmic overpotential in the bulk of the electrolyte. b) Charge transfer overpotential in the interface electrode/electrolyte. c) Mass transfer overpotential in the interface electrode/electrolyte. d) Deposition overpotential in the inner Helmholtz layer. (See reference [83])

2.2 Mass Spectrometry

Mass spectrometry is a technique used in chemistry to study nature and composition of gaseous mixtures. It is based on the separation of ionized gaseous compounds according to mass/charge ratio (m/z or mass number). Commonly, the gaseous ions are produced in an ion source. The ions are then separated by application of an electric and/or magnetic field into the appropriate mass-charge groups. Finally, the ions are detected by a detector. In an ideal mass spectrometer the ion travels form source to detector without interactions with the other ions. To reach this condition, the pressure inside the mass spectrometer has to be lower than $10^{-5}$ mbar (see reference [85], chapter 8). There are several types of instruments and they are
classified in static and dynamic instruments. The former are based on constant electric and magnetic field, the latter on periodic electro-magnetic field (see reference [85], chapter 2).

The ion source has to produce the ion beam from gaseous molecules. There are some common features that an ideal ion source should posses. The produced ion beam has to be sufficiently intense for accurate measurements of the separated ions; the total intensity of the beam should reach $10^{-10}$ A (see reference [85], chapter 4). The ion beam has to be stable. The energy spread of the ion source has to be as low as possible, to obtain the highest resolving power. The intensity of the background signal produced by the ion source as to be as low as possible. The memory effect or cross contaminations between successive samples have to be reduced to the minimum. Mass discrimination has to be negligible (all the ions should have the same probability to enter the mass analyzer).

The most common ion source is the electron-impact source; it was also used during this PhD work. This source is very stable, has a low energy spread, and intensity of $10^{-9}$ A. It has the disadvantage to produce a quite intense background signal, due to residual gases. The gaseous molecules are ionized by impact with an electron beam. The produced ions depend on the energy of the electron beam. The threshold for ionization is the ionization potential of the molecule. If the energy is lower than it, no ionization occurs. At energies slightly above this threshold, ions of the corresponding molecule are produced (parent ions), mainly positive:

$$M + e^- = M^+ + 2e^-$$

where M indicates the gaseous molecule. If the energy of the electron beam is very high, the molecule can be fragmented, due to the instability of the ion produced:

$$M^+ = m_1^+ + m_2$$

where $m_1$ and $m_2$ are two fragments of the molecule M. It also happens that in the ionization process two fragments with opposite charge are formed:

$$M + e^- = m_1^+ + m_2^- + e^-$$

Some mass discrimination occurs in the source of this type, and is due to the trajectory of the ions and the exit slit, which separate the ion source from the mass analyzer. It is also possible to obtain ions with multiple charges.
The mass spectrometer used during this PhD work is a quadrupole mass spectrometer. The quadrupole mass spectrometer was developed by Paul et al. in 1955. The separation of the mass numbers takes place in a quadrupole, radio-frequency electric field. The ion injected in the quadrupole field start to oscillate. If the oscillations of the ion are stable, it can reach the detector. In the opposite case, the ion is deviated outside the quadrupole and strikes one of the electrodes. There is a region of stability, which depends on the values of the constant and alternate electric field generated by the quadrupole, the distance between the quadrupoles and the frequency of the alternate electric field. Also the shape of the electrodes is important in the determination of the stability window. In the original instrument of Paul and coworkers, the poles had a hyperbolic cross section. The stability region is represented in a diagram with the dimensionless parameters $A$ and $Q$:

$$A = \frac{8eU}{mr^2\omega^2} ; \quad Q = \frac{4eV}{mr^2\omega^2}$$  \hspace{1cm} (2.4)

where $U$ is the constant electric potential of the quadrupole, $V$ the r-f electric potential of the quadrupole, $r$ a dimension depending on the geometry of the system, and $\omega$ the angular frequency of the electric field.
frequency of the r-f electric potential (see reference [85], chapter 2). Constant values of A/Q define the resolution of the instrument, and changing \( \omega \) or U and V proportionally, the mass spectrum of the molecule is scanned (see figure 2.4). By increasing the ratio A/Q, the resolution of the instrument increases. There is a limit value of A/Q; all the ions are deviated outside the quadrupole at values above it. The shape of the peaks results trapezoidal at low resolution and triangular at high resolution. The detector of the quadrupole mass spectrometer is an electrical detector. The electrical detector collects the ion current, and amplifies it. In this way it is possible to detect ionic currents up to \( 10^{-15} \) A.

2.3 Differential Electrochemical Mass Spectrometry (DEMS)

The differential electrochemical mass spectrometry method (DEMS) allows the qualitative and quantitative analysis of the electrochemically developed gases in an electrochemical system, by using a mass spectrometer. The electrochemical cell is shifted from its equilibrium condition by changing the voltage of the cell (cyclic voltammetry) or applying a current intensity (galvanostatic cycling). If a reaction involving gaseous products takes place, the developed gases can be detected from the mass spectrometer. The mass spectrometer used is normally monoenergetic; it can detect the signal of one mass number per time. The intensity of the mass signal is registered continuously and correlated with the voltage of the cell (potential of the working electrode if a reference electrode is used).

It is possible to detect the intensity of many mass signals. In this way, a punctual mass spectrum can be obtained, which gives more information on the composition of the gaseous phase. The more mass signals are detected, the more precise is the mass spectrum, and the few points are registered in the time unit (loss of time resolution). An optimum between the resolution of the mass spectrum and of the time scale has to be found. A typical curve of the intensity of the mass signals vs. the potential (mass signal cyclic voltammogram, MSCV) or vs. the time (comparative plot) shows one or more peaks in a potential window where the mass signal is sensitive to a gas developed (see figure 2.5). Normally, mass spectroscopic cyclic voltammograms also report the current intensity flowing through the electrochemical cell, and comparative plots report several mass numbers and the voltage of the cell (or the potential of the working electrode).
The intensity of each mass signal has a background line, which depends on the mass number (see figure 2.5). This background intensity depends on three factors: the background intensity of the instrument (see the previous paragraph 2.2); the transport of the gaseous phase from the surface of the electrode to the mass spectrometer; and the presence of low boiling compounds in the electrolyte. Impurities and memory effects are also reflected in the signal, but the instrument and the setup for the experiment can be purged to minimize them. Generally, the higher is the background intensity, the lower is the resolution of the developed gasses. In extreme cases, the gas signal is not detectable due to the background intensity.

![Graph](image_url)

**Figure 2.5:** Comparative plot of the intensity of the mass signal $2$, $I_2$, for a graphite KS44 sample acquired during a cyclic voltammetry at 0.2 mV s$^{-1}$ in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte. The peaks indicate development of a gas in the potential window 0.5 – 0.01 V vs. Li/Li$^+$ at each cycle, while the value 0.15 nA can be assumed as the background intensity of mass signal $I_2$.

The background intensity of the instrument cannot be avoided. It depends on the mass number. It can be recorded and then subtracted by closing the instrument input and measuring the mass spectrum, once the equilibrium condition is reached. Its value will be normally constant. The background signal due to the transport of the gaseous phase depends on the
construction of the electrochemical cell. The gases can be sucked directly from the electrode, if a membrane impermeable to the liquid electrolyte is used, or are removed continuously from the top of the electrochemical cell. In both cases the flux of a carrier gas is needed. The carrier gas generates a mass spectrum which adds to the instrument background intensity. This background intensity is proportional to the concentration of the carrier gas in the gas flux. If a concentration of few tenth or hundreds ppm of electrochemically developed gases has to be measured, the concentration of the carrier gas remains constant and also the background signal. The background signal due to the carrier gas can be calculated. If low boiling compounds are present in the electrolyte, they are also removed continuously from the cell and injected into the mass spectrometer. The vapors of the solvents of the electrolyte results in another part of the background intensity. The intensity of the background depends on the amount of evaporated solvent. Very precise instruments will be affected also by high boiling solvents. Depending on the solvents of the electrolyte, the intensity of this background can be intense and hide the detection of some important products.

Generally, the background intensity is defined by hand and then subtracted. During this thesis work, an analytical procedure to eliminate the influence of the background intensity was developed. If the pressure in the mass spectrometer is lower than $10^{-5}$ mbar, the ions in the ion beam are not interacting (see reference [85], chapter 8). In this case the total intensity of the mass signals observed is the sum of the background intensity of the instrument and the number of molecules generating that mass number times the sensitivity of the molecule to that mass number (see reference [85], chapter 9):

$$I_m(t) = B_m + P_{IS}(t) \left[ \sum_{i=0}^{N-1} y_i(t) S_{i,m} \right]$$

(2.5)

where $I_m$ is the intensity of the mass signal $m$, $B_m$ the background signal of the instrument for mass number $m$, $P_{IS}$ the pressure inside the ion source, $y_i$ the molar fraction of the $i$-th molecule, $S_{i,m}$ the sensitivity factor of the $i$-th molecule with respect to the mass number $m$, and $N$ the total number of species in the gaseous phase. It is known that the sum of the molar fractions is equal to 1. If the carrier gas is taken as reference, and indicated with the index 0, eq. (2.5) is rewritten as:

$$J_m(t) = \frac{I_m(t) - B_m}{P_{IS}(t)} = S_{0,m} + \sum_{i=1}^{N-1} y_i(t) (S_{i,m} - S_{0,m})$$

(2.6)
S\textsubscript{0,m} can be evaluated by injecting the pure carrier gas in the mass spectrometer and measuring the mass spectrum; it is independent from the time. If S\textsubscript{0,m} is known, it can be subtracted from the intensity of the mass signal:

\[ J_m(t) - S_{0,m} = \sum_{i=1}^{N} y_i(t) (S_{i,m} - S_{0,m}) \]  

(2.7)

In this way it is possible to keep the DEMS measurement free from the background signal due to the instrument and the gas carrier. The intensities obtained by eq. (2.7) are still affected by the signal of the evaporated solvents, which is changing in time. By giving the index 1 to the electrolyte solvent, eq. (2.7) is written as:

\[ J_m(t) - S_{0,m} = y_1(t) (S_{1,m} - S_{0,m}) + \sum_{i=2}^{N} y_i(t) (S_{i,m} - S_{0,m}) \]  

(2.8)

To eliminate the background intensity of the solvent of the electrolyte, it is necessary to find a mass number m that is not influenced by the electrochemically developed gases and the carrier gas, i.e. S\textsubscript{i,m} and S\textsubscript{0,m} equal to 0. In this case it results:

\[ y_i(t) = \frac{J_{m'}(t)}{S_{1,m'}} \]  

(2.9)

At a time t\textsubscript{0} after the purging of the cell and before starting the electrochemical test, the y\textquotesingle s are equal to 0:

\[ J_m(t_0) - S_{0,m} = y_1(t_0) (S_{1,m} - S_{0,m}) \]  

(2.10)

Finally, the value of the background intensity due to the solvent is equal to:

\[ y_1(t_0) (S_{1,m} - S_{0,m}) \frac{y_1(t_0)}{y_1(t_0)} = \left[ J_m(t_0) - S_{0,m} \right] \frac{J_m(t)}{J_{m'}(t_0)} \]  

(2.11)

By substitution of eq. (2.11) in eq. (2.8), the signal of the developed gases can be separated by the other part of the signal. This analytical procedure eliminates at least 95% of the background line. The remaining part of the background signal has to be subtracted by hand. It is due to unknown molecules and/or residual memory effects.

The signals J\textsubscript{m} with the background intensity subtracted have to be transformed into the values of the y\textquotesingle s. It is necessary to know the values S\textsubscript{i,m}. This step needs a calibration of the instrument. A calibration is required every time the settings of the ion source are changed, because the sensitivity factors depend on them. The calibration is performed by injecting in
the mass spectrometer the \(i\)th gas is known concentration. If only the \(i\)th gas and the gas carrier are injected in the mass spectrometer, eq. (2.8) becomes:

\[
J_m(t) = S_{0,m} + y_i(t)(S_{i,m} - S_{0,m})
\]  

(2.12)

The signal of several mass numbers can be measured for different concentrations of the \(i\)th gas. A linear regression of the data gives the value of \(S_{i,m}\) (see figure 2.6). As can be observed from figure 2.6, eq. (2.12) correctly predicts the linear behavior of the calibration curve.

The quantitative analysis of the developed gas can be carried out only if the temperature, the pressure, and the gas flux in the electrochemical cell are known. If it is the case, the law of the ideal gases gives the correlation between the number of moles per time unit of the \(i\)th gas and the molar fraction \(y_i\). There is a time delay between the time at which the gas is generated and the time at which it is detected. By increasing the gas flux rate, the time delay decreases, but contemporaneously the gas concentration in the flux is lower (loss of resolution). The best compromise has to be found and depends on the experimental setup.

![Figure 2.6: Calibration curve of oxygen in argon as carrier gas for the mass number m/z = 32. The sensitivity factor \(S_{32}(O_2)\) is equal to \(4.67 \times 10^{-8}\) nA. This value can change with the settings of the ion source.](image-url)
2.4 Electrochemical Impedance Spectroscopy

By using the electrochemical impedance spectroscopy technique (EIS), information on the electrochemical reactions in the system and transport of reactants/products is obtained. This technique is applied on an electrochemical system which is in equilibrium or under steady state conditions. EIS is based on the application of a sinusoidal voltage (or current) signal on the electrochemical cell. The response of the cell to the sinusoidal perturbation is a sinusoidal current (or voltage), which has the same frequency as the perturbation and is normally shifted in phase. It is possible to transform the voltage perturbation and the current response in the Euler representation. The ratio between the perturbation and the answer is a frequency-dependent complex number, called impedance.

\[
\frac{Z_1}{Z_4} = \frac{Z_2}{Z_3}
\]

Figure 2.7: Schematic representation of an impedance bridge. The balancing arm \( Z_2 \) can be modified, while \( Z_1 \) is the arm with unknown impedance. When the current flowing through the amperometer \( A \) is equal to 0, the balancing condition is reached.

The first instrument used to measure the impedance of an electrochemical cell was the impedance bridge (or universal bridge) (see reference [86], chapter 3). The basic principle of an impedance bridge is similar to the principle of a balance comparing unknowns with their built-in standards. The balance is established by adjusting the balancing arm manually. Once the balancing condition is reached, the current flowing across the bridge is equal to 0 (see figure 2.7). In the last century, this method was used, e.g., to measure the impedance of the electrolyte solutions. The method is very time consuming, because the balancing arm has to
be adjusted manually, and in practice more than 60 points are required to obtain a good impedance spectra in a standard frequency range.

Modern instruments to measure impedance spectra are the frequency response analyzers (FRA), commercially available since the 1970's. The oldest FRA’s were external instruments to connect to a potentiostat, while the modern ones are directly integrated in the potentiostats. The working principle of the FRA is normally the Fourier analysis of a periodic signal. Electrochemical systems are typically not linear systems with respect to the potential. For this reason, if a sinusoidal voltage perturbation is applied to the cell, the current response will be periodic, with the same period of the perturbing signal, but not sinusoidal. By reducing the amplitude of the voltage perturbation, it is possible to reduce the non-linearity of the system. If the signal is reduced too much, the current response will be too noisy to be detected. Under the conditions of a standard electrochemical experiment, a good compromise between the two conditions is the AC voltage amplitude of 10 mV. The Fourier series decomposes a periodic function \( S \) in a series of sinusoidal functions (see reference [86], chapter 3):

\[
S(t) = \sum_{n=0}^{\infty} [a_n \cos(n \omega t) + b_n \sin(n \omega t)]
\]

where \( T \) is the period of the function \( S \), \( \omega \) the angular frequency of the function \( S \), and \( n \) is the order of the harmonic. The FRA performs the Fourier analysis on the applied voltage perturbation and on the measured current response, and it calculates the first (and/or higher) harmonic for both signals by integrating for one or more periods. The value of the impedance at angular frequency \( \omega \), \( Z(j \omega) \) is equal to:

\[
Z(j \omega) = |Z(\omega)| e^{-j \theta(\omega)}
\]

\[
|Z(\omega)| = \sqrt{a_{1,\varphi}^2 + b_{1,\varphi}^2}
\]

\[
\theta(\omega) = \tan^{-1} \left( \frac{a_{1,J}}{b_{1,J}} \right)
\]

where the index \( \varphi \) refers to the voltage perturbation, and \( I \) to the current response. The FRA can calculate also the harmonics of higher order. Under standard conditions they are
negligible. If the voltage amplitude higher than 20 mV is used, the second order harmonic can be normally measured, and it gives more information about the symmetry of the electrochemical processes.

![Graphical representation of simulated impedance data at different value of the amplitude of the perturbation (namely 10 mV and 50 mV) and simulated model describing the electrochemical system. The simulated system is a single electrode at which a redox reaction occurs. The mass transport was neglected. The parameter used for the simulation are: resistance of electrolyte equal to 3 Ω, the charge transfer resistance equal to 11 Ω, and the double layer capacitance equal to 20 µF.](image)

In figure 2.8 an electrochemical system is simulated, using the resistance of the electrolyte equal to 3 Ω, the charge transfer resistance equal to 11 Ω, and the double layer capacitance equal to 20 µF. By increasing the amplitude of the perturbation, the value of the impedance decreases (see figure 2.8). This effect is due to the exponential dependence of the
current on the potential drop and it influences only the absolute values of the impedance data; the shape of the impedance data (phase shift) is independent from the amplitude of the perturbation. In the first oscillation of the sinusoidal perturbation, the system is not stabilized and the current response shows a not periodic behavior for some oscillations (generally the first three). This is another non-linear effect, which can be eliminated by waiting some oscillations of the voltage perturbation (delay time) before the integration of the current response.

The value of the impedance is registered for numerous frequencies. At each frequency, the FRA has to perform one or more oscillations of the voltage perturbation (generally at least three plus the delay time). At high frequencies (above 1 Hz) the procedure is very fast. When the frequency is below 10 mHz, each frequency requires more than 5 minutes, and the time scale can shift to hours for frequencies below 1 mHz. The fast Fourier transform (FFT) was implemented in most of the modern FRA's to shorten the time needed for the measurements at low frequencies. The periodic voltage perturbation applied to the electrochemical system is a sum of several sinusoidal voltage perturbations at different frequencies. The input and output signals are then decomposed and the first harmonic of each signal is calculated. The disadvantage of the FFT method consists in the interferences that can rise from the interaction of a higher harmonic of a low frequency perturbation with the first harmonic of a high frequency perturbation.

In a standard EIS experiment, the impedance of the system is registered in the frequency range 100 kHz – 100 mHz. Above this frequency range there are normally serious distortion problems due to the geometry of the cell and the interaction of the cables of the instrument with the measurement (inductivity of the cables and antenna effect). To avoid distortions of the measured impedance due to the antenna effect of the cell, it is useful to put the cell and the cables in a Faraday cage. At very high frequencies the two electrodes behave as the plates of a capacitor, and the electrolyte is the dielectric medium. Also the electrolyte contributes to the distortions, because of high frequency effects (Debye-Falkenhagen effect) (see reference [83], chapter 2). The standard frequency range explores the main features of the electrochemical system, which have a time constant between $10^{-5}$ and 10 s. The lower is the investigated frequency, the slower are the phenomena observed. Below the standard frequency range secondary reactions are sometimes observed. In this frequency domain, it is very important to
ensure a constant temperature and pressure of the cell, and very stable conditions of the current lines. Solid-state diffusion can require very long time to be observed, depending on the dimension of the particles, and experiments are performed over a period of several days at frequencies down to 10 µHz.

Using the complex representation of Euler for a sinusoidal function, the measured impedance, $Z_m$, can be written as:

$$Z_m(j\omega) = \frac{\Delta \varphi_m}{I_m(j\omega)}$$

(2.15)

where $\Delta \varphi_m$ is the amplitude of the perturbation and $I_m$ the complex number representing the amplitude and shift in phase of the current response. If a two electrode configuration is used (see figure 2.9 a), $Z_m$ is the impedance of the whole cell. Preferably a single electrode is studied, the so called working electrode. In this case a three electrode configuration has to be used (see figure 2.9 b). The introduction of the third electrode changes the position at which the voltage perturbation is applied, and therefore also the meaning of the measured impedance. The three electrode cell can be divided in five basic parts: the working electrode; the electrolyte between the working and the reference electrode; the reference electrode; the electrolyte between the reference and the counter electrode; the counter electrode. If the reference electrode has an ideal behavior, the current flowing from the working electrode to the reference electrode is 0 (see figure 2.9 b). In this case the obtained impedance value is referred only to the impedance of the working electrode. In general, some current can flow through the reference electrode. In this case the impedance measured will be equal to:

$$Z_m = Z_{WE} + \left(Z_{WE} + Z_{RE}\right)\frac{I_{WR}}{I_{WC}}$$

(2.16)

The current flowing through the reference electrode depends on the input impedance of the potentiostat, $Z_{PS}$, which measures the potential difference $\Delta \varphi_m = \Delta \varphi_{WE} - \Delta \varphi_{RE}$. The presence of a reference electrode introduces a distortion due to the current flowing through it and to its polarizability. If the potentiostat has very high input impedance, the distortion is negligible.
Figure 2.9: Distribution of the potential drops in an electrochemical system with three electrodes. In an ideal case, the current $I_{WR}$ is 0. The observed current is $I_{WC}$, and the observed potential is $\Delta \phi_m = \Delta \phi_{WE} - \Delta \phi_{RE}$. The total voltage of the electrochemical cell is $\Delta \phi_T = \Delta \phi_{WE} - \Delta \phi_{CE}$. (Based on reference [86], chapter 3)

The current flowing through the potentiostat, $I_{WR}$, and the total voltage of the cell, $\Delta \phi_T$, are expressed as:

$$I_{WR} = \frac{\Delta \phi_m}{Z_{PS}} ; \quad \Delta \phi_T = (Z_{WE} + Z_{CE})I_{WC} + Z_{WE}I_{WR} \quad (2.17)$$

Substitution of eq. (2.17) in eq. (2.16) gives:

$$Z_m = Z_{WE} + (Z_{WE} + Z_{RE})\frac{\Delta \phi_m (Z_{WE} + Z_{CE})}{\Delta \phi_T Z_{PS} - \Delta \phi_m Z_{WE}} \quad (2.18)$$

To avoid distortions due to the presence of the reference electrode, it is necessary to use some precautions: a potentiostat with input impedance significantly higher than the impedance of the working electrode has to be used; the impedance of the counter electrode has to be low, and the impedance of the reference electrode has to be low. When a two electrode configuration cell is used, eq. (2.18) is transformed in:

$$Z_m = \frac{Z_{PS} (Z_{WE} + Z_{CE})}{Z_{PS} - (Z_{WE} + Z_{CE})} \quad (2.19)$$

In this case, a potentiostat with input impedance significantly higher than the impedance of the electrochemical cell is necessary to avoid distortions of the impedance data. The prediction of the distortions was performed considering the cell one-dimensional. In a real three-dimensional cell there are also distortions generated by the position of the reference
electrode. In particular, it is compulsory that the reference electrode is located externally to
the main current path, between the working and the counter electrode. Also the relative
position of working and counter electrode and the geometry of the cell can influence the
behavior of the system at high frequencies [87].

The value of the impedance is a complex number, which is dependent on the frequency
of the voltage perturbation. There are different graphical representations of a set of impedance
data. The most common representation is the Nyquist plot. The Nyquist plot shows in the x-
axis the real part of the impedance and in the y-axis the opposite of the imaginary part of the
impedance. It is important that the x-axis and y-axis have the same scale length. The shape of
the Nyquist plot is representative of the electrochemical processes at the surface of the
electrodes and in the bulk of the electrolyte. It is possible to recognize immediately the
resistance of the electrolyte, the resistance of the charge transfer, and other properties of the
system. Moreover, the kinetic parameters can be obtained from the plot in the case of simple
redox systems. The disadvantages of the Nyquist plot are related with the values of the
impedance data. Generally, the real and imaginary part of impedance can change of some
orders of magnitude in the frequency range 100 kHz – 100 mHz. An enlargement of the high
frequency region is necessary to recognize the electrochemical processes. The Bode plot
reports separately the decimal logarithm of the absolute value of the impedance and the phase
shift as function of the frequency. With this plot the values of the impedance are evident in
the whole range of frequency; the phase shift is related to the electrochemical and transport
processes, but the connection between phase shift and processes is not as obvious as in a
Nyquist plot. The Cole-Cole plot reports the complex capacitance of the system. The complex
capacitance is obtained from the impedance by the following transformation:

\[
C'(j\omega) = [j\omega Z(j\omega)]^{-1}
\]

The Cole-Cole plot is the equivalent of the Nyquist plot for the complex capacitance. It
reports the real part of the complex capacitance versus the negative imaginary part of the
complex capacitance. In this plot the adsorption/desorption processes are evidenced, while the
faradaic processes are darkened (see reference [86], chapter 1). The three plots are represented
in figure 2.10 for the electrochemical system simulated in figure 2.8.
The analysis of impedance data is the most challenging part of the EIS technique. The Kramers-Kronig transformations (KK transformations) relate the imaginary part of the impedance, $Z_{\text{Im}}$, at a single frequency with the complete set of real values of impedance, $Z_{\text{Re}}$, and vice versa:

$$Z_{\text{Im}}(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{Z_{\text{Re}}(x) - Z_{\text{Re}}(\omega)}{x^2 - \omega^2} \, dx$$

$$Z_{\text{Re}}(\omega) = R_\infty + \frac{2}{\pi} \int_0^\infty \frac{xZ_{\text{Im}}(x) - \omega Z_{\text{Im}}(\omega)}{x^2 - \omega^2} \, dx \tag{2.21}$$

Figure 2.10: Graphical representations of simulated impedance spectra. The parameter used for the simulation are: resistance of electrolyte equal to 3 $\Omega$, the charge transfer resistance equal to 11 $\Omega$, and the double layer capacitance equal to 20 $\mu$F. a) Nyquist plot. b) Cole-Cole plot. c) Bode plot.
where \( R_\infty \) is the resistance at infinite frequency. Eqs. (2.21) are valid if the system fulfills the conditions of stability, linearity and causality. The Kramer-Kronig analysis (KK analysis) is based on eqs. (2.21); it individuates and eliminates the non-linear, instable and stochastic effects from the set of measured impedance data. After this analysis, the quality of the fitting increase notably. To perform the KK analysis, the whole set of impedance data, from 0 to infinite frequency, should be available. To overcome the problem, a general model to describe the impedance spectrum is used. This model describes the impedance spectra as an infinite series of a resistance and a capacitance in parallel (see figure 2.11). Each element can be described by a time constant, \( \tau \), and a weighting factor \( G(\tau) \) [88]:

\[
Z_A(j\omega) = R_0 \int_0^{\infty} \frac{G(\tau)d\tau}{1 + j\omega \tau}
\]  

(2.22)

where \( R_0 \) is the resistance at 0 frequency. \( G(\tau) \) is the spectrum of the time constant of the system. The model described by eq. (2.22) respects the KK transformations. The data obtained by the fitting of the measured data with eq. (2.22), \( Z_A \), are used in a fitting routine with the model describing the electrochemical processes. The goal of deriving eq. (2.22) is to transform the measured data in another format. Eq. (2.22) requires an infinite distribution of time constant. From its expression, it is clear that the weighting factors of the time constant much lower or much higher than \( 1/\omega \) do not influence the final value of the impedance. It is sufficient to create a set of time constants which range from \( 10/\omega_{\text{min}} \) to \( 0.1/\omega_{\text{max}} \). For electrochemical systems with non-faradaic processes (the time constant of the electrochemical process is very high) the model described by eq. (2.22) needs a broader range of the time constants. Alternatively, an infinite parallel of a resistance in series with a capacitor can be used (see figure 2.11). This general model can be described by:

\[
Z_A(j\omega) = \frac{R_0}{\int_0^{\infty} \frac{j\omega \tau}{1 + j\omega \tau} G_p(\tau)d\tau}
\]  

(2.23)

The weighting factor \( G_p \) is the spectrum of time constant of the system. Eq. (2.23) can be used in the same way of eq. (2.22) to obtain data free from the effect of non-linearity, instability, and non-causality.
The kinetic parameters of the investigated systems can be obtained by fitting the impedance data, measured or after the KKT analysis, with a model. Sometimes the model can be described by a connection in parallel and series of simple elemental circuits, such as capacitances and resistances (equivalent circuit). This point of view helps in understanding the physico-chemical phenomena occurring during the overall reaction. The equivalent circuit is useful only as a visualization of the mathematical description of the model. Several models were developed during this PhD work and they are presented in the following chapter 3. To fit a model to a set of impedance data, it is necessary to define an object function, which has to be minimized. A general object function, $f_O$, for complex data can be defined as:

$$f_O = \sum_{i=1}^{N} \left\{ w_{Re,i} \left[ Z_{Re}(\omega_i) - Z_{m,Re,i} \right]^2 + w_{Im,i} \left[ Z_{Im}(\omega_i) - Z_{m,Im,i} \right]^2 \right\}$$  \hspace{1cm} (2.24)$$

where $w_{Re,i}$ and $w_{Im,i}$ are the weighting factors of the i-th point for the real and imaginary part of the impedance respectively. In this PhD work two object functions were defined. The first is in common use; it is indicated as $\chi^2$ and is equal to:

$$\chi^2 = \frac{1}{N - N_p} \sum_{i=1}^{N} \left\{ \frac{\left[ Z_{Re}(\omega_i) - Z_{m,Re,i} \right]^2 + \left[ Z_{Im}(\omega_i) - Z_{m,Im,i} \right]^2}{Z_{m,Re,i}^2 + Z_{m,Im,i}^2} \right\}$$  \hspace{1cm} (2.25)$$

Figure 2.11: Equivalent circuits of the general models represented by eq. (2.22) (a) and by eq. (2.23) (b) [88].
where $N$ is the number of points of the set of impedance data, $N_p$ the number of parameters in the model (see reference [86], chapter 3). The second object function was indicated as $\chi^2_{\text{mod}}$ and defined as:

$$\chi^2_{\text{mod}} = \frac{1}{2(N - N_p)} \sum_{i=1}^{N} \left\{ \left[ \frac{Z_{\text{Re}}(\omega_i) - Z_{m,\text{Re},i}}{Z_{m,\text{Re},i}} \right]^2 + \left[ \frac{Z_{\text{Im}}(\omega_i) - Z_{m,\text{Im},i}}{Z_{m,\text{Im},i}} \right]^2 \right\}$$

(2.26)

The fitting routine was always performed with the object function $\chi^2_{\text{mod}}$, and $\chi^2$ was used to verify the goodness of the fitting. In general it seems that $\chi^2$ is always smaller than $\chi^2_{\text{mod}}$. The better is the fitting, the nearer are the two numbers.
3 Development of the Mathematical Models

EIS technique is a powerful tool for the study of the kinetics of electrochemical systems. It has a high time resolution (up to $10^{-5}$ s), and it can be used for the study of the electrochemical processes and the spatial distribution of current densities. The high time resolution is contemporary the weak point of the EIS technique; the analysis of impedance data requires the development of sufficiently precise mathematical models. Even if a model can be visualized through an equivalent circuit, it is not true that every equivalent circuit corresponds to a physical model. The model describing the electrochemical system has to satisfy the physico-chemical equations for the reaction rate, for the accumulation of species (charged and neutral), and for the geometry of the system. In the following chapter the models developed during this PhD work are presented. The models are expressed in the time domain. The EIS experiment is simulated by starting from an equilibrium condition of the system. A sinusoidal voltage perturbation is applied to the equilibrium condition. The impedance of the model is obtained considering all the time-dependent physical variables to change sinusoidally with the same frequency of the voltage perturbation. The alternate part of a physical variable is indicated with the symbol $\sim$, and it is treated as a differential of the variable itself. At the end of the thesis a list of the used symbols is given.

3.1 Model of the Intercalation Process

In this paragraph the intercalation process is treated as a two step mechanism. The first step is the adsorption of the intercalating ion; the second step is the accommodation of the species in the structure of the electrode. The valence state of the intercalating ion in the solution and in the structure of the electrode can be different. The real valence state of the intercalated ion in the structure of the electrode depends on the nature of the electrode. During the adsorption the ion can also change its valence state, depending if an electrochemical adsorption or an ion sorption occurs; it could be also possible to have a distribution of electrochemical adsorption and ion sorption. Because both adsorbing processes are inner-sphere reactions, the average charge of the lithium in the inner Helmholtz plane depends on
the properties of the surface of the electrode. This detail strongly influences the polarizability of the electrode.

The first step is assumed to be a distribution of electrochemical adsorption and ion sorption. In the second step a distribution of the charge of the intercalated species in the solid phase is considered. The kinetic parameters describing the system are average values. The intercalation of lithium is explicitly considered; the model can readily be extended to other cases. The adsorption of the lithium and the accommodation of the lithium in the structure of the electrode are described by the following electrochemical reactions:

\[ \text{Li}^{+}(\varepsilon) + (1 - \delta_1) \epsilon^{(o)} \xrightarrow[k_{1,o}]{k_{1,R}} \text{Li}^{\delta_1 +} (3.1) \]

\[ \text{Li}^{\delta_1 +} (\sigma) + (\delta_1 - \delta_2) \epsilon^{(o)} \xrightarrow[k_{2,o}]{k_{2,R}} \text{Li}^{\delta_2 +} (3.2) \]

where \( \varepsilon \) represents the electrolyte phase, \( i \) the inner Helmholtz plane, \( \sigma \) the solid phase, \( \delta_1 \) the average valence state of the lithium in the inner Helmholtz plane, \( \delta_2 \) the average valence state of the lithium inside the solid phase (\( \delta_2 = \delta_1 \)). Both ion sorption and electrochemical adsorption are described by the reaction (3.1) (\( \delta_1 = 1 \), ion sorption; \( \delta_1 = 0 \), electrochemical adsorption).

The rates of reaction of the two steps, \( r_1 \) and \( r_2 \), are treated with the kinetic theory of standard chemical reactions; the effect of the potential drop is included in the kinetic coefficients. It is considered that the lithium cannot move in an occupied adsorbing or intercalating site:

\[ r_1 = C_\varepsilon (1 - \theta) k_{1,R} - N_i \theta k_{1,o} \]

\[ r_2 = N_i \theta (1 - \beta_0) k_{2,R} - N_\sigma \beta_0 (1 - \theta) k_{2,o} \]

(3.3)

where \( C_\varepsilon \) is the concentration of lithium ions in the solution, \( N_i \) the number of absorbing sites available, \( \theta \) the occupancy of the absorbing sites, \( N_\sigma \) the number of intercalation sites available, \( \beta_0 \) the occupancy of the intercalating sites at the interface solid/electrolyte. The current density flow, \( i \), at the interface solid/electrolyte is expressed by (see figure 3.1):

\[ i = -F\lambda r_1 + C_1 \frac{d\Delta \varphi_i}{dt} = -\delta_1 F\lambda r_2 - (1 - \delta_1) F\lambda r_1 + C_2 \frac{d(\Delta \varphi_i - \Delta \varphi_j)}{dt} \]

(3.4)
where $C_1$ and $C_2$ are the double layer capacitance of the electrolyte and solid phase respectively, $\lambda$ the jumping distance, and $\Delta \phi_i$ the potential drop in the inner Helmholtz plane. The term $-(1-\delta_1)F\lambda r_1$ rises from the tunneling of the electrons from the solid phase to the inner Helmholtz plane, due to reaction $r_1$ (see figure 3.1). The mass balances of $\theta$ and $\beta$ are:

$$\frac{d\theta}{dt} = r_1 - r_2$$
$$N_0 \frac{d\beta}{dt} = -\frac{\partial j_\beta}{\partial x} + G(x, t)$$  \hspace{1cm} (3.5)

where $j_\beta$ is the transport of lithium in the solid phase, and $G$ the generation (trapping) of lithium from Li containing species in the solid phase. Both transport and generation of lithium depend on the transport mechanism in the solid phase. It is discussed at the end of this paragraph.

![Figure 3.1](image-url)

**Figure 3.1:** (a) Potential distribution at the interface solid phase/electrolyte. $\Delta \phi_i$ is the potential drop in the inner Helmholtz plane. The potential drop in the solid phase was neglected. (b) Graphical representation of the current flow through the interface solid phase/electrolyte.

From the kinetic reactions (3.1) and (3.2) the relationship between the potential drop in the inner Helmholtz plane and the potential drops influencing the reaction rates $r_1$ and $r_2$, $\Delta \phi_1$ and $\Delta \phi_2$, respectively, are obtained:

$$\Delta \phi_1 = \Delta \phi_T - \delta_1 (\Delta \phi_T - \Delta \phi_i)$$
$$\Delta \phi_2 = \delta_1 (\Delta \phi_T - \Delta \phi_i)$$  \hspace{1cm} (3.6)

The kinetic constants of the electrochemical reactions are equal to:
\[ k_{1,R} = k_{1,R,0} \exp \left( -\frac{F\Delta\phi_i}{2RT} \right) \]
\[ k_{1,O} = k_{1,O,0} \exp \left( \frac{F\Delta\phi_i}{2RT} \right) \]
\[ k_{2,R} = k_{2,R,0} \exp \left( -\frac{F\Delta\phi_2}{2RT} \right) \]
\[ k_{2,O} = k_{2,O,0} \exp \left( \frac{F\Delta\phi_2}{2RT} \right) \]

The expressions for the kinetic constants (3.7) derive from the adiabatic electron transfer theory, assuming the transfer coefficients equal to 0.5 (see reference [83], chapter 5). The last assumption is not necessary, but simplifies the mathematical development of the model.

The influence of the occupancy of the adsorbing sites on the distribution of potential drops at the interface solid phase/electrolyte is obtained by eqs. (3.4-3.6):

\[ d\Delta\phi_i = \gamma d\Delta\phi_T + \delta_i \gamma_i \frac{RT}{F} d\theta \]  

(3.8)

with the parameters \( \gamma \), and \( \gamma_i \) equal to:

\[ \gamma = \frac{C_2}{C_1 + C_2} \]; \[ \gamma_i = \frac{C_i}{C_1 + C_2} \]

(3.9)

Eq. (3.8) means: if the ions adsorbed are neutral (electrochemical adsorption), the potential in the inner Helmholtz plane is always proportional to the total potential drop; if the ions adsorbed are charged (ion sorption), the potential in the inner Helmholtz plane depends also on the occupancy of the adsorbing sites. In the latter case, the effect causes always the decrease of the reaction rate. At \( \theta = 0 \), \( \Delta\phi_i \) is proportional to \( \Delta\phi_T \). The integral form of eq. (3.8) is:

\[ \Delta\phi_i = \gamma \Delta\phi_T + \delta_i \gamma_i \frac{RT}{F} \theta \]  

(3.10)

Eq. (3.10) can be substituted in eq. (3.6) and the whole intercalation mechanism at the interface solid phase/electrolyte be described by three equations (excluding the transport of lithium in the electrolyte and in the solid phase).

In equilibrium conditions the time derivatives are equal to 0 and the current flowing through the system is 0. The value \( \beta_0 \) is equal to:

\[ \beta_0 = \frac{1}{1 + \frac{N_0 k_{1,0,0} k_{2,0,0}}{C_i k_{1,0,0} k_{2,0,0}} \exp \left[ \frac{F\Delta\phi_T}{RT} \right]} \]  

(3.11)

Eq. (3.11) regards only the surface of the intercalating electrode; the bulk concentration and the total amount of intercalated lithium depend on the expression of the mass balance.
(transport and trapping term). The occupancy of the adsorbing sites depends on the potential applied and on the mechanism of adsorption. The differential of $\theta$ with respect to the total potential drop at the interface solid phase/electrolyte is equal to:

$$\frac{RT}{F} \frac{d\theta}{d\Delta \Phi_T} = -\frac{(1 - \delta_i + \delta_i' \gamma)\theta(1 - \theta)}{1 + \theta(1 - \theta)\delta_i' \gamma_i}$$

(3.12)

Eq. (3.12) is valid in equilibrium conditions. The charge accumulated in the surface of the electrode is negligible with respect to the total one; therefore the shape of the equilibrium curves (3.11) and (3.12) cannot be observed in intercalating compounds.

If a voltage perturbation is applied to the system, the alternate part of the reaction rates can be expressed by their differentials. It results:

$$\tilde{\lambda}_s = \frac{1}{F \lambda} \left[ -\frac{1 - \Gamma}{R_1} \Delta \Phi_T - k_{1,0} \tilde{\theta} + k_\epsilon \tilde{C}_\epsilon \right]$$

$$\tilde{\lambda}_r = \frac{1}{F \lambda} \left[ -\frac{\Gamma}{R_2} \Delta \Phi_T + k_{2,0} \tilde{\theta} - k_\beta \tilde{\beta}_0 \right]$$

(3.13)

where $\Gamma$ is equal to $\delta_i(1-\gamma)$. The coefficients in eqs. (3.13) are obtained by the partial derivative of the reaction rates with respect to the considered alternate variable:

$$\frac{1}{R_1} = (C_\epsilon k_{1,R} + N_i k_{1,O}) \theta(1 - \theta) \frac{F}{RT} \lambda$$

$$k_{1,0} = (C_\epsilon k_{1,R} + N_i k_{1,O}) \left[ 1 + \theta(1 - \theta)\delta_i' \gamma_i \right] \frac{F \lambda}{R_1}$$

$$k_\epsilon = (1 - \theta)k_{1,R} F \lambda$$

$$\frac{1}{R_2} = [N_i (1 - \beta_0) k_{2,R} + N_\alpha \beta_0 k_{2,O}] \theta(1 - \theta) \frac{F}{RT} \lambda$$

$$k_{2,0} = [N_i (1 - \beta_0) k_{2,R} + N_\alpha \beta_0 k_{2,O}] \left[ 1 + \theta(1 - \theta)\delta_i' \gamma_i \right] \frac{F \lambda}{R_2}$$

$$k_\beta = -[N_i \theta k_{2,R} + N_\alpha (1 - \theta) k_{2,O}] \frac{F \lambda}{R_2}$$

(3.14)

The value of $\theta$ is obtained substituting eqs. (3.13) in the mass balance of the absorbing sites:

$$\tilde{\theta} = \left( \frac{\Gamma}{R_2} - \frac{1 - \Gamma}{R_1} \right) \frac{\Delta \Phi_T}{(k_{1,0} + k_{2,0}) [j \omega \tau + 1]} + k_{\beta} \tilde{\beta}_0 + k_\epsilon \tilde{C}_\epsilon$$

$$\tau = \frac{\lambda F N_i}{k_{1,0} + k_{2,0}}$$

(3.15)

The alternate current density flowing through the interface solid phase/electrolyte, $\tilde{i}$, can be expressed by:

$$\tilde{i} (j \omega) = \left[ j \omega C_d + \frac{1}{Z_{m_0}(j \omega)} + \frac{1}{Z_1(j \omega)} \right] \Delta \Phi_T - K_\epsilon (j \omega) \tilde{C}_\epsilon + K_\beta (j \omega) \tilde{\beta}_0$$

(3.16)
where \( C_{dl} \) is the capacity of the double layer of the interface, \( Z_{ad} \) is the impedance of the adsorbing sites, \( Z_I \) the impedance of the total intercalation process, \( K_\varepsilon \) the proportion coefficient for the transport of the lithium in the solution, and \( K_\beta \) the proportion coefficient for the transport of the lithium in the solid phase. The terms of the total current density of the system are equal to:

\[
\begin{align*}
C_{dl} &= \frac{C_1 C_2}{C_1 + C_2} \\
Z_{ad}(j\omega) &= \left[ \frac{(1-\Gamma)^2}{R_1} + \frac{\Gamma^2}{R_2} \right] \left[ 1 + \frac{1}{j\omega}\right] \\
Z_I(j\omega) &= (R_1 + R_2) [j\omega + 1] \\
K_\varepsilon &= \left[ \frac{1 - \Gamma}{j\omega + 1} \right] \\
K_\beta &= \left[ \frac{\Gamma}{j\omega + 1} \right]
\end{align*}
\]

Neglecting the transport of the lithium in both electrolyte and solid phase, eq. (3.16) can be visualized by an equivalent circuit (see figure 3.2). The equivalent circuit is composed by three parallel branches. The first branch contains two capacitances in series (double layer branch). The second branch contains a capacitance and a resistance in series (adsorption branch). The third branch contains an inductance and a resistance in series (intercalation branch). Substituting eq. (3.15) in eqs. (3.13) one obtains:

\[
\begin{align*}
\bar{\tau}_1 &= \frac{1}{F\lambda} \left[ \frac{1}{R_1 + R_2} \frac{1 - \Gamma}{j\omega + 1} \Delta \phi \right] - \frac{\bar{R}_2}{R_1 + R_2} \frac{1}{j\omega + 1} k_\beta \bar{\beta}_0 + \frac{j\omega + 1}{R_1 + R_2} k_\varepsilon \bar{C}_\varepsilon \\
\bar{\tau}_2 &= \frac{1}{F\lambda} \left[ \frac{1}{R_1 + R_2} \frac{\Gamma}{j\omega + 1} \Delta \phi \right] - \frac{\bar{R}_2}{R_1 + R_2} \frac{1}{j\omega + 1} k_\beta \bar{\beta}_0 + \frac{\bar{R}_1 + R_2}{j\omega + 1} k_\varepsilon \bar{C}_\varepsilon
\end{align*}
\]

The mass balance equation in the host material is very important for the expression of the equilibrium potential as function of the oxidation state of the electrode. This influences the shape of the charge/discharge curve of the electrode. The classical point of view of transport
considers only diffusion occurring in the solid phase [89-91]. The diffusion transport mechanism can simulate a sloppy charge/discharge curve of the electrode; it describes the transport of lithium in single-phase systems. The moving boundary model considers the transport of lithium as a front that moves inside the host material [92,93]. It can be visualized as a host material where only migration occurs. The host material is divided in two zones, one rich in lithium, the other without lithium. This model can describe the two-phase systems.

\[
\begin{align*}
\Gamma^+ &= \\Gamma^- \\
R_I &= \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tau \\
C_{dl} &= \frac{C_1 C_2}{C_1 + C_2} \\
R_{ad} &= \left(\frac{(1-\Gamma)^2 + \Gamma^2}{R_1} + \frac{\Gamma^2}{R_2}\right)^{-1} \\
C_{ad} &= \left(\frac{(1-\Gamma)^2 + \Gamma^2}{R_1} + \frac{\Gamma^2}{R_2}\right) \tau \\
L_I &= (R_1 + R_2) \tau 
\end{align*}
\]

Figure 3.2: (a) The equivalent circuit of the intercalation model. The limitations due to the transport of the lithium in the electrolyte and solid phase were neglected. (b) The correlation between the electric elements in the equivalent circuit and the parameters of the kinetic model.

In both diffusion and moving boundary models the term G(x,t) in eq. (3.5) is neglected. G(x,t) could eventually represent the trapping of the lithium in the structure of the host material. When trapped, the lithium is not available for the diffusion or for the migration. G(x,t) influences the charge/discharge curve of the electrode. In this PhD work, the classical point of view on the transport of lithium in the structure of the solid phase was used; only the diffusion of the lithium through the host material was considered (3.5).

Some comments on $C_1$ and $C_2$ are necessary. $C_1$ represents the process of charge/discharge of the double layer on the side of the electrolyte. $C_1$ is equal to the series of the capacitance of the compact double layer (before the inner Helmholtz plane) and the capacitance of the diffuse double layer in the outer Helmholtz layer. $C_2$ represents the process of charge/discharge of the double layer on the side of the solid electrode. It is equal to the...
series of the capacitance of the compact double layer (after the inner Helmholtz plane) and the capacitance of the solid phase.

3.2 Models of the Porous Electrode

The model describing the intercalation process, presented in the previous paragraph, can be applied as it is only for a flat surface of a solid electrode. The electrodes used in lithium-ion batteries are composed by many particles, bounded with a polymeric binder. The electrode is porous, the current is generated in different positions along the pores and a model correlating the current density and the position in the porous electrode is needed. In the literature two classes of models are present: two-phase models and single-phase models.

In 1948 the first model for porous electrode appears. It was developed in 1948 by V. S. Daniel-Bekh [94]. This is a two-phase model; the liquid electrolyte and the solid electrode are treated as separated phases. The pores have a well defined geometrical shape: cylindrical or conical. Daniel-Bekh neglected the effect of the transport of reactants and products. In 1960 J. Euler and W. Nonnenmacher [95] described the porous electrode as a single phase. The single-phase model considers the current to be generated in the volume of the porous electrode. The electrode is treated as being a homogeneous phase of the liquid electrolyte and solid electrode. Euler and Nonnenmacher simulated the current density distribution along the porous electrode, by neglecting diffusion of the reactants and products and assuming the current density along the pore to be directly proportional to the overpotential (small overpotential).

In 1962 J. Newman and C. W. Tobias [96], starting from the model described by Euler and Nonnenmacher [95], introduced the effect of diffusion and the dependence of the polarization resistance on the current density distribution. The transmission line model (TLM), developed by de Levie [97-99] in 1963-1965, is based on the two-phase model of Daniel-Bekh. Diffusion of reactants and products was considered to occur only along the radius of the pore. It is a good approximation when the consumption (generation) rate of reactants (products) is small with respect to the concentration of them in solution.

Starting from the TLM, many works were developed considering different pore shape and pore size distribution [100-103]. De Levie argued that crosslinked pores can be described
with a single characteristic dimension \([99]\). It appears that pore size distribution is not an important parameter in porous electrodes composed by bounded particles. Meyers et al. \([91]\) used the single-phase model to describe a porous electrode composed by intercalating particles. The diffusion paths in the solid phase were considered spherical.

In this chapter a simplified generalized model of porous electrodes based on the TLM of de Levie \([97]\) is presented. The porous electrode is considered immersed in an electrolyte solution containing a single monovalent binary salt, which cations participate in an electrochemical reaction. In figure 3.3 a schematic drawing of the porous electrode is shown. The zero of the \(x\) axis is put in the boundary between the porous electrode and the current collector. The porous electrode has a thickness \(L\) and the current collector is assumed to be inert in the electrolyte solution. The pores of the electrode can have different size and shape, both changing along the \(x\)-axis. It is postulated that the centers of mass of each section of the pore are aligned along the \(x\)-axis. Focusing attention to a single current tube (a bundle of electronic and ionic current lines) passing through the electrode, everywhere the current tube is near the solid phase/electrolyte interface, a part of the electronic current is converted into ionic current through the electrochemical process (see figure 3.3).

![Figure 3.3](image)

Figure 3.3: (a) Schematic drawing of a porous electrode. (b) Schematic drawing of a current tube.

At \(x = 0\) the ionic current is zero and at \(x = L\) the electronic current is zero (i.e., all the electronic current lines are converted into ionic current lines). There is a free path \(a_k\) between \(k\)-th and \((k+1)\)-th reaction site (see figure 3.4). It is a statistical parameter and represents the free path that an electron (solid phase) and an ion (electrolyte) can move before coming sufficiently close to the solid phase/electrolyte interface where they could be involved in the
electrochemical reaction. The value of the free path length is equal to \( a_k = A_{p,k}/P_{p,k} \), where \( A_{p,k} \) is the sectional area of the pore at position \( k \), and \( P_{p,k} \) the sectional perimeter of the pore at position \( k \). The equivalent electrical circuit representing the model is similar to the TLM electrical circuit introduced by de Levie [97] (see figure 3.4).

![Figure 3.4: Electrical equivalent circuit representing the current lines and reacting sites in the porous electrode.](image)

Each current tube is \( n \) steps long. The potential difference in the electrolyte and in the solid phase between two points \( k \) and \( k-1 \) depends on the ohmic potential drop (\( \Delta \phi_{\text{ohm}}' \) and \( \Delta \phi_{\text{ohm}}'' \), respectively); the effect of the concentration gradients (diffusion potential drop) is neglected. The potential drop at the interface solid phase/electrolyte in the \( k \)-th position is represented by \( \Delta \phi_k \) (see figure 3.4); it generates the current \( I_k \) through the electrochemical processes occurring at the surface of the electrode. From the Kirchhoff's loop rule applied between \( k \)-th and \( (k+1) \)-th position it follows:

\[
\Delta \phi_k + \Delta \phi_{\text{ohm}k}' - \Delta \phi_{k+1} - \Delta \phi_{\text{ohm}k}'' = 0 \quad (3.19)
\]

The ohmic potential drops in the electrolyte solution and in the solid phase can be related to the current intensities:

\[
\begin{align*}
\Delta \phi_{\text{ohm}k}' &= \frac{\rho_s a_k}{A_{p,k}} I_k' \\
\Delta \phi_{\text{ohm}k}'' &= \frac{\rho_E a_k}{A_{p,k}} I_k''
\end{align*}
\quad (3.20)
\]

where \( \rho_s \) is the resistivity of the electrolyte solution (inside the pores), \( \rho_E \) the average resistivity of the solid phase (inside the pores), \( A_{p,k} \) the cross sectional area of the pore at the
position \( k \), and \( I'_k \) and \( I''_k \) the ionic and electronic current intensities, respectively, at the \( k \)-th position (see figure 3.4). The ionic current intensity at position \( k \) is equal to the sum of the \( I'_k \)'s from 0 to \( k \). The electronic current intensity at position \( k \) is equal to the sum of the \( I''_k \)'s from \( k \) to \( L \). Passing from the finite elements to the infinitesimal ones, i.e., for \( n \to \infty \), and using the expressions (3.20), the Kirchhoff’s loop rule (3.19) becomes:

\[
\frac{\partial \Delta \phi}{\partial x} = \frac{\rho_s + \rho_E}{A_p(x)} \int_a^{x'} I'(x') \, dx' - \frac{\rho_E}{A_p(x)} I_T
\]

(3.21)

where \( I_T \) is the total current intensity flowing through the porous electrode. Eq. (3.21) can be differentiated again. Assuming \( \rho_S \) and \( \rho_E \) are independent of \( x \), the result is:

\[
\frac{\partial}{\partial x} \left( A_p \frac{\partial \Delta \phi}{\partial x} \right) = \left( \frac{\rho_s + \rho_E}{a} \right) I
\]

(3.22)

For a numerical solution of eq. (3.22), it is better to use dimensionless coordinate. Calling \( X \) the normalized position along the pore axes, \( x/L \), eq. (3.22) can be rewritten as:

\[
\frac{\partial}{\partial X} \left( A_p \frac{\partial \Delta \phi}{\partial X} \right) = \left( \frac{\rho_s + \rho_E}{a} \right) L^2 I
\]

(3.23)

Eq. (3.22) describes porous systems and is independent of the type of experiment and reactions occurring at the surface of the electrode.

Eq. (3.23) needs two boundary conditions. The first one comes from eq. (3.21) calculated at \( x = 0 \) and \( x = L \). The second one is obtained from the total potential drop in the porous electrode, \( \Delta \phi_p \), which is sum of the potential drop in the solid phase, in the interface solid phase/electrolyte, and in the electrolyte:

\[
\Delta \phi_p = \frac{\rho_E}{\rho_s + \rho_E} \Delta \phi_0 + \frac{\rho_s}{\rho_s + \rho_E} \Delta \phi_i + R_U I_T
\]

(3.24)

\[
R_U = R_S + \frac{\rho_S \rho_E}{\rho_s + \rho_E} \int_0^{X'} \, dx'
\]

where \( R_S \) is the bulk electrolyte resistance, outside the pores. It is possible to add another relationship between the potential and the total current intensity:

\[
I_T = \frac{1}{(\rho_s + \rho_E)} \left[ A_p \frac{\partial \Delta \phi}{\partial X} \bigg|_1 - A_p \frac{\partial \Delta \phi}{\partial X} \bigg|_0 \right]
\]

(3.25)
The response of the porous electrochemical system depends strictly on the values of the resistivities of solution and material. If the resistivities in the electrolyte and in the solid phase are both very small, or the current is always very small, then at each point $\Delta \varphi$ is constant and equal to $\Delta \varphi_p$. In this case the current density distribution is constant.

The description of the porous electrode given by eq. (3.23) reproduces the behaviour of the porous electrode only if the electrolyte inside one current tube is physically separated by the electrolyte inside another current tube. In a more realistic picture of the porous electrode, the pore structure can be assumed as composed by main pores, perpendicular to the current collector, with lateral branches (closed pores) and networks (interconnections between main pores), where the electrochemical processes occur as in the main pores (see figure 3.5).

![Figure 3.5: Electrical equivalent circuit representing the current lines and reacting sites in the porous electrode described by the BTLM (a) and NTLM (b).](image)

These advanced models describing the structure of the pores were called branched transmission line model (BTLM) and network transmission line model (NTLM). The presence of the lateral pores (branches and interconnections) generates a lateral current density distribution, which influences the main current density distribution (in the main pores). The effect of the lateral current density distribution on the main current density distribution
depends on the ratio between the reacting area located inside the lateral pore and the reacting area located in the main pores, and on the resistance of the solution inside the lateral pores (see figure 3.5).

The values of the physico-chemical quantities in the lateral pores (branches and interconnections) are indicated with the index \( m \). The BTLM and NTLM are presented together; they have many common features. The distance between two lateral pores is equal to \( b \). If the current flowing from/to the lateral pores can be treated using infinitesimal elements (the number of the lateral pores is high), eq. (3.23) for the \( K \)-th main pore has to be replaced by:

\[
\frac{\partial X}{\partial \Delta X} \left[ A_{p,K} \frac{\partial \Delta \phi_{K}}{\partial X} \right] = \left( \frac{\rho_s + \rho_e}{a_k} \right) + \sum_{m} \frac{1}{b_m} \left( \rho_s \Gamma_{T,m,K} + \rho_e \Gamma_{T,m,K} \right) \tag{3.26}
\]

where the ionic and electronic currents flowing from/to the lateral pores, \( \Gamma_{T,m,K} \) and \( \Gamma_{T,m,K} \) respectively, have same values if the lateral pore is a branch, and different values if the lateral pore is an interconnection. The BTLM and NTLM give a three-dimensional description of the porous electrode.

The lateral pores are described by a differential equation similar to eq. (3.23). The 0 of the \( y \)-axis is chosen in the point where the lateral pore and the main pore meet. The normalized axis of the branch will be called \( Y \)-axis. \( L_m \) was assumed to be the length of the branch or half of the length of an interconnection. The following differential equation describes the lateral pore:

\[
\frac{\partial}{\partial Y} \left[ A_{p,m} \frac{\partial \Delta \phi_{m}}{\partial Y} \right] = \left( \frac{\rho_s + \rho_e}{a_m} \right) L_m^2 I_m \tag{3.27}
\]

The boundary conditions of eq. (3.27) depend on the model used:

\[
\begin{align*}
(BTLM) & \quad \left. \frac{\partial \Delta \phi_{m}}{\partial Y} \right|_{Y=1} = 0 \quad ; \quad \left. \Delta \phi_{m} \right|_{Y=0} = \Delta \phi_K (x) \\
(NTLM) & \quad \left. \Delta \phi_{m} \right|_{Y=2} = \Delta \phi_K (x) \quad ; \quad \left. \Delta \phi_{m} \right|_{Y=0} = \Delta \phi_K (x)
\end{align*}
\tag{3.28}
\]

where the index \( K' \) refers to the other main pore meeting the interconnection. Applying the Kirchhoff’s loop rule to the whole lateral pore, the following relationship is obtained:

\[
\left. \frac{A_{p,m}}{L_m} \frac{\partial \Delta \phi_{m}}{\partial Y} \right|_{Y=0} = \left( \rho_s \Gamma_{T,m,K} + \rho_e \Gamma_{T,m,K} \right) \tag{3.29}
\]

Substituting in eq. (3.26) one obtains:
\[
\frac{\partial}{\partial X} \left[ A_{p,K} \frac{\partial \Delta \phi}{\partial X} \right] = \left( \rho_s + \rho_e \right) L^2 \left( \frac{I_k}{a_k} - \sum_m \frac{A_{p,m}}{(\rho_s + \rho_E) b_m L_m} \frac{\partial \Delta \phi_m}{\partial Y} \right)_{Y=0} \] 
\] (3.30)

The solution of eq. (3.30) depends on the nature of the lateral pores. It is possible to mix together also different types of pore structures, because this general form is independent from the exact structure of the porous electrode. Each lateral pore has to be solved apart for the calculation of the total response of the porous electrode.

An easy solution of eq. (3.30), which was considered by de Levie [99], is obtained when there is no generation of current inside interconnections and the electric and ionic resistances inside the lateral pores are negligible (small reacting surface area in the lateral pores). In this case the porous structure can be defined by a single equation:

\[
\frac{\partial}{\partial X} \left[ A_{p,K} \frac{\partial \Delta \phi}{\partial X} \right] = \left( \rho_s + \rho_e \right) L^2 \frac{A_{p,K}}{a_k} \] 
\] (3.31)

Summing for all the pores and dividing for their number N, the final result is

\[
\frac{\partial}{\partial X} \left[ \left( \frac{1}{N} \sum_{K=1}^{N} A_{p,K} \right) \frac{\partial \Delta \phi}{\partial X} \right] = \left( \rho_s + \rho_e \right) L^2 \left( \frac{1}{N} \sum_{K=1}^{N} \frac{A_{p,K}}{a_k} \right) \] 
\] (3.32)

which can be transformed into eq. (3.23). Random electrodes (as the electrodes composed by different particles connected by a binder), for which a distribution of pore dimension is expected, can be generally described by a single \( a_K \). The effect of the pore size distribution [103] is not reasonable in electrodes where the reacting area in the lateral pores is small compared to the reacting area in the main pores.

If the surface of the lateral pores is high with respect to the surface of the main pores, eq. (3.32) cannot describe the porous electrode accurately. It is necessary to use another simplification. In a random electrode, it can be assumed reasonably that \( a_K(x) \), \( a_m(x,y) \) and \( b_m(x) \) are independent from K, m, and y. Under these conditions, eq. (3.30) is simplified:

\[
\frac{\partial}{\partial X} \left[ A_p \frac{\partial \Delta \phi}{\partial X} \right] = \left( \rho_s + \rho_e \right) L^2 \left( \frac{1}{a} - \sum_m \frac{A_{p,m}}{(\rho_s + \rho_E) b m L_m} \frac{\partial \Delta \phi_m}{\partial Y} \right)_{Y=0} \] 
\] (3.33)

Eq. (3.33) is independent from the nature of the lateral pore. Moreover, to solve the differential equation describing the lateral pores, eq. (3.27), the boundary conditions (3.28) given by the BTLM can be used. This is due to the symmetry plane passing through the
middle of the lateral pore (see figure 3.5). The boundary conditions (3.24) can be used to solve eq. (3.33).

When the porous electrode is in equilibrium conditions, the potential drop at the interface solid phase/electrolyte is constant along the X-axis of the main pores and Y-axis of the lateral pores. Moreover, the concentration profile of the reactants and products is also constant. Starting from this condition, if a sinusoidal voltage perturbation is applied to the porous electrode, the total current response depends on the alternate current density distribution. The differential equation (3.23) is written as:

\[
\frac{\partial}{\partial X} \left[ A_p \frac{\partial \Delta \phi}{\partial X} \right] = \frac{\left( \rho_s + \rho_e \right)}{\alpha} L^2 \tilde{I}(j\omega) \tag{3.34}
\]

It was considered here that the porous electrode could be approximated by the TLM model (see figure 3.4). Neglecting the limitations due to the transport of reactants and products, eq. (3.16) can be substituted in eq. (3.34):

\[
\frac{\partial}{\partial X} \left[ A_p \frac{\partial \Delta \phi}{\partial X} \right] = \left( \rho_s + \rho_e \right) A_p L^2 \Delta \phi
\]

\[
\frac{1}{Z(j\omega)} = j\omega C_{\text{di}} + \frac{1}{Z_{\text{ad}}(j\omega)} + \frac{1}{Z_{1}(j\omega)}
\]

\( Z \) is the impedance of the single reacting site. \( Z \) is independent from the position \( X \), because the porous electrode is in equilibrium conditions. In a random electrode, \( A_p \) and \( \alpha \) are averagely independent from the position \( x \); eq. (3.35) can be written as:

\[
\frac{\partial^2 \Delta \phi}{\partial X^2} = \left( \rho_s + \rho_e \right) L^2 \Delta \phi \tag{3.36}
\]

The impedance of the porous electrode, \( Z_p = \Delta \phi_p / I_T \), results equal to:

\[
Z_p(j\omega) = \frac{\rho L}{A_p N} \left\{ \frac{\cosh(\kappa) + \alpha}{\kappa \sinh(\kappa)} \right\} + R_u
\]

\[
\rho = \frac{\rho_s^2 + \rho_e^2}{\rho_s + \rho_e} ; \quad \alpha = \frac{2\rho_s \rho_e}{\rho_s^2 + \rho_e^2} ; \quad \kappa^2 = \frac{(\rho_s + \rho_e)L^2}{\alpha Z}
\]

The dependence of the impedance of the porous electrode on the impedance of the single reacting site is included in the expression of \( \kappa \). When the value of \( \kappa \) is high (high current flow), the impedance of the porous electrode is proportional to the square root of the impedance of the single reacting site. When the value of \( \kappa \) is small (low current flow), the
impedance of the porous electrode is directly proportional to the impedance of the single reacting site.

If the NTLM is used instead of the TLM, a very similar result is obtained. Eq. (3.37) can be used as it is if the expression of $\kappa$ is replaced by:

$$\kappa^2 = \left(\frac{\rho_s + \rho_E}{aZ}\right)^2 \left[1 + \frac{a_m L_m}{ab} \tanh\left(\kappa'\right)\right]$$

$$\kappa'^2 = \frac{(\rho_s + \rho_E)^2}{aZ} L_m^2$$

(3.38)

In the intercalation porous electrode, the limitations rising from the transport of the reactants and products through the pore and through the solid phase are not negligible, eqs. (3.37, 3.38) cannot be used as they are. The differential equation (3.34) has to be implemented with two mass balances, one for the lithium ions in the electrolyte, the other one for the lithium in the solid phase.

3.3 Models of the Transport in Pores

The transport of species along the pores of a porous electrode was firstly treated by J. Newman and C. W. Tobias [96] in 1962. By using a one-phase model based on the model of Euler and Nonnenmacher [95], the authors introduced the effect of diffusion by assuming the reactants (products) to be consumed (produced) as in a bulk reaction. An average concentration of the reactants and products was used to describe the reaction at the interface solid phase/electrolyte. This assumption is intrinsic to the single-phase model. The model is described by a system of two coupled differential equations. In 1966 G. Darby [104,105] treated the diffusion of oxygen in a porous electrode, used as cathode for fuel cell. Again, the porous electrode model was based on the one-phase model. In his calculation of DC current and impedance spectra response, Darby neglected the effects due to the resistance of the electrolyte and of the solid phase. The TLM, formulated by de Levie [97-99] in 1963, and based on the two-phase model of Daniel-Bekh [94], considered diffusion of reactants and products occurring only along the radius of the pore. By using this assumption the mass balance equation is solved separately; the electrode is described by a one-dimensional differential equation.
The solution to the transport problem given by de Levie [97-99] is a good approximation at short time (high frequency range), when the pores are not yet completely depleted from reactants (filled with products) and transport along the x-axes of the pore gives a negligible contribution to the total transport. On the other hand, for longer time this assumption has no more sense and the Newman-Tobias [96] assumption can be used to simulate the data. During this PhD work a model for the transport in pores was developed to unify the advantages of the models of de Levie and Newman-Tobias. The model presented in this paragraph, called the average concentration model (ACM), proposes a recursive integration of the approximated solution of the mass balance equation.

When the two-phase model for the description of the porous electrode is used, the real mass balance equation in the pores has to be three-dimensional. Normalized cylindrical coordinates are used to describe the transport in the pores: the normalized x coordinate, X, is equal to x/L; the normalized r coordinate, R, is equal to r/2a. The time constant of the diffusion process is defined as 

$$\tau_{D,i} = \frac{L^2}{D_i},$$

where $D_i$ is the diffusion coefficient of the species i. It is assumed that the pores have a cylindrical shape, the mass balance equation can be written in normalized cylindrical coordinates as:

$$\tau_{D,i} \frac{\partial C_i}{\partial t} = \frac{\partial^2 C_i}{\partial X^2} + \left( \frac{L}{2a} \right)^2 \frac{1}{R} \frac{\partial}{\partial R} \left( \frac{R \frac{\partial C_i}{\partial R}}{2a} \right)$$

(3.39)

where $C_i$ is the concentration of species i. The boundary conditions of equation (3.39) are:

$$C_i = C_{S,i}, \quad t = 0 \quad \forall X, R$$

$$\frac{\partial C_i}{\partial X} = 0, \quad X = 0 \quad \forall t, R$$

$$C_i = C_{S,i}, \quad X = 1 + \delta \quad \forall t, R$$

(3.40)

$$\frac{\partial C_i}{\partial R} = \pm \frac{1}{2} \left( \frac{2a}{L} \right)^2 \frac{\tau_{D,i}}{a} r(X, t) \quad R = 1 \quad \forall t, X$$

$$\frac{\partial C_i}{\partial R} = 0 \quad R = 0 \quad \forall t, X$$

where $r$ is the rate of reaction of the electrochemical process occurring at the surface of the pore and involving species $i$, $\delta$ is the thickness of the Nernst layer normalized by the length of the pore, and $C_{S,i}$ the concentration of species $i$ in the bulk of the electrolyte. In the fourth boundary condition (3.40), $+$ has to be used if species $i$ is a reactant, $-$ if it is a product. The average value of $C_i$ in the cross section, $C_{av,i}$, is defined as:
\[ C_{av,i}(X,t) = \frac{1}{2} \int_0^R C_i(R,X,t) dR \]  \hspace{1cm} (3.41)

Averaging the mass balance equation (3.39) along the radius, and using the definition of \( C_{av,i} \) and boundary conditions (3.40), one obtains:

\[ \tau_{D,i} \frac{\partial C_{av,i}}{\partial t} = \frac{\partial^2 C_{av,i}}{\partial X^2} + \frac{\tau_{D,i}}{a} r \]  \hspace{1cm} (3.42)

Eq. (3.42) has the same form of the differential equation developed by Newman and Tobias in 1962 [96]. The simplification used by Newman and Tobias, which is implicit in single-phase model, considers the reaction rate dependent on the average concentration in the cross section instead of dependent on the concentration at the wall of the pore. This happens because in the single-phase model, the solid and liquid phases are considered not separated, as the radius of the pores were 0. The more realistic two-phase model should be solved by using eq. (3.39), which is possible only by numerical approximation. To avoid numerical integration along two coordinates, eq. (3.42) is used, by defining a coefficient \( \Xi_i(X,t) \):

\[ C_{av,i} = \Xi_i(X,t) C_{w,i} \]  \hspace{1cm} (3.43)

where \( C_{w,i} \) is the concentration of species i at the wall of the pore. \( r(X,t) \) can be written as a function of \( C_{av,i} \) instead of \( C_{w,i} \). The mass balance equation is reduced to a one-dimensional differential equation.

The coefficient \( \Xi_i(X,t) \) has to be calculated. The real solution of equation (3.39) is defined as:

\[ C_i = \xi_i(R,X,t) C_{i,w} \]  \hspace{1cm} (3.44)

where \( \xi_i \) is a coefficient depending on position and time. Substituting the solution (3.44) in the definition of the average concentration in the cross section, one obtains

\[ \Xi_i(X,t) = 2 \int_0^1 R \xi_i(R,X,t) dR \]  \hspace{1cm} (3.45)

The real coefficient \( \Xi_i \) is equal to the average of the coefficient \( \xi_i \) in the cross section. The calculation of \( \Xi_i \) needs the evaluation of the coefficient \( \xi_i \); the mass balance equation has to be solved. In the following part, two approximations of the mass balance equation to calculate \( \xi_i \) are presented with the name ACM-I and ACM-II, respectively.
(ACM-I) In pores with $L \gg r_p$ (it is the most common situation in porous electrodes), it can be argued that the radial transport and the axial transport occur in two different times, in particular the former is faster. Because the $\xi_i$ coefficient represents the changing of the concentration along the radius, in its calculation, the axial transport is neglected. Using the definition (3.44) for $\xi_i$, eq. (3.40) is simplified as

$$\tau_{D,i} \frac{\partial}{\partial t} \left[ \frac{\xi_i'}{\Xi_i'} \right] + \tau_{D,i} \xi_i' \frac{\partial \ln C_{av,i}}{\partial t} = \left( \frac{L}{2a} \right)^2 \frac{1}{R} \frac{\partial}{\partial R} \left( R \frac{\partial \xi_i'}{\partial R} \right)$$

(3.46)

where $\xi_i'$ and $\Xi_i'$ are the approximated values of $\xi_i$ and $\Xi_i$, respectively. Assuming the first term in the left hand side negligible with respect to the second one, eq. (3.46) is solved analytically:

$$\Xi_i'(X, t) = \frac{2}{k I_0(k)} \frac{I_1(k)}{I_0(k)} \frac{1}{k^2}$$

$$\Xi_i'(X, \infty) = 1$$

(3.47)

where $I_n$ indicates the modified Bessel function of order $n$. The axial transport did not disappear; it is included in equation (3.42). The error implicit in $\Xi_i'$ depends on the correctness of the approximations made. In particular, in the time domain where the radial transport is important, the axial transport has to be negligible, that means, in the time domain where $\xi_i$ is strongly dependent on the time, the second term in the right hand side of eq. (3.42) has to be larger than the first one. As explained before, this happens if $L \gg r_p$.

(ACM-II) Eq. (3.47) implicitly imposes that, when $t \rightarrow \infty$, $\xi_i' \rightarrow 1$; in steady state conditions the ACM-I model predicts a constant concentration of the species $i$ along $R$. The real mass balance equation in steady state conditions predicts changes of the concentration of the species $i$ along $R$ if the reaction involving the species $i$ occurs. To obtain a better approximation with respect to the solution of ACM-I, the average transport in the axial direction is added to eq. (3.46). Using the same simplifications as in the ACM-I, one obtains:

$$\Xi_i'(X, t) = 1 + \frac{2a}{L} \left( \frac{r}{a C_{w,i}} \right) \tau_{D,i} \left( \frac{k I_0(k) - 2 I_1(k)}{2 k^2 I_1(k)} \right)$$

$$\Xi_i'(X, \infty) = 1 + \frac{1}{8} \left( \frac{2a}{L} \right)^2 \left( \frac{r}{a C_{w,i}} \right) \tau_{D,j}$$

(3.48)
The solutions (3.47, 3.48) have not to be treated as mass balances. The meaning of solutions (3.47, 3.48) is to approximate the concentration profile shape along the R axis and the X axis of the pore (see figure 3.6).

Figure 3.6: Concentration profile along the R axis (a) and X axis (b) as predicted by the Newman-Tobias model (NTM), ACM-I, and ACM-II models (the species i is a reactant).

Under alternate voltage perturbation, $\xi'_i$ results to be a constant in time, depending on $j\omega$. The value of $\Xi'_i$ in the two previously introduced ACM models can be obtained by substituting the value of $k^2$ in solutions (3.47, 3.48) with:

$$k^2 = j\omega \tau_{Dj} \left( \frac{2a}{L} \right)^2$$

(3.49)

When $\omega \neq 0$, $\Xi'_i$ of the ACM-I tends to 1. The ACM-I gives the same result of the Newman-Tobias model in the low frequency domain. It can also be demonstrated that, at high frequency, by neglecting the axial transport in eq. (3.42), the same result as de Levie is obtained. These observations imply that the ACM-I can unify the advantages of the previous cited models. In the high frequency domain, it follows only the radial transport, but when the frequency becomes sufficiently small, the axial transport is also introduced.

The transport of lithium in the solid phase is generally treated as a spherical diffusion [90,91]. This can be used only if the particle is spherical, and the potential drop at the
interface solid phase/electrode is the same in the whole surface of the intercalation particle. This is sufficiently true if the particles are small compared to the thickness of the porous electrode. If it is not the case, the mass balance of the lithium in the solid phase can be calculated by using eq. (3.42) with modified boundary conditions along the X-axis. If the transport through the X-axis can be neglected, eq. (3.42) gives the same result of a circular diffusion transport. In this PhD work the circular diffusion transport was considered a better approximation of the real transport in the solid phase and used instead of the spherical diffusion transport.

3.4 Mathematical Simulations

The impedance of the intercalation porous electrode in a lithium-ion battery can be calculated solving the following system of differential equations:

\[
\begin{align*}
\frac{\partial^2 \Delta \phi}{\partial X^2} &= \left( \rho_s + \rho_e \right) \frac{L^2}{a} \tilde{j}(j\omega) \\
\frac{\partial^2 C_{av,\varepsilon}}{\partial X^2} &= \tau_{D,\varepsilon} \tilde{j} \omega \tilde{C}_{av,\varepsilon} + \frac{\tau_{D,\varepsilon}}{a} \tilde{r}_1 \\
\tau_{D,\varepsilon} N_e \tilde{j} \omega \tilde{C}_{av} &= \frac{\tau_{D,\varepsilon}}{a} \tilde{r}_2
\end{align*}
\] (3.50)

The expression of \( \bar{U}, U_1 \) and \( U_2 \) are obtained by eqs. (3.16, 3.18, 3.43). The system is written considering the following models: the intercalation is a two-step process, described by the electrochemical reactions (3.1, 3.2); the porous electrode is described by one parameter, \( a \); the mass balance of the lithium ions in the electrolyte considers only diffusion transport of \( \text{Li}^+ \); the mass balance of the lithium in the solid phase considers only circular diffusion transport.

The system (3.50) can be rewritten in the following form:

\[
\begin{align*}
\frac{\partial^2 \Delta \phi}{\partial X^2} &= A \Delta \phi + BC_{av,\varepsilon} \\
\frac{\partial^2 C_{av,\varepsilon}}{\partial X^2} &= C \Delta \phi + D \tilde{C}_{av,\varepsilon}
\end{align*}
\] (3.51)

where \( A, B, C, D \) are constant along X and depend on the angular frequency, \( \omega \). The system (3.51) can be transformed in a fourth order linear differential equation with respect to \( \Delta \phi \):  

\[
\frac{\partial^4 \Delta \phi}{\partial X^4} - (A + D) \frac{\partial^2 \Delta \phi}{\partial X^2} + (AD - BC) \Delta \phi = 0
\] (3.52)

The general solution of the differential equation (3.52) is equal to:
\[ \Delta \tilde{\phi} = I_1 \sinh (K_1 X) + I_2 \cosh (K_1 X) + I_3 \sinh (K_2 X) + I_4 \cosh (K_2 X) \]

\[ K_{1,2} = \frac{1}{2} \sqrt{\frac{(A + D)}{2} \pm \sqrt{\left(\frac{(A + D)^2}{4} - (AD - BC)\right)}} \]  

The integration constants \( I_1, I_2, I_3, \) and \( I_4 \) are obtained from the boundary conditions. Assuming that \( \rho_S >> \rho_E \), the impedance of the intercalation porous electrode can be written as:

\[ Z_p(j\omega) = \frac{\Delta \tilde{\phi}_1}{A_{p,j} \partial \Delta \tilde{\phi}_1 \partial X} + R_U \]  

An analytical solution of the intercalation electrode is obtained and can be used for the mathematical simulations and for a fitting routine (see paragraph 2.4).

The mathematical simulations of the impedance spectra of an intercalation porous electrode are used to explain some effects observed in real systems. The values of the parameters are chosen in agreement to a realistic system: \( D_e = 2 \cdot 10^{-6} \) cm\(^2\) s\(^{-1}\); \( D_p = 2 \cdot 10^{-9} \) cm\(^2\) s\(^{-1}\); \( L = 2 \cdot 10^{-2} \) cm; \( a = 1 \cdot 10^{-4} \) cm; \( \tau = 10^{-3} \); \( R_p = 2.5 \Omega \); \( R_U = 1 \Omega \); \( C_{dl} = 1 \cdot 10^{-6} \) F cm\(^{-2}\); \( R_1 = 10 \Omega \) cm\(^2\); \( \Gamma = 0.5 \).

In figure 3.7 the Nyquist plots of the simulated impedance spectra are reported, for different values of the resistance of the intercalation process, \( R_2 \). The simulations are performed in the frequency range 100 kHz – 0.1 Hz. When the resistance of the intercalation process tends to infinite, the only reaction occurring at the interface solid state/ electrolyte is the adsorption of the ion. A distorted semicircle is observed, followed by a pure capacitative behavior of the system. The distortion of the semicircle is due to the resistance of the pores; it is the transport of charge in the pores, both electronic and ionic. The impedance spectra simulated for \( R_2 = 8 \) has a second semicircle in the intermediate frequency range; this second process is not an electrochemical reaction, but it is due to the transport of the adsorbed species along the pores. When the intercalation process becomes possible (\( R_2 \) has a finite value), the shape and the modulus of the impedance spectra change. The impedance spectra can change considerably, depending on the value of the parameters. For \( R_2 > R_1 \) the high frequency semicircle remains quite the same in intensity and shape. The low frequency part of the impedance spectra changes, because of the intercalation process. By decreasing the value
of $R_2$, the semicircle in the high frequency region becomes smaller. When $R_2 < R_1$ a second semicircle is observed, due to the intercalation process itself.

Figure 3.7: Nyquist plot of the simulated impedance spectra in the frequency domain 100 kHz - 0.1 Hz for an intercalation porous electrode. The parameters used for the mathematical simulation are: $D_\varepsilon = 2 \times 10^{-6}$ cm$^2$ s$^{-1}$; $D_\beta = 2 \times 10^{-9}$ cm$^2$ s$^{-1}$; $L = 2 \times 10^{-2}$ cm; $a = 1 \times 10^{-4}$ cm; $\tau = 10^3$ s; $R_\phi = 2.5$ $\Omega$; $R_U = 1$ $\Omega$; $C_{dl} = 1 \times 10^{-6}$ F cm$^{-2}$; $R_1 = 10 \Omega$ cm$^2$; $\Gamma = 0.5$.

In figure 3.8 the Nyquist plots of the simulated impedance spectra are reported, for different values of the parameter $\Gamma$. The value of the other parameters and the frequency domain is the same value used in the simulations of figure 3.7. $R_2$ was considered equal to $0.1R_1$. When $\Gamma = 0$ (the adsorbed species is neutral), only one semicircle in the high frequency
range is observed. By increasing $\Gamma$, the semicircle in the high frequency region decreases in absolute value and it splits in two semicircles. The two semicircles represent the two steps of the total intercalation reaction. If the adsorbed species is uncharged, the step 3.2 is independent from the potential; it cannot be directly observed. The simulated impedance data in the low frequency region, representing the diffusion in the host material, are independent from the state of charge of the adsorbed species.

**Figure 3.8:** Nyquist plot of the simulated impedance spectra in the frequency domain 100 kHz - 0.1 Hz for an intercalation porous electrode. The parameters used for the mathematical simulation are: $D_\varepsilon = 2 \times 10^{-6}$ cm$^2$ s$^{-1}$; $D_\beta = 2 \times 10^{-9}$ cm$^2$ s$^{-1}$; $L = 2 \times 10^{-2}$ cm; $a = 1 \times 10^{-4}$ cm; $\tau = 10^3$; $R_p = 2.5$ $\Omega$; $R_0 = 1$ $\Omega$; $C_{dl} = 1 \times 10^{-6}$ F cm$^2$; $R_1 = 10$ $\Omega$ cm$^2$; $R_2 = 1$ $\Omega$ cm$^2$. 
4 Experimental Setup

4.1 Preparation of the Electrodes

The electrode for the electrochemical experiments was prepared by mechanically mixing electro-active materials with conductive additives (if any) in the powder form. This mixture was subsequently dissolved in a solution of polyvinylidene fluoride (PVdF 6020) in N-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry, which was then spread onto a current collector via the doctor-blading technique. The coated-electrodes were dried at 80 °C under moderate vacuum for 2 h in order to remove the NMP solvent. Subsequently, the electrodes were dried at 120 °C under vacuum for overnight to remove any remaining traces of NMP solvent present in the electrodes. Finally, the electrodes were transferred into a glove box with high-purity argon atmosphere (O\textsubscript{2} and H\textsubscript{2}O < 2 ppm each). The final composition of the electrode after drying, depends on the type of electro-active material used for each study and is indicated on the relevant place.

The PVdF acts as a binder, which provides mechanical stability to the electrode. Meanwhile, the current collector has to be electrochemically and chemically inert when in contact with the electrolyte for the entire range of the working potential window of the electrochemical system. However, at the same time, the current collector also has to be an electron conductor. In general, copper mesh/foil is applied on the negative electrode, while aluminium mesh/foil are applied on the positive electrode. However, in some cases, titanium can also be used as the current collector on either the negative or positive electrode.

In this doctoral research work, graphite was investigated as the electro-active material for the negative electrodes. As the graphite particles have high electronic conductivity, no additional conductive additive is necessary for the preparation of the negative electrodes. The final composition of the graphitic negative electrodes is 90 wt.% graphite (electro-active material) and 10 wt.% PVdF 6020 (binder). In addition, the Li\textsubscript{1+x}(Mn\textsubscript{1/3}Ni\textsubscript{1/3}Co\textsubscript{1/3})\textsubscript{1-x}O\textsubscript{2} (NMC) was investigated as electro-active material for the positive electrode. Since the NMC compound is an oxide, it has low electronic conductivity. Therefore, conductive additives
such as carbon black and graphite were added in order to enhance the overall electronic conductivity of the electrode. The final composition of the NMC positive electrodes is 82 wt.% \( \text{Li}^{1+x}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3})_{1-x} \text{O}_2 \) (electro-active material), 7 wt.% carbon black (Super P, TIMCAL) (additive), 4 wt.% graphite (KS6, TIMCAL) (additive), and 7 wt.% PVdF 6020 (binder).

4.2 Synthesis of the Electro-Active Materials

\( \text{Li}^{1+x}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3})_{1-x} \text{O}_2 \) (NMC) compounds were synthesized via the co-precipitation of the hydroxides of the transition metals. An aqueous solution consisting of 1 M LiOH and 3 M \( \text{NH}_4\text{OH} \) and a solution of 1 M \( \text{Me(NO}_3)_2 \) in ethanol (Me are the transition metals) were prepared in the first instance. The solution containing the transition metals was prepared in ethanol in order to speed up the drying process. Stoichiometric amount of the as-prepared solutions were mixed by slowly dropping the transition metals-based solution into the lithium-based solution under magnetic stirring. Due to the high pH of the resulting mixture, hydroxides of the transition metals precipitated. The resulting suspension was left overnight under agitation. The suspension was later dried in rotavapor until all solvents were removed. The dried precipitate was kept overnight in moderate vacuum at 80 °C for the complete removal of water traces.

The dried precipitate, in powder form, was collected by scraping and grinding in an agate mortar. The ground powder was placed in an alumina crucible and calcinated in air. The calcination process is divided into three steps: the powder is heated up to the calcination temperature in 6 hours; followed by maintaining the calcination temperature for the next 6 hours; and finally cooled down to 25 °C in 6 hours. Three calcination temperatures were chosen for this doctoral work, namely at 700, 850, and 1000 °C. The calcinated powder was subsequently ground in an agate mortar. A total of 9 samples were prepared by varying 3 different stoichiometries (\( x = 0, x = 0.1, \) and \( x = 0.2 \)) with the three calcination temperatures.

4.3 Standard Electrochemical Experiments

Standard electrochemical experiments were performed on all the negative and positive electrodes. The standard electrochemical tests were galvanostatic cycling and cyclic voltammetry (CV). The electrochemical cell used for the standard electrochemical
experiments is a coin-type cell, with a two-electrode configuration; where the working electrode consists of the investigated electro-active material and the counter electrode is metallic lithium (a half-cell configuration). The counter electrode serves as reference electrode as well. Throughout the entire thesis, all potentials are given in respect to the metallic lithium electrode (Li/Li$^+$). A separator is used to avoid the electric contact between the working and counter electrode. The separator used in this study is made of glass fibers and soaked in the electrolyte. The electrolyte used in the standard experiments is a solution of 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and di-methyl carbonate (DMC). The solvents were mixed in the proportion of 1:1 by weight (EC:DMC). The cell was then assembled inside a glove box, under a high-purity argon atmosphere ($O_2$ and $H_2O < 2$ ppm each). After completing the cell assembly, the cell was left inside the glove box for approximately half an hour in order to make sure the electrodes were completely soaked with electrolyte.

Both the galvanostatic cycling and cyclic voltammetry (CV) measurements were performed by means of a computer-controlled cell capture (CCCC) system (Astrol Electronics AG, Oberrohrdorf, Switzerland). The electrochemical cell was put inside a temperature-controlled chamber, where the operating temperature is maintained at $25 \pm 0.1^\circ C$. The galvanostatic cycling experiments for the negative electrodes were performed at a specific current of 10 mA g$^{-1}$ (based on the graphite weight). The cell was cycled between 1.500 and 0.005 V. As for the positive electrodes, the galvanostatic cycling experiments were performed at a specific current of 25 mA g$^{-1}$ (based on the oxide weight). In the “low voltage” experiments, the cell was cycled between 3.0 and 4.3 V; while in the “high voltage” experiments, the cell was cycled between 3.0 and 5.0 V. The CV measurements for the positive electrodes were performed between 3.0 and 5.0 V at two different scan rates, namely at 0.02 and 0.05 mV s$^{-1}$.

4.4 Differential Electrochemical Mass Spectrometry (DEMS)

The differential electrochemical mass spectrometry (DEMS) experiments were performed in a special electrochemical cell (also known as the DEMS cell) [106,107]. The current collectors used for the working and the counter electrodes are also applied as the body of the cell (see Figure 4.1). The current collectors used are titanium plates. One of the titanium plate contains a quartz window in the upper part of the body, for monitoring the level
of the electrolyte in the cell. Another titanium plate provides the inlet of the electrolyte (bottom of the cell) and also the inlet and outlet for the argon carrier gas (top of the cell). The latter titanium plate also has other two additional holes on the top for optional use (if necessary). The argon flux continuously removes the gases accumulated on the top of the DEMS cell and carries these accumulated gases to the mass spectrometer. The DEMS cell normally works without the separator. The separator could retain partially gas bubbles released from the working electrode. The distance between the electrodes is maintained by a polyethylene ring to avoid short-circuit of the DEMS cell. The DEMS cell has normally a two-electrode configuration and is assembled in a glove box with high-purity argon atmosphere (O\textsubscript{2} and H\textsubscript{2}O < 2 ppm each). The DEMS cell was always assembled in a half-cell configuration, unless otherwise specified. The electrolyte used in the DEMS cell is specified in the Experimental Chapters 5 and 6.

![Figure 4.1: Schematic representation of the DEMS cell.](image)

A new cell for the DEMS experiment was built during this doctoral work. In the new DEMS cell, a reference electrode could be placed on the bottom of the titanium body (see Figure 4.2). The reference electrode is electrically insulated from the remaining part of the titanium body via insulation with epoxy resin. A hole at the back of the reference electrode holder provides the electrical connection with the potentiostat/galvanostat. The new DEMS cell has the advantage of a three-electrode configuration thus providing a reference potential for the working electrode. In general, the reference electrode applied was metallic lithium. However, the holder of the reference electrode can also support other electro-active materials as the reference electrode.
The electrochemical part of the DEMS experiment is a cyclic voltammetry, where it is performed at room temperature with a potentiostat (MODEL 2049, AMEL Instruments). The CV measurement has to be performed relatively fast compared to the other standard experiments. The scan rate applied is 0.2 mV s\(^{-1}\). The choice of the scan rate is related to the resolution needed for the mass spectrometry results, as explained below. Before starting the electrochemical experiment, the gas pipe line and the DEMS cell are purged with Ar carrier gas for 5 h to remove traces of air (possibly remaining after assembly in the interconnections of the DEMS cell with the mass spectrometer unit). The DEMS experiments of the graphitic negative electrodes were performed between 3.00 and 0.09 V (vs. Li/Li\(^{+}\)) in the first reductive half-cycle, followed by the reductive cycling between 1.50 and 0.09 V (vs. Li/Li\(^{+}\)) in all subsequent cycles. The DEMS experiments for the oxide positive electrodes were performed between 3.40 and 5.30 V (vs. Li/Li\(^{+}\)) in the first oxidative half-cycle, followed by the oxidative cycling between 5.30 and 2.50 V (vs. Li/Li\(^{+}\)) in all subsequent cycles.

The gases developed in the DEMS cell are removed by a flux of argon carrier gas. The argon flux carries the gas phase on the top of the DEMS cell to the mass spectrometer (see Figure 4.3). The argon flux is controlled by a mass flow controller (GSC-A9SA-DD21, Voegtlín Instruments AG). The GSC can control the mass flow of the gas between 0.05 and 5.00 mL min\(^{-1}\), with an estimated error of 0.05 mL min\(^{-1}\). The mass flow controller is located before the DEMS cell, in order to prevent any vapors from the solvents from entering the mass flow controller and, subsequently, to condensate inside.

**Figure 4.2:** Schematic representation of the new DEMS cell. The electric connection provides the necessary electrical contact for the reference electrode.
The background line in the DEMS measurement is due to the argon (carrier gas) flux and also the vapors from the solvents. In particular, the dimethyl carbonate (DMC) is a low boiling-point compound ($T_b = 91 \, ^\circ\text{C}$). The mass spectrum of the argon flux has no mass number in common with the mass spectrum of the typically developed gases; its influence on the background line is therefore small. The spectrum of DMC has many mass numbers in common with the typical developed gases; the background line generated by the DMC is therefore very important.

In order to increase the sensitivity of the DEMS data, it is necessary to either decrease the concentration of DMC in the gas flow or increase the concentration of the developed gases. The amount of gases developed in the time unit is dependent on the scan rate of the cyclic voltammetry; the higher the scan rate, the higher the concentration of the developed gases. The amount of DMC in the gas flow is independent of the scan rate. If the flux of argon in the DEMS cell is increased, the concentration of DMC in the gas flow decreased slightly, while the concentration of developed gas decreased linearly. Therefore, in order to increase the sensitivity of the DEMS data, it is necessary to increase the scan rate and to decrease the flux of the argon carrier gas. The applicable scan rate is limited by the kinetics of the system, where the optimum scan rate was found to be approximately $0.2 \, \text{mV s}^{-1}$. On the other hand, the flux of the argon carrier gas is limited by the sensibility of the mass flow controller and retro-diffusion of oxygen from the air to the mass flow controller. If the flux of the argon carrier gas is lower than $1 \, \text{mL min}^{-1}$, the retro-diffusion of air from the outlet of the gas pipe line will generates a background signal.

Due to the above-mentioned technical issues, a new gas pipe line was built to increase the ratio between the concentration of the developed gases over the concentration of those developed by the DMC (see Figure 4.3) solvent in the cell. The new gas pipe line is connected to two mass flow controllers; the first one is a GSC-type, while the second one is a F-200CV-type (Bronkhorst AG). The F-200CV can control the gas flow between 0.02 and 1.00 mL min$^{-1}$, with an estimated error of 0.01 mL min$^{-1}$. In this case, the F-200CV controls the flow of argon into the DEMS cell at approximately 0.05 mL min$^{-1}$. The gas outlet of the DEMS cell goes into a T-connection, where it is mixed with a stream of pure argon (0.95 mL min$^{-1}$) controlled by the GSC. The new gas pipe line permits a higher ratio (ca. 15 times higher with respect to the old gas pipe line) between the concentrations of the gas developed gases.
over the concentration of those developed by the DMC solvent in the cell. The total gas flow to the DEMS cell is approximately 1 mL min\(^{-1}\) in order to avoid the retro-diffusion of air.

![Diagram](image)

**Figure 4.3:** a) DEMS experimental setup with a single mass flow controller. b) New DEMS experimental setup with two mass flow controllers in parallel. Ar indicates the bottle of argon.

The mass spectrometer applied in our DEMS system is a quadrupole-type mass spectrometer (Prisma QME 200, Pfeiffer Vacuum). The ion source is built-in in the mass spectrometer. The ion source is an electron beam source, where the filament used is tungsten. For this DEMS experimental setup, the gas inlet into the mass spectrometer was modified. The gas inlet now consists of a sheet (thickness 20 µm) of stainless steel with a laser-punched hole of approximately 2 µm in diameter. The pressure inside the mass spectrometer reached up to \(4 \times 10^{-6}\) mbar. As the pressure decreases with time, the stainless steel sheet would have to be replaced when the pressure is lower than \(1.5 \times 10^{-6}\) mbar. In general, a large portion of the gas flow exits the gas pipe line from the gas outlet (see Figure 4.3). Only a small portion of the gas flow reaches the mass spectrometer and is analyzed. The time delay between the release of the gas on the top of the DEMS cell and the detection of the gas in the mass spectrometer is approximately 16 s. It was measured experimentally by injecting air into the DEMS cell, which was filled with electrolyte. Thus, at a scan rate of 0.2 mV s\(^{-1}\) the uncertainty in the potential associated to the gas development is about 3 mV.
4.5 Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) experiments were performed in a special electrochemical cell (also known as the EIS cell) [108] (see Figure 4.4). The cell is divided into three parts: the main central part and the remaining two electrode-holders. The body of the cell is made of polyetheretherketone (PEEK), while the current collectors are titanium plates of approximately 1.33 cm$^2$ in geometrical surface area. The cell can also function without the use of a glass fiber/Celgard separator. The distance between the electrodes is maintained by the central part of the cell. The central part of the cell has four holes. The holes can be used to fill the cell with the electrolyte and also to place a reference electrode. The reference electrode normally consists of a small piece of lithium fixed at the tip of a titanium wire ($\Theta = 225 \, \mu m$) insulated in a tube. The reference electrode remains external to the current lines flowing from the working electrode to the counter electrode. The cell was assembled in a glove box with high-purity argon atmosphere ($O_2$ and $H_2O < 2 \, ppm$ each).

![Figure 4.4: Drawing of the EIS cell.](image)

The EIS experiments were performed under strict temperature control at approximately 25(±0.1) °C using a potentiostat/galvanostat (Model 273A, EG&G Princeton Applied
Research) coupled with a Frequency Response Analyzer (SI 1255, Solartron). The impedance data were acquired with a Power Suite software (Princeton Applied Research). Only the graphite negative electrodes were investigated with this EIS technique. The EIS cell was assembled in a half-cell configuration. Conditioned metallic lithium with high surface area was used as the counter electrode, due to the low impedance. The impedance data of the graphite negative electrodes were acquired before cycling and also after a desired number of cycles, respectively, at a constant DC potential of approximately 1.5 V (vs. Li/Li') in the frequency range from 100 kHz to 10 mHz by imposing an alternate current with a small amplitude of 2 mV on the electrode in the steady state. Before starting the frequency sweep, the graphite negative electrode was stabilized at 1.5 V (vs. Li/Li') for 2 h. Meanwhile, for the cycling of the graphite negative electrode, cyclic voltammetry was performed between 1.50 and 0.09 V (vs. Li/Li') at a scan rate of approximately 0.2 mV s⁻¹. This experimental setup was used to investigate the changes in the graphite electrodes due to high scan rate cycling.

4.6 Multiple-Working-Electrode Cell (MWE)

The multiple-working-electrode cell (MWE) is a special home-made cell, which was developed during this doctoral work. The MWE cell is based on the coffee bag cell design [109,110]. One or more electrodes can be used in the cell as working electrodes (see Figure 4.5). The working electrodes are placed in series and are electrically insulated by means of a separator, and, at the same time, ionically connected through the electrolyte. Each working electrode consists of a self-standing electrode pressed onto a metallic mesh that acts as a current collector. The electrode was prepared in the similar way as described earlier in Paragraph 4.1. The current collectors used in this study are expanded metal meshes of approximately 30 µm in thickness. The use of metal mesh guarantees the ionic contact between the working electrodes. The type of material for the current collector is chosen according to the electrode, as described earlier in Paragraph 4.1. Meanwhile, the counter electrode is a strip of metallic lithium foil fixed to a copper mesh. In general, only one lithium electrode is needed for the whole MWE cell. The separators used are normally made of polypropylene and are 25 µm thick (Celgard 2500). Between the working electrodes and the counter electrode, a glass fiber separator is placed in order to adsorb more electrolyte to create a buffer layer of electrolyte solution. Finally, the separators are soaked in the electrolyte solution before sealing of the coffee bag cell.
The coffee bag foil used for the assembly of the MWE cell is a multi-layered foil composed of two layers of polyethylene (PE), one layer of aluminium (Al) and also one layer of oriented polyamide (OPA). Once all elements of the cell are stacked, the MWE cell is sealed to protect the cell from oxygen and moisture in the air. The MWE cell is assembled and sealed in a glove box with high-purity argon atmosphere (O\textsubscript{2} and H\textsubscript{2}O < 20 ppm each). The coffee bag measures approximately 10 cm by 10 cm, and prior to any electrochemical measurement, cables were soldered to the current collectors, in order to connect it to the potentiostat.

The MWE cell can be used for standard electrochemical experiments as well as for EIS measurements. A reference electrode can be added to the MWE cell. The MWE cell is aimed at the study of the current density distribution throughout the working electrodes applied. The current density flowing from the working electrodes can be acquired separately.
5 Study of the Negative Electrodes

5.1 Introduction

Graphite is the most used active material for the negative electrode of commercially available lithium-ion batteries. The term graphite indicates an ordered compound formed by graphene sheets stacked along the c-axis (see figure 5.1). The graphene sheets are kept together by Van der Waals forces; the structure can expand along the c-axis and accommodate lithium-ions. By intercalation of Li\(^{+}\) in the structure of graphite, Li\(_x\)C\(_6\) is formed, with 0 = x = 1 [27]. Graphite particles are formed by many graphite crystals, differently oriented, called crystallites.

![Schematic representation of the crystalline structure of graphite.](image)

Graphite has many advantages: the practical and theoretical reversible specific charge are similar and around 372 mAh g\(^{-1}\); the equilibrium potential of the lithium-graphite compounds is near the equilibrium potential of metallic lithium [28], therefore can be used in high energy lithium-ion batteries; it can be charged and discharged many times without lose of the electrochemical performances; it is cheap and environmentally friendly. The disadvantages of graphite based electrodes are related to the advantages. Because of the strongly reductive equilibrium potential of the Li\(_x\)C\(_6\) compounds, the components of the common organic electrolyte are not thermodynamically stable. The reduction of the electrolyte is an irreversible process; the irreversible charge used in the reduction of the
electrolyte is “lost” (loss of the performance of the battery). The products of the reduction of the electrolyte are mainly gaseous, the pressure inside the lithium-ion battery increases (safety problem). Moreover, when the lithium ions intercalate in the graphite structure, the solvation shell of Li⁺ is not blocked by the surface of graphite; the solvation shell co-intercalates into the graphite structure, where it is reduced. The gaseous products of the reduction of the solvation shell expand the layers between graphene sheets, destroying the crystal structure of graphite near the surface (exfoliation). The exfoliation process generates fresh surface in contact with the electrolyte, and the new surface speeds up the process of exfoliation. The exfoliation process irreversibly consumes a huge amount of charge; under exfoliating conditions the graphite based electrodes cannot be used as negative electrodes for commercial lithium-ion batteries.

The reduction of the electrolyte is kinetically blocked by the formation of a passivation film at the surface of graphite particles. The passivation film is called solid electrolyte interphase (SEI) and prevents also the reductive co-intercalation of solvent molecules. The SEI layer is a very complex, rather random composite of organic and inorganic electrolyte decomposition products of the (organic) solvents and (inorganic) lithium salt(s) [111]. An effective SEI layer permits lithium ions to pass through but is insulating for electrons and, ideally, impermeable for solvent molecules. A good quality SEI is critical for the proper functioning of electrodes based on highly crystalline graphite. Ethylene carbonate (EC) containing electrolytes are able to form a good quality SEI. Propylene carbonate (PC) containing electrolytes are not able to form an SEI which blocks the co-intercalation of solvent molecules. If a mixture of EC and PC is used as solvent for the electrolyte, the final behavior of the graphite is strongly dependent on the surface chemistry of the graphite particles [26]. The formation of the SEI irreversibly consumes a part of the charge used for charging the graphite electrode. For a better performance of the graphite electrode, it is desired that a good quality SEI formed with the smallest amount of charge.

For safety reason, the potential of the graphite electrode has to be always higher than about 50 mV (Li/Li⁺), to avoid the electroplating of the lithium at the surface of the graphite particles. The under abuse conditions deposited lithium could have a needle-like shape and break locally the separator, causing a short circuit. The equilibrium potential of the LiC₆ phase is around 100 mV (Li/Li⁺); only 50 mV of overpotential can be used to charge the
graphite particles. Depending on the kinetic and mass transport limitations, there is a maximum specific current, which can be used to charge the graphite particles.

The DEMS measurements are particularly suitable for the study of the SEI formation. The gaseous molecules generated by the reduction of the electrolyte can be detected by the mass spectrometer, and their nature can be correlated with the reduced solvent molecules. The correlation between the intensity of several mass numbers and the potential of the graphite electrode could give an indication of the mechanism of SEI formation. It is also possible to investigate the eventual reductive co-intercalation of solvent molecules.

The EIS measurements are suited for the study of the kinetic limitations of the graphite electrode. The effect of the pore structure on the total response of the graphite electrode can be separated and analyzed. The pore structure is also the cause of a non-homogeneous usage of the graphite electrode; its study is believed to be the key for the engineering of a fast graphite electrode for high power lithium-ion batteries. Moreover, it is possible to observe the effect of aging on the kinetic parameters of the graphite electrodes, and correlate it with the morphology and orientation of the crystallites.

The surface chemistry of the graphite is very important for the formation of the SEI and the intercalation of the lithium ions in the structure of graphite. Different orientation of the crystallites and different manufacturing processes of the graphite particles have different effects on the surface chemistry of graphite (surface groups). Four samples of synthetic (KS and SFG) and natural (GN) graphites (TIMREX®, TIMCAL SA, Bodio, Switzerland) were selected to examine the influence of the particle morphology, and orientation of the crystallites. Also different particle sizes were selected to examine the influence of the particle size on the SEI formation and pore structure. Table 5.1 summarizes the main characteristics of the graphite particles investigated during this PhD work.

<table>
<thead>
<tr>
<th></th>
<th>BET / m² g⁻¹</th>
<th>d₅₀ / µm</th>
<th>d₉₀ / µm</th>
<th>Purity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS44</td>
<td>9.0</td>
<td>18.6</td>
<td>45.4</td>
<td>98.2%</td>
</tr>
<tr>
<td>SFG44</td>
<td>5.0</td>
<td>23.8</td>
<td>48.8</td>
<td>98.0%</td>
</tr>
<tr>
<td>GN44</td>
<td>4.9</td>
<td>22.9</td>
<td>49.5</td>
<td>98.0%</td>
</tr>
<tr>
<td>KS6</td>
<td>20</td>
<td>3.4</td>
<td>6.5</td>
<td>98.1%</td>
</tr>
</tbody>
</table>

Table 5.1: Basic characteristics of the investigated graphites. d₅₀ and d₉₀ represent the average dimension of the particles at which the cumulative distribution is equal to 50 % and 90 %, respectively.
5.2 Standard Electrochemical Measurements

The electrochemistry of graphite particles is well known. In a standard electrochemical measurement, only graphite KS6 was investigated by using galvanostatic cycling, to gain information on the irreversible loss during the SEI formation. The laboratory coin-type cell, containing the KS6 electrode, was cycled between 1.5 and 0.005 V. The electrolyte was 1 M LiPF$_6$ in EC:DMC (1:1 by wt.). The galvanostatic cycling was performed at 10 mAh g$^{-1}$, to complete the formation of the SEI layer in the first cycle. The curve potential $E$ vs. charge $Q$ in the first cycle shows the common main features of the graphite electrodes (see figure 5.2). The open circuit potential of the KS6 electrode is around 3.1 V (Li/Li$^+$); when the (negative) current intensity is imposed, the potential decreases rapidly up to 1.0 V (Li/Li$^+$). In the potential window 3.0 – 1.0 V (Li/Li$^+$) the electrochemical processes at the interface graphite/electrolyte involve reduction of surface groups and reduction of trace of water in the electrolyte; both processes are irreversible.

Figure 5.2: Galvanostatic cycling measurements at 10 mAh g$^{-1}$ in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte for KS6 based electrodes (1$^{st}$ cycle).
In the potential window 1.0 – 0.3 V (Li/Li⁺) the electrochemical process is the formation of the SEI. The charge consumed in the formation of the SEI is higher than the charge consumed in reducing the surface groups. If a good quality SEI is formed, in this potential window the charge consumption in the following cycles is drastically reduced and is almost reversible; the so called dilute phase is formed (see figure 5.3).

In the potential window 0.3 – 0.005 V (Li/Li⁺) the main electrochemical process is the intercalation of lithium in the graphite structure. Three plateaus are observed, which correspond to three different lithium-graphite compounds, namely Li_{1/3}C_6, Li_{1/2}C_6, and LiC_6. The charge consumed in the lithium intercalation is reversible; the charge is recovered during the anodic oxidation of the lithium-graphite compounds. During the electrochemical intercalation of lithium, the co-intercalation of the solvent molecules is also possible, if the SEI is not sufficiently protective. The co-intercalation of the solvent is followed by the reduction of the solvent (exfoliation), which is an irreversible process.

![Graph of electrochemical behavior](image)

**Figure 5.3:** Galvanostatic cycling measurements at 10 mAh g⁻¹ in 1 M LiPF₆, EC:DMC (1:1 by wt.) electrolyte for KS6 based electrodes (5th cycle).
In the following cycles, the curves $E$ vs. $Q$ during reduction and oxidation of the KS6 electrodes have the same shape, but are shifted in potential (see figure 5.3). The shift of the potential is due to the overpotential; it represents the kinetic limitations of the graphite sample. After the first cycle, the irreversible specific charge decreases, while the reversible specific charge remains stable or increases slightly in the second cycle and then stabilizes. The decrease of the irreversible specific charge indicates the formation of a good quality SEI. The rate of charge and discharge in the galvanostatic cycling experiment was very low (namely 10 mA g$^{-1}$), allowing the complete charge of the graphite particles.

To study the effect of fast charging and ageing on the graphite performance during the first few cycles, cyclic voltammetry experiments were performed on all graphite samples (cf. table 5.1). The cyclic voltammetry experiments were performed at a scan rate of 0.2 mV s$^{-1}$, using as the electrolyte 1 M LiPF$_6$ in EC:DMC (1:1 by wt.). The EIS cell with a three electrode configuration was used for the experiment. The potential window investigated was 1.50 – 0.09 V (Li/Li$^+$). The limit of 0.09 V (Li/Li$^+$) was chosen because the graphite electrodes come off the current collector at lower potentials if the electrode is not pressed by the separator. Metallic lithium was used as counter and reference electrode. The metallic lithium counter electrode was preconditioned by imposing a current of 1.5 mA for 2 hours in another cell and then mounted into the EIS cell.

In figure 5.4 the first electrochemical cycles of all examined samples are compared. It is observed that, during the first reduction, all three types of graphite exhibit an irreversible reduction peak around 600 mV vs. Li/Li$^+$. This reduction peak is attributed to the formation of the SEI surface layer. The charge consumed during the SEI formation correlates with the BET specific surface area of the graphite which translates into the dependence of the magnitude of this particular peak on the BET value (see table 5.2 and table 5.1) [112]. But the KS44 electrode shows an additional reduction current maximum around 350 mV vs. Li/Li$^+$. This second current maximum looks a lot like a plateau and, with respect to the first maximum at ca. 600 mV; the specific current is higher in this potential region. This second reduction peak was also attributed to the SEI formation coupled with the exfoliation of some graphite particles [113]. The intercalation peak is located around 0.15 V (Li/Li$^+$); the current peak corresponds to the formation of the compound Li$_{1/3}$C$_6$. At lower potential the reductive current intensity increases again; it indicates the formation of a new lithium-graphite phase,
Li_{1/2}C_6. Because the scan rate is switched at 0.09 V (Li/Li⁺), the intercalation process is not complete, the second reductive current maximum is not observed. The oxidation of the lithium-graphite compounds shows a double peak, which correspond to the de-intercalation of the lithium from the partially formed Li_{1/2}C_6 and Li_{1/3}C_6, respectively.

![Figure 5.4: Cyclic voltammograms at 0.2 mVs⁻¹ in EC:DMC, 1 M LiPF₆ for the investigated graphite samples (1st cycle).](image)

In figure 5.5 the different electrochemical cycles of the KS44 sample are compared. The sample KS44 is representative of the behavior of the other graphite samples. After the first cycle, the potential window 1.50 – 0.25 V (Li/Li⁺) is electrochemically inactive. The reductive current peak at low potential decreases in intensity and is shifted to more cathodic potential. The oxidative current peaks at low potential also decrease in intensity and are shifted to more anodic potential. The shift of the peaks in the opposite direction of the potential scale indicates an increase of the resistance of the system. Also the decreasing of the intensity in the current peaks is an indication of the increased resistance of the system. The
The difference between the potential of the second anodic current peak and the potential of the cathodic current peak is equal to two times the average overpotential.

Figure 5.5: Cyclic voltammograms at 0.2 mVs$^{-1}$ in EC:DMC, 1 M LiPF$_6$ for graphite KS44.

<table>
<thead>
<tr>
<th></th>
<th>$Q_{IRR}$ / mAh g$^{-1}$</th>
<th>$Q_{REV}$ / mAh g$^{-1}$</th>
<th>$Q_p$ / mAh g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
<td>5th</td>
</tr>
<tr>
<td>KS44</td>
<td>93.6</td>
<td>13.0</td>
<td>3.7</td>
</tr>
<tr>
<td>SFG44</td>
<td>21.7</td>
<td>4.2</td>
<td>1.7</td>
</tr>
<tr>
<td>GN44</td>
<td>19.8</td>
<td>3.2</td>
<td>1.3</td>
</tr>
<tr>
<td>KS6</td>
<td>61.5</td>
<td>10.2</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 5.2: Basic electrochemical data from cyclic voltammetric experiments of the investigated graphites. $Q_{IRR}$ is the irreversible charge, $Q_{REV}$ is the reversible charge, and $Q_p$ is the irreversible charge measured between 1.50 and 0.50 V vs. Li/Li$^+$ in the first cycle.

In Table 5.2 the irreversible and reversible charge for the entire cycle and the $Q_p$ (the charge in the potential window $\geq$500 mV vs. Li/Li$^+$ under the reductive peak in the first cycle, related to the SEI formation) is compared for the different graphite samples and given cycles. The cycling was performed by cyclic voltammetry at a fairly fast potential sweep rate of
0.2 mVs\(^{-1}\) with immediately reversing the current at the lower potential limit. In such an experiment the (faster) surface reactions can be considered as completed but this is not true for the (slower) lithium intercalation into the bulk graphite. The KS44 sample has the highest irreversible charge consumption, but the sample KS6 has the higher value of \(Q_b\), which is related to the irreversible charge consumed in the formation of the SEI. The values of the irreversible charge consumption listed in table 5.2 are for the SEI formation on the original surface of the respective samples but also include the charge consumption for the exfoliation and passivation of so created new surface. In the case of the KS44 graphite, most of the irreversible charge consumption is related with the exfoliation process, as evidenced by figure 5.4 and table 5.2.

5.3 EIS measurements

To have a better insight on the effect of ageing on the graphite performance during the first few cycles, the cyclic voltammetry experiments described in paragraph 5.2 were coupled with electrochemical impedance spectroscopy (EIS) measurements. EIS experiments were performed at 1.5 V vs. Li/Li\(^+\) after a given number of cycles, in particular before the formation of the SEI layer (“0\(^{th}\) cycle”) and after the 1\(^{st}\), 2\(^{nd}\), 5\(^{th}\), and 10\(^{th}\) cycle, respectively. EIS was performed in the frequency range 100 kHz - 10 mHz, imposing an alternate current of a small amplitude of 2 mV on the electrode in a steady state. Before starting the frequency sweep, the graphite electrode was stabilized at 1.5 V vs. Li/Li\(^+\) for 2 hours.

To extract useful information from the acquired EIS data, all the impedance spectra were analyzed using Kramers-Kronig transformations, as explained in paragraph 2.4. Using the model described by equation (2.23), it was possible to eliminate an eventual instability and non-linearity of the system. Equation 2.23 fits the impedance data with a general model, which describes an infinite parallel of a resistance in series with a capacitor; this model can fit every set of EIS data responding to the principles of linearity, stability and causality. Every parallel branch corresponds to a time constant. For the real analysis of the experimental EIS data, 5 time constants per decade of the investigated frequency range were used. The so analyzed data and the experimentally acquired ones showed discrepancies at very low and very high frequencies, respectively, but the relative errors were always less than 3% (see figure 5.6). The model used in Kramers-Kronig analysis doesn’t describe the real electrochemical process occurring in the system.
The influence of the SEI layer on the electrochemical response of graphite electrodes is obvious from the difference between the impedance spectra acquired at 1.5 V vs. Li/Li$^+$ on fresh (“0$^{\text{th}}$ cycle”) and cycled electrodes (“1$^{\text{st}}$ cycle”), respectively. At 1.5 V the surface of fresh electrodes is not yet covered by a noteworthy SEI film and the cycled electrodes do not show first-order transitions due to intercalation of Li$^+$. In figure 5.7 representative impedance spectra of a GN44 electrode in a standard EC:DMC battery electrolyte are compared in a Bode plot. It is clear from the figure that the electrochemical processes changed significantly; the evidence is given by the different slope of the modulus of a cycled electrode with respect to a fresh one. Moreover, the value of the modulus of the impedance in the high and medium frequency range (above 1 Hz) is higher for the cycled electrode. In the low frequency range (below 1 Hz) the value of the modulus of the impedance is lower for the cycled electrode.
In figure 5.8 the modulus of the specific electrochemical impedance measured on fresh KS44, SFG44, GN44, and KS6 electrodes is shown for the “0th cycle”. Undoubtedly, for the KS samples the impedance value at low frequencies is about 3 times less than for the SFG44 and GN44 graphites. Clearly, there is an influence of the BET specific surface area (see table 5.1) but one can certainly conclude that the impedance value correlates with the irreversible charge consumption.

In figure 5.9 the modulus of the specific electrochemical impedance measured on cycled KS44 electrodes is shown for different cycles. In the high frequency region (above 1 Hz) the value of the specific impedance increases with the cycle number. In the low frequency region (below 1 Hz) the value of the specific impedance decreases slightly; the relative difference between the value of the impedance acquired at 10 mHz at the 1st cycle and at the 10th cycle is about 14%. The behavior of the KS44 sample is representative of the other graphite samples. It seems that by increasing the cycle number the resistance in the high frequency region, corresponding to the resistance of polarization of the electrode, increases.
Figure 5.8: Modulus of the specific electrochemical impedance acquired for the different graphite samples in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte at 1.5 V vs. Li/Li$^+$ before the SEI formation.

Figure 5.9: Modulus of the specific electrochemical impedance acquired for the KS44 samples in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte at 1.5 V vs. Li/Li$^+$ after the SEI formation at different cycles.
Essential information about the processes at/in the graphite electrodes can be extracted from the electrochemical impedance spectra. The electrodes have inherent energetic limitations (due to the charge transfer resistance at the interface, lithium diffusion inside the host material, lithium adsorption at the interface, etc.) and geometric limitations (due to the resistance of both the electrode and the electrolyte in the pores, diffusion gradients in the pores, etc.). Deep understanding of these limitations allows engineering of the electrode in order to obtain maximum performance of the electro-active material and to utilize the electrode homogeneously. For this purpose the electrochemical impedance spectroscopy is a very useful tool because it permits a rather easy quantification of a number of different processes.

In figure 5.10 a Nyquist plot of the experimental electrochemical impedance spectrum of a fresh GN44 electrode is shown as an example. At high frequencies a depressed capacitive semicircle is observed, due to the influence of the porosity on the electrode’s AC response, as explained in paragraph 3.4. For this reason, independently from the physical model to apply to simulate the electrochemical processes at the graphite electrode interface, a model to include the spatial effects cannot be disregarded. The solution developed in paragraph 3.4 was used to fit the impedance spectra. It was necessary to find an expression for $\kappa^2$, which depends on the physical model of the interfacial electrochemical processes through $Z$. The examination of the Nyquist plots for fresh graphite electrodes (all graphite samples) has suggested that the electrochemical process before the SEI formation can be described as an adsorption process. The expression of $Z$ can be calculated from eq. (3.16), imposing $R_2 > 8$. Correlations between the fitted parameters from an equivalent circuit model with the microscopic properties of the electrode (such as reaction rate, wetted surface area, and number of adsorbing sites) depend on the value of $\Gamma$, but this parameter cannot be obtained directly from the EIS data. It was observed that, at low frequencies the experimental impedance spectra deviated from the spectra calculated using the classical adsorption model. This deviation from the model can be attributed to a current leakage at the interface. From the point of view of physical chemistry, a current leakage represents a current passing through the electrode because of side reactions and/or because the experiments were performed under quasi-steady-state conditions (which means that the adsorbing sites were not fully equilibrated). Considering an equivalent circuit, a leakage current can be simply represented by a conductance, $G_{lc}$, in parallel with the capacitance of double layer.
Figure 5.10: Nyquist plot of the electrochemical impedance of a GN44 electrode in the 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte at 1.5 V vs. Li/Li$^+$ before the SEI formation.

Fitting the impedance spectra with the adsorption model gives realistic results for the samples SFG44 and GN44, respectively, but not for the KS samples (KS44 and KS6). In the latter case a second time constant is observed. This time constant can be attributed to several secondary effects, or to an additional parallel process or to a process in series with the adsorption process. Several alternatives were analyzed: the NTLM model was used instead of the TLM model; a secondary parallel process of adsorption at a second type of surface sites was added; a two-step adsorption process trough surface states was substituted to the standard adsorption process. Note that a reaction trough surface states is a typical phenomenon for junctions semiconductor/electrolyte, investigated and discussed for many systems [114].
For our electrochemical system, the two-step adsorption through the surface states was chosen as the most plausible process. This choice is based on comparing the fitting parameters obtained from the models, especially considering the influence of porosity and comparing the data for the KS samples with those obtained for SFG44 and GN44, respectively. It should be stressed that the models were obtained by solving the physico-chemical equations describing the system and that all non-idealities were attributed to the leakage current. The equations used for fitting the impedance spectra are more than an assembly of plausible parameters, and the fitted values can be correlated directly with the physicochemical properties of the electrochemical system.

The geometrical properties of the system are contained in the model for porous materials. Because graphite has a comparatively high electrical conductivity (order of magnitude of $10^4$ S·cm$^{-1}$ in the bulk material) with respect to the ionic conductivity of the electrolyte solution (order of magnitude of $10^{-2}$ S·cm$^{-1}$), the parameter $\alpha$ in eq. (3.37) was assumed to be close to 0. The impedance spectra were therefore fitted using as object function $\chi^2_{\text{mod}}$ (see eq. (2.26)). In Tables 5.3 and 5.4 the parameters obtained from fitting the impedance spectra measured before the SEI formation are reported for the standard adsorption process and for the adsorption process through surface states, respectively. The standard deviation of the fits was always very low ($\chi^2$ less than $10^{-3}$). The resistance of the pores $R_p$ is equal to

$$R_p = \frac{\rho l}{N_A \rho M}$$  \hspace{1cm} (5.1)

where $M$ is the mass of the sample. The resistance $R_p$ of the pores depends on the geometry of the system (in particular on the geometric area of the current collector) and is normalized to the mass, thus, when the mass is higher, the electrode is considered to be thicker and the resistance of the pores higher.

It has to be stressed that the order of magnitude of $R_p$ is always the same, regardless which of the two models is used for the fitting, and nearly independent of the graphite type. The minor differences originate most probably from the different shape and dimension of the particles of each graphite type. In particular, KS6 sample has an $R_p$ value double with respect to the other graphite types, which means smaller dimensions of the pores. For this reason we argue that the investigated pores are generated by the connection between the particles, not
intrinsically present in the material. Note that in a porous system the apparent value of the electrolyte resistivity in pores is higher with respect to the resistivity of the bulk electrolyte solution. The ratio between the two values is the so-called tortuosity which depends on the geometry of the pores and, thus, on the shape of the particles in the electrode. The tortuosity can be considered also as the ratio between the true length of the current lines and the thickness of the electrode.

\[
R_p / \Omega \text{ g}^{-1} = 1.33 \cdot 10^3 \\
C_{dl} / F \text{ g}^{-1} = 5.95 \cdot 10^{-3} \\
R_{ad}/ \Omega \text{ g} = 2.21 \cdot 10^{-3} \\
\tau_{ad}/ s = 7.71 \cdot 10^{-4} \\
\chi^2 = 4.51 \cdot 10^{-4}
\]

Table 5.3: Parameters obtained by fitting the impedance spectra of GN44 and SFG44 electrodes measured in EC:DMC, 1 M LiPF$_6$ at 1.5 V vs. Li/Li$^+$ before the SEI formation with the model describing standard adsorption process.

<table>
<thead>
<tr>
<th></th>
<th>SFG44</th>
<th>GN44</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p / \Omega \text{ g}^{-1}$</td>
<td>1.33 $\cdot 10^3$</td>
<td>1.42 $\cdot 10^3$</td>
</tr>
<tr>
<td>$C_{dl} / F \text{ g}^{-1}$</td>
<td>5.95 $\cdot 10^{-3}$</td>
<td>3.48 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>$R_{ad}/ \Omega \text{ g}$</td>
<td>2.21 $\cdot 10^{-3}$</td>
<td>1.65 $\cdot 10^{-2}$</td>
</tr>
<tr>
<td>$\tau_{ad}/ s$</td>
<td>7.71 $\cdot 10^{-4}$</td>
<td>4.92 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>4.51 $\cdot 10^{-4}$</td>
<td>2.28 $\cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 5.4: Parameters obtained by fitting the impedance spectra of all investigated electrodes measured in EC:DMC, 1 M LiPF$_6$ at 1.5 V vs. Li/Li$^+$ before the SEI formation with the model describing an adsorption process through surface states.

<table>
<thead>
<tr>
<th></th>
<th>KS44</th>
<th>SFG44</th>
<th>GN44</th>
<th>KS6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p / \Omega \text{ g}^{-1}$</td>
<td>1.32 $\cdot 10^3$</td>
<td>1.13 $\cdot 10^3$</td>
<td>1.40 $\cdot 10^3$</td>
<td>3.15 $\cdot 10^3$</td>
</tr>
<tr>
<td>$C_{dl} / F \text{ g}^{-1}$</td>
<td>1.23 $\cdot 10^{-2}$</td>
<td>4.60 $\cdot 10^{-3}$</td>
<td>2.22 $\cdot 10^{-3}$</td>
<td>1.47 $\cdot 10^{-2}$</td>
</tr>
<tr>
<td>$R_{ad}/ \Omega \text{ g}$</td>
<td>1.42 $\cdot 10^{-5}$</td>
<td>3.95 $\cdot 10^{-3}$</td>
<td>1.30 $\cdot 10^{-2}$</td>
<td>3.00 $\cdot 10^{-2}$</td>
</tr>
<tr>
<td>$C_{ad}/ F \text{ g}^{-1}$</td>
<td>8.28 $\cdot 10^{-1}$</td>
<td>3.33 $\cdot 10^{-1}$</td>
<td>2.97 $\cdot 10^{-1}$</td>
<td>1.43</td>
</tr>
<tr>
<td>$R_{SS}/ \Omega \text{ g}$</td>
<td>9.74 $\cdot 10^{-4}$</td>
<td>3.46 $\cdot 10^{-3}$</td>
<td>5.37 $\cdot 10^{-3}$</td>
<td>6.65 $\cdot 10^{-4}$</td>
</tr>
<tr>
<td>$C_{SS}/ F \text{ g}^{-1}$</td>
<td>3.19 $\cdot 10^{-1}$</td>
<td>1.77 $\cdot 10^{-2}$</td>
<td>1.86 $\cdot 10^{-3}$</td>
<td>1.39 $\cdot 10^{-1}$</td>
</tr>
<tr>
<td>$\tau_{SS}/ s$</td>
<td>3.11 $\cdot 10^{-4}$</td>
<td>6.13 $\cdot 10^{-5}$</td>
<td>8.32 $\cdot 10^{-6}$</td>
<td>9.27 $\cdot 10^{-5}$</td>
</tr>
<tr>
<td>$\tau_{ad}/ s$</td>
<td>1.13 $\cdot 10^{-3}$</td>
<td>2.49 $\cdot 10^{-3}$</td>
<td>5.49 $\cdot 10^{-3}$</td>
<td>5.76 $\cdot 10^{-3}$</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.15 $\cdot 10^{-4}$</td>
<td>4.20 $\cdot 10^{-4}$</td>
<td>2.27 $\cdot 10^{-4}$</td>
<td>3.41 $\cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

It follows a discussion on the results summarized in Tables 5.3 and 5.4. Because the adsorption process and charging of surface states are processes in series, the time constants for the surface state charge $\tau_{SS}$ and the adsorption $\tau_{ad}$, respectively, are defined as:

\[
\tau_{SS} = R_{SS} C_{SS} \\
\tau_{ad} = (R_{SS} + R_{ad})(C_{SS} + C_{ad})
\]

(5.2)
For both, the SFG44 and GN44 electrodes the impedance data were fitted using both models: standard adsorption and adsorption through surface states. From the latter model the time constant $\tau_{SS}$ is very low. Therefore, nothing is observed in the experimental impedance spectrum but a tiny distortion of the high frequency semicircle. Generally, the order of magnitude of $\tau_{SS}$ changes with the graphite type. It was hypothesized that this could be related to the variation of the graphite surface’s properties known to be dependent on the manufacturing process and, thus, on the graphite type. (There is also a dependence on the particle size of the same graphite type because of the influence of the milling process on the surface quality.) Another interesting observation is that the value of $\tau_{ad}$ is in the same order of magnitude for all types of graphite. The $\tau_{ad}$ values are related with the surface energetic of a particular interface, not with the surface area exposed to the electrolyte. Therefore, the lithium-ion adsorption process has obviously comparable surface energetic for all three types of graphite.

The next interesting point to discuss is the value of $C_{ad}$. Independent of the theory used to correlate the macroscopic properties of the electrode with the microscopic surface phenomena, $C_{ad}$ is proportional to the number of adsorbing (“active”) surface sites. One observes that the values of $C_{ad}$ are comparable when normalized with respect to the BET specific surface area of the respective sample. It is observed that the $C_{ad}$ values correlate well with the irreversible charge $Q_p$ consumed for the SEI formation. It is therefore possible to offer an interpretation of the nature of the adsorption sites, assuming them as electrochemically active surface sites reacting with the electrolyte solution at higher overpotentials. The active adsorption sites are occupied by species from the electrolyte and are the basis for the SEI nucleation and growth. Actually, the active adsorption sites could be considered as the very first layer of the SEI. Care must be taken when interpreting data when significant graphite exfoliation is involved (here the case of the KS44 sample) because the $C_{ad}$ values determined at 1.5 V vs. Li/Li$^+$ do not reflect the additional surface created by exfoliation.

The impedance spectra acquired for cycled electrodes (after the SEI layer was formed) were examined qualitatively. Clearly, there is a difference to the case without the SEI (see figure 5.7). Obviously, the model used for fitting the impedance spectra acquired for the different graphite types before the formation of the SEI cannot be used for fitting and
analyzing the impedance spectra acquired in the following cycles. A more sophisticated model including the influence of the SEI layer needs to be developed which could be the subject of future work.

5.4 DEMS Measurements

The understanding of the mechanism of formation of the SEI at the surface of negative electrodes based on graphite is very important for enhancing the performances of lithium-ion batteries. As explained in the previous paragraphs of this chapter, the SEI is composed of organic and inorganic lithium compounds, formed by the reduction of the electrolyte components. The specific charge consumed for the formation of the SEI is not recovered during the discharge of the lithium-ion battery. The SEI is necessary for the protection of the surface of the particles of graphite from the process of exfoliation, but the irreversible specific charge consumed for the SEI formation has to be as low as possible. The reduction of the electrolyte components produces volatile compounds, which can be detected with a mass spectrometer. The DEMS technique is an easy and powerful tool for the study of the mechanism of the SEI formation and the effectiveness of the SEI. If the SEI is not effective in protecting the surface of the particles of graphite from the exfoliation process, volatile compounds produced by the exfoliation process can be detected during the intercalation of Li⁺.

All the DEMS experiments were performed at room temperature in the DEMS cell with the reference electrode. The reference and counter electrodes were made of metallic lithium. The working electrodes were based on the graphites KS44 and KS6 (see table 5.1). Before starting the voltammetric DEMS experiment, a 5 hours delay was allowed to purge completely the entire gas system from traces of air, possibly remaining in the interconnections of the DEMS cell with the mass spectrometer unit. During the purging period, the potential of the graphite electrode was held constant at 3.00 V (Li/Li⁺). The first reductive half-cycle was then performed between 3.00 and 0.09 V (Li/Li⁺) and all subsequent cycles between 1.50 and 0.09 V (Li/Li⁺) at a potential sweep rate of 0.2 mVs⁻¹. During the DEMS experiments multiple mass signals (m/z) were recorded. The particular choice of the monitored mass signal channels was based on previous experiments. The signals of hydrogen and ethylene (known side products of the SEI formation [115]) were always recorded. The mass signals were analyzed using the technique explained in paragraph 2.3. The background signal composed of the mass spectrum of the argon carrier gas, and the low-boiling electrolyte component(s) in
the vapor phase were subtracted. The mass signal m/z = 59 was identified as being influenced only from the vapors of the electrolyte components and was used to subtract the base line in the procedure of analysis of the DEMS data. The time delay between gas evolution in the cell and detection in the mass spectrometer is circa 16 s (corresponding to a potential shift of circa 3 mV) and was estimated by injection of air into the electrolyte after the measurement.

In paragraphs 5.2 and 5.3, it was shown that the different graphite types in the 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte behave in the same way. It was also observed that the charge consumed during the SEI formation is proportional to the BET surface area. The KS type graphite was chosen as a reference material for this study because of its higher surface area, which permits an easier detection of the volatile compounds coming from the SEI formation. In figure 5.11 the comparative plot of the normalized mass signal intensities $I_2$ and $I_{27}$ as measured for the KS6 and KS44 samples in the 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte is reported. The mass signals $I_2$ and $I_{27}$ were typically observed during the SEI formation. It turned out that, in respect of both the onset of the gas development and the relative amounts of the volatile products, the results are comparable. Although the main features of the mass signals are independent from the type of graphite particles, the intensity of the mass signals, $I_m$, change strongly; in particular the intensity of $I_m$ for the sample KS6 is circa doubled with respect to $I_m$ for the sample KS44. Therefore, only representative results for KS6 electrodes are shown.

In figure 5.12 a comparative plot of the analyzed mass signal intensities, $I_m$, for the KS6 sample in the 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte is reported. The second cycle is also representative for the following cycles. The following observations were made: the signal intensities of mass number channels m/z = 26, 27, 28, and 44, respectively, reveal distinct peaks during the first reduction of the graphite electrode, there are no major peaks during the subsequent cycles; the signal intensities of mass number channels m/z = 2 and 41, respectively, show peaks re-appearing in each cycle, their magnitude decreases after the first cycle but then remains quite constant in the subsequent cycles; all relevant channels show peaks during the reduction of the electrode (which means during the SEI formation and/or lithium intercalation), but there are no significant mass signals during the lithium de-intercalation from the graphite.
Figure 5.11: Comparative plot of the mass signal intensities $I_\text{m}$ ($\mu$A g$^{-1}$) as measured for the KS6 and KS44 samples in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.
Figure 5.12: Comparative plot of the analyzed mass signal intensities $J_m$ (nA g\(^{-1}\)) (see paragraph 2.3) for the KS6 samples in 1 M LiPF\(_6\), EC:DMC (1:1 by wt.) electrolyte.
From the analysis of mass spectra of various reference gases and their mixtures it is most likely that the peaks of the mass signals $J_{26}$ and $J_{27}$ are due to the fragments of ethylene. The peak of the mass signal $J_{44}$ was undoubtedly assigned to CO$_2$. The peak of the $J_{28}$ signal could arise due to fragments from CO$_2$ and/or ethylene but it could be also from the reductive formation of CO. Because the shape of mass signal $J_{28}$ is equal to the shape of the mass signals $J_{27}$ and $J_{26}$, it is believed that no CO is produced. The intensity changes in the mass signal $m/z = 2$ are believed to be due to the generation of hydrogen. The changes in the mass signal $J_{44}$ could not yet be attributed to a particular compound. It can be excluded that the signal $J_{41}$ comes from propylene because then $J_{42}$ (not shown) should also change at the same potential which was not the case. It is noteworthy that $J_2$ and $J_{41}$ have exactly the same shape. The signals $J_2$ and $J_{41}$ could therefore indicate two different volatile products of the same reaction or the two mass numbers are two different fragments generated by the ionization of the same molecule.

![Graph](image.png)

**Figure 5.13:** First cycle CV and MSCV of mass signal $J_2$ at 0.2 mV s$^{-1}$ of the KS6 sample in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.
Figure 5.14: First cycle CV and MSCV of mass signal $J_{27}$ at 0.2 mV s$^{-1}$ of the KS6 sample in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.

The first cycle cyclic voltammograms (CV) and the corresponding mass signal cyclic voltammograms (MSCV) for mass numbers 2 and 27 are reported respectively in figures 5.13 and 5.14. In the reductive half-cycle the signals $I_2$ (hydrogen) and $I_{27}$ (ethylene) rise both at about 0.75 V vs. Li/Li$^+$, i.e., in the SEI formation region. Two peaks are observed for $J_{27}$ and one peak for $J_2$. The peak of the signal of mass number 2 is located in the low potential region, where the intercalation of the Li$^+$ occurs. It is believed to be due to a probable exfoliation of some graphite particles. The $J_{27}$ signal has a first peak located at 0.5 V (Li/Li$^+$) (due to the SEI formation) and second ones at about 0.1 V vs. Li/Li$^+$, the latter in a region where the Li$^+$ intercalation occurs. The second peaks can be therefore assigned to the SEI formation on the extra surface created by graphite exfoliation.

The first cycle cyclic voltammograms (CV) and the corresponding mass signal cyclic voltammograms (MSCV) for mass numbers 2 and 27 are reported respectively in figures 5.13 and 5.14. In the reductive half-cycle the signals $J_2$ (hydrogen) and $J_{27}$ (ethylene) rise both at about 0.75 V vs. Li/Li$^+$, i.e., in the SEI formation region. For the mass signal $J_2$ only one peak
is observed, at the more cathodic potential. The mass signal $J_{27}$ shows two maxima: the first maximum is located at about 0.5 V vs. Li/Li$^+$ (due to the SEI formation); the second maximum is at the more cathodic potential. The second peak of $J_{27}$ and the peak of $J_2$ can be therefore assigned to the SEI formation on the extra surface created by graphite exfoliation or co-intercalation of solvent molecules. It could be also possible that the volume increase of the graphite due to the lithium intercalation increases the contact area of the electrolyte with the electrode and creates thus a new surface where SEI is formed.

Figure 5.15: First cycle CV and MSCV of mass signal $m/z = 44$ corresponding to $\text{CO}_2$ at 0.2 mV s$^{-1}$ of the KS6 sample in 1M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.

Figure 5.15 shows the CV and MSCV for the mass signal $m/z = 44$ corresponding to $\text{CO}_2$. It can be observed that, in contrast to both H$_2$ and ethylene signals rising around 0.75 V (Li/Li$^+$), the CO$_2$ development starts at more anodic potentials, namely circa at 1 V (Li/Li$^+$). The CO$_2$ development in this potential region could be an indicator of a first coverage of the graphite surface with some electrolyte reduction products and/or related to the reduction of graphite’s surface groups [115,116]. The very low intensity of the CO$_2$ signal stresses that it is a side reaction product. It is known that, the reduction of ethylene carbonate generates a radical ion, by splitting the C-O bond in the ethylene position. This radical ion can be further
reduced and gives Li₂CO₃ and ethylene [117,118]. From spectral studies of the SEI compounds on metallic lithium, Aurbach et al. have deduced that the radical anions can disproportionate and generate ROCO₂Li [78]. Subsequent reaction of this compound with traces of water will generate Li₂CO₃, R·OH, and CO₂. It could be also that the reduced ethylene carbonate is split in one C-O bond near the carbonyl bond, which may subsequently develop CO₂ and other products, such as Li₂O and ethylene or polymeric compounds of the SEI.

5.5 Multiple-Working-Electrode Measurements

As evidenced in the previous paragraphs of this chapter, the irreversible specific charge of the negative electrode based on graphite particles is very important for the performance of the lithium-ion battery. The irreversible specific charge in the first cycle is related to the SEI formation at the surface of the particles of graphite, exfoliation of the surface of the particles of graphite, and the reduction of the electrolyte. It could be expected that, for a given graphite and electrolyte, the irreversible specific charge (normalized to the weight of the graphite) in the first cycle is independent from the mass of the graphite sample. In the real experiments, however, it was observed that there is a decrease of the relative irreversible specific charge in the first cycle by increasing the thickness of the electrode. In figure 5.16 the relative irreversible specific charge in the first cycle is reported as a function of the areal density for graphite SFG44 electrodes. The galvanostatic cycling measurements were performed in a standard laboratory coin-type cell. The cell was cycled between 1.0 and 0.005 V (Li/Li⁺), imposing a specific current equal to 10 mAh g⁻¹. At 1.0 and 0.005 V (Li/Li⁺) a potentiostatic step was added. The potentiostatic step lasted until the specific current dropped to 5 mAh g⁻¹. The relative irreversible specific charge in the first cycle, QIRR, clearly decrease from circa 20% to circa 7% when the areal density of the graphite electrode changes from circa 1.5 mg cm⁻² to circa 11 mg cm⁻². The decrease of QIRR with the areal density of the sample was believed to depend on the increasing thickness of the sample. From galvanostatic cycling measurements made on compressed graphite electrodes, however, it turned out that the decrease of QIRR is not dependent on the thickness but on the real areal density of the electrode.
Figure 5.16: Relative irreversible specific charge in the first cycle vs. areal density of the electrode for SFG44 samples in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.

To understand the reason of the decreasing of $Q_{IRR}$ by increasing the areal density, a new cell was designed: the multiple-working-electrode cell (MWE cell), described in paragraph 4.6. With the MWE cell it is possible to divide the working electrode (in this case made of graphite) in several layers (cf. scheme in figure 4.5). The layers are in series, and they simulate the thickness of the electrode. The current intensity flowing through each layer can be measured separately; in this way it is possible to study $Q_{IRR}$ at several positions along the thickness of the working electrode. Moreover, the design of the cell ensures that the differences between the three layers are connected with the limitations due to the transport of ions in the electrolyte solution, while the limitations generated by the transport of electrons and ions in the solid phase are the same in the three layers. Both galvanostatic cycling and cyclic voltammetry experiments can be performed with the MWE cell. The measurement with the MWE cell needs 4 potentiostats.

In figure 5.17 it is shown how the 4 potentiostats are connected to the cell in the case of three layers of the working electrode. The working electrodes of the three potentiostats $p_i$ are connected to the three respective layers of the graphite electrode, while the counter electrodes
of the three potentiostats $p_i$ are connected with each other. An artificial short circuit is created by imposing a difference of potential between the working and the counter electrode of the potentiostats $p_i$, $V_i$, equal to 0. In this way the three layers of the working electrode are short circuited for electrons, as they are in a standard laboratory cell, and contemporary the current flowing through each layer is measured independently. Finally the counter electrode of the potentiostat $P$ is connected to the counter electrode of the MWE cell, while the working electrode is connected to the three counter electrodes of the potentiostats $p_i$. The potentiostat $P$ controls the whole cell; it can control the potential of the cell or impose the total current that has to flow through the three layers of the working electrode. On the other side, the current of each potentiostat $p_i$ changes so that the three layers are always at the same potential.

![Schematic drawing of the electric circuit used in the experiments with the MWE cell (case of three working electrodes).](image)

Figure 5.17: Schematic drawing of the electric circuit used in the experiments with the MWE cell (case of three working electrodes).

The MWE cell was built in a glove box. The working electrode is made from graphite SFG44 particles; the counter electrode is from metallic lithium. The cell is assembled in a two electrode configuration, as explained in paragraph 4.6. The galvanostatic cycling experiments were selected for the graphite characterization. The cell was cycled as the standard laboratory coin-type cell: a total specific current equal to 10 mAh g$^{-1}$, with respect to the total weight of the graphite in the layers of the working electrode, was applied between 1.0 and 0.005 V (Li/Li$^+$); at 1.0 and 0.005 V (Li/Li$^+$) a potentiostatic step was added, until the total specific current dropped to 5 mAh g$^{-1}$. The electrolyte used in the experiments was 1 M LiPF$_6$ in EC:DMC (1:1 by wt.)

In figure 5.18 the curves $U_E$ vs. $Q$ for the three layers of the working electrode are reported. The differences between the three curves can be classified in overpotential.
differences and charge differences. The shape of the charge / discharge curve is strongly dependent on the position of the layer: the nearer is the layer to the counter electrode, the smaller are the overpotentials due to the transport (both migration and diffusion) of the lithium ions in the electrolyte solution. In the \( U_E \) vs. \( Q \) curve of the first layer the three plateaus indicating the formation of the lithium-graphite compounds are clearly observed; in the \( U_E \) vs. \( Q \) curve of the second and third layer the plateaus due to the formation of \( \text{LiC}_6 \) and \( \text{Li}_{1/2}\text{C}_6 \) compounds are not differentiated anymore (overpotential differences).

![Figure 5.18: Galvanostatic cycling measurements for the graphite SFG44 sample in 1 M LiPF₆, EC:DMC (1:1 by wt.) electrolyte with the MWE cell. The curves \( U_E \) vs. \( Q \) were separated for the three layers (cf. figure 5.17). The potential \( U_E \) is relative to Li/Li⁺.](image)

Both the reversible and irreversible specific charges in the three different layers are different. While in the first reductive half cycle the first layer consumes 447 mAh g⁻¹, the second layer consumes only 395 mAh g⁻¹, and the third layer around 391 mAh g⁻¹. The reversible and irreversible specific charge for the three layers is reported in table 5.5. The
irreversible specific charge was divided in two parts: $Q_{\text{SEI}}$ is the irreversible charge obtained between 1.0 and 0.4 V (Li/Li$^+$); $Q_{\text{RED}}$ is the irreversible charge obtained between 0.4 and 0.005 V (Li/Li$^+$). From table 5.5 it is deduced that the biggest part of the irreversible charge observed in the three layers is consumed in the low voltage region, below 0.4 V (Li/Li$^+$).

<table>
<thead>
<tr>
<th>Layer</th>
<th>$Q_T$</th>
<th>$Q_{\text{REV}}$</th>
<th>$Q_{\text{IRR}}$</th>
<th>$Q_{\text{SEI}}$</th>
<th>$Q_{\text{RED}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>446.7</td>
<td>339.3</td>
<td>107.4</td>
<td>14.6</td>
<td>89.2</td>
</tr>
<tr>
<td>Layer 2</td>
<td>394.7</td>
<td>337.7</td>
<td>57.0</td>
<td>13.0</td>
<td>41.1</td>
</tr>
<tr>
<td>Layer 3</td>
<td>390.5</td>
<td>324.6</td>
<td>65.9</td>
<td>12.2</td>
<td>51</td>
</tr>
</tbody>
</table>

Table 5.5: Total, reversible and irreversible specific charge (mAh g$^{-1}$) in the three layers of a working electrode based on graphite SFG44 particles in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte. $Q_{\text{SEI}}$ is the irreversible specific charge between 1.0 and 0.4 V (Li/Li$^+$). $Q_{\text{RED}}$ is the irreversible specific charge between 0.4 and 0.005 V (Li/Li$^+$).

The reason of the described behavior is not yet clarified. Here we offer a hypothesis based on the observed phenomena and on the theoretical principles of electrochemistry. At the beginning of the first reductive half cycles, all the layers of the working electrodes are in equilibrium conditions, no current intensity is flowing. When the total specific current is applied, it is distributed in the three layers following the model described by equation (3.23) and figure 3.4. Most of the highest amount of current intensity flows through the first layer, smaller in the following layers. The solid electrolyte interphase is formed in the three layers quite contemporary and consuming the same amount of charge because the overpotentials, mainly due to migration of the ions in the electrolyte, are small.

When the intercalation of lithium ions starts: because the high amount of lithium ions consumed in the intercalation process, the overpotentials due to diffusion of lithium ions in the electrolyte solution are high and it is possible to observe the differences between the three layers in the curves $U_{\text{E}}$ vs. Q. The reduction of the electrolyte is stopped by the SEI, which lets the lithium ions pass through, but is an insulator for the electrons. When low potentials are reached, the first layer is fully charged, while the others are not yet. When the first layer is fully charged, the distribution of overpotential in it changes. The lithium ions in the first layer cannot pass from the structure of the SEI to the structure of the graphite; Li$^+$ is accumulated at the interface SEI/graphite, the SEI is strongly polarized and the potential drop in the SEI increases. Due to the higher potential drop in the SEI, the electrons can be transported through
the SEI and reduce the electrolyte. This hypothesis could possibly explain why the first layer has a higher irreversible specific charge with respect to the other two layers.

Of course this is only a hypothesis; it has to be confirmed through other experimental results. The curve $U_E$ vs. $Q$ for the first layer shows clearly the three plateaus for the formation of the three lithium-graphite compounds. It is possible to calculate the amount of the irreversible charge in the formation of the compound $\text{LiC}_6$, which is the compound with the higher concentration of lithium. If the hypothesis suggested above is correct, it would be expected the irreversible charge in this stage to be very high. From the experimental data it results that the irreversible specific charge in the first layer for the formation of the compound $\text{LiC}_6$ is equal to circa 52 mAh g$^{-1}$, which corresponds to more than 50% of $Q_{\text{RED}}$. 
6 Study of the Positive Electrodes

6.1 Introduction

The most common active material for the positive electrode of lithium-ion batteries is LiCoO$_2$. LiCoO$_2$ has a layered structure; layers containing cobalt ions (slab) and layers containing lithium ions (interslab) alternate in the structure (see figure 6.1). During charging of the positive electrode, the lithium ions de-intercalate from the structure and the cobalt ions are oxidized from the Co$^{3+}$ to Co$^{4+}$. While negative electrodes based on graphite can achieve very good performances (high cycling stability and reversible specific charge of up to 370 mAhg$^{-1}$), LiCoO$_2$ possesses low practical specific charge with respect to the theoretical specific charge (circa 50%) [56], is carcinogenic, and exhibits an exothermic peak at ca. 150 °C when heated in the de-intercalated state (safety problem).

![Crystallographic structure of the LiCoO$_2$ compound and similar layered compounds.](image)

The oxide family with the general formula Li$_{1+x}$(Ni$_y$Mn$_z$Co$_{1-y-z}$)$_{1-x}$O$_2$, called NMC, is believed to be one of the most promising substitute of the current industrial standard [1-3].
The NMC compounds are layered oxides, with the same crystallographic structure of the LiCoO$_2$ (see figure 6.1). The most studied NMC compounds are the ones with $z = y$. $x$ is called the overlithiation degree. It indicates the excess of lithium in the structure of the NMC compounds. The lithium ion excess is located in the layers of the transition metals (slab).

As general rule, manganese and cobalt are present in the structure as Mn$^{+4}$ and Co$^{+3}$ respectively, while nickel is observed as a mixing of Ni$^{2+}$ and Ni$^{3+}$ [67]. The performances of the NMC compounds depend from the values of $x$, $y$, and $z$. The presence of cobalt ions decreases the disorder in the interslab. If the nickel ions are in divalent state, the NMC compound shows a higher thermal stability [68-70]. The NMC compounds can reach high specific charge density with respect to LiCoO$_2$ [1] (circa 170 mAh g$^{-1}$ for the NMC compound with $x = 0$ when cycling in the potential window from 2.5 to 4.4 V vs. Li/Li$^+$), and a good cycling stability.

During this PhD work, the effect of overlithiation degree on the performances of the NMC compounds was investigated. The NMC compounds with general formula Li$_{1+x}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{1-x}$O$_2$ were synthesized and studied. The synthesis was performed by coprecipitation of hydroxides of the transition metals, as explained in Chapter 4. 9 samples were prepared and analyzed in total, by crossing 3 stochiometries ($x = 0$, $x = 0.1$, and $x = 0.2$) with three calcination temperatures ($T = 700$°C, $T = 850$°C, and $T = 1000$°C). The chemical and structural analysis and the standard electrochemical measurements were performed for each sample. Two of the 9 samples were selected as the most promising ones and further analyzed by differential electrochemical mass spectrometry (DEMS).

6.2 Structural, Morphological and Chemical Analysis

For each synthesized sample the structural, morphological, and chemical analysis was performed, to verify the nature and composition of the final compound. These analyses were done in collaboration with Mr. Rosciano from PSI electrochemistry laboratory. X-ray diffraction was performed to verify the crystallographic structure of the synthesized active materials. All the NMC samples synthesized at 850°C have shown the layered structure of the NMC compounds (see figure 6.2). The NMC compounds synthesized at 1000°C have also a layered structure. The NMC compounds synthesized at 700°C have broader peaks, and the doublet located at 65° becomes a single peak (see figure 6.3). The passage from a doublet to a
single peak with the decrease of the temperature of calcination could be connected to the broadening of the peaks or to the formation of a different crystallographic structure, the spinel structure.

The morphological analysis of the NMC samples was carried out with the scanning electron microscopy technique (SEM). The morphological structure of the synthesized NMC samples depends on the temperature of calcination and seems independent from the overlithiation degree. By increasing the temperature of calcination, the dimension of the crystallites increases. The dimension of the crystallites is around 120 nm for the samples calcined at 700°C, while increases to 800 nm for the samples calcinated at 1000°C (see figures 6.4 and 6.5).

![X-ray pattern for the three pristine NMC compounds synthesized at 850°C with different overlithiation degrees.](image)

**Figure 6.2:** X-ray pattern for the three pristine NMC compounds synthesized at 850°C with different overlithiation degrees.
Figure 6.3: X-ray pattern for the three pristine NMC compounds with overlithiation degree equal to 0.1 and synthesized at different calcination temperatures $T$.

Figure 6.4: SEM image of the NMC sample calcined at 700°C and with overlithiation degree equal to 0.1.
Figure 6.5: SEM image of the NMC sample calcined at 1000°C and with overlithiation degree equal to 0.1.

The iodometric titration method was used for the chemical analysis of the NMC samples; it permits to find experimentally the value of the overlithiation degree. The solution for the iodometric titration was prepared mixing 5 ml of an aqueous solution of HCl (37% by wt), 5 ml of an aqueous solution of KI (10% by wt), 10 ml of water, circa 30 mg of the investigated NMC sample. The resulting solution was left to react at 60°C overnight. The titrating solution is an aqueous solution of 0.01 M Na$_2$S$_2$O$_3$; it was slowly dripped in the solution containing the transition metals. The volume of the titrating solution used during the iodometric titration, $V_{\text{tit}}$, and the average oxidation degree of the transition metals, $d$, are related by the formula:

$$d = 2 + \left[ \frac{\text{Na}_2\text{S}_2\text{O}_3}{\text{M}} \right] \cdot \frac{m_s}{q_m} \cdot V_{\text{tit}}$$  \hspace{1cm} (6.1)

where $m_s$ is the mass of the sample, $M$ the molar weight of the sample, and $q_m$ the stoichiometric coefficients for the transition metal in the sample. The average oxidation degree of the transition metals and the overlithiation degree of the NMC sample are related by the formula:

$$x_{\text{sp}} = \frac{3 - d}{1 - d}$$  \hspace{1cm} (6.2)
The results of the iodometric titration are reported in table 6.1. The iodometric titration has evidenced that the nominal and experimental overlithiation degree coincide for $x_{\text{nom}}$ equal to 0 and 0.1. For $x_{\text{nom}}$ equal to 0.2, the experimental overlithiation degree is lower. XPS experiments have shown that in the NMC compounds Mn and Co have always an oxidation degree equal to 4 and 3, respectively; nickel is observed as a mixing of Ni$^{2+}$ and Ni$^{3+}$ [67]. There is a maximum value of d and consequently there is a maximum value of $x_{\text{sp}}$. The sample with $x_{\text{sp}}$ equal to 0.2 cannot be synthesized for thermodynamic limitations.

<table>
<thead>
<tr>
<th>$x_{\text{nom}}$</th>
<th>$m_S$ / mg</th>
<th>M / g mol$^{-1}$</th>
<th>$q_m$</th>
<th>$V_{\text{tit}}$ / ml</th>
<th>$x_{\text{sp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>35.0</td>
<td>96.46</td>
<td>1</td>
<td>36</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>30.9</td>
<td>91.39</td>
<td>0.9</td>
<td>36.9</td>
<td>0.095</td>
</tr>
<tr>
<td>0.2</td>
<td>36.5</td>
<td>86.34</td>
<td>0.8</td>
<td>47.5</td>
<td>0.167</td>
</tr>
</tbody>
</table>

Table 6.1: Results of the iodometric titration for the NMC samples calcined at 850°C. $x_{\text{nom}}$ is the nominal overlithiation degree of the NMC sample, $m_S$ is the mass of the sample, M is the molar weight of the sample, $q_m$ is the stoichiometry of the transition metal of the sample, $V_{\text{tit}}$ is the volume of the titrating solution used, $x_{\text{sp}}$ the overlithiation degree obtained from the titration.

6.3 Standard Electrochemical Measurements

The standard electrochemical measurements were performed on a coin-type laboratory cell in a half-cell configuration (counter electrode of metallic lithium). 1 M LiPF$_6$ in EC:DMC (1:1 by wt.) was used as electrolyte. Two galvanostatic cycling experiments were performed: the low voltage galvanostatic cycling and the high voltage galvanostatic cycling. In the low voltage galvanostatic cycling the cell is cycled between 3.0 and 4.3 V (Li/Li$^+$). In the high voltage galvanostatic cycling the cell is cycled between 3.0 and 5.0 V (Li/Li$^+$). The imposed specific current was 25 mA g$^{-1}$ in both cases. The galvanostatic cycling experiments of the different NMC samples were used to study the fading of the reversible specific charge with the number of cycles. The galvanostatic cycling experiments are strongly dependent on the synthesis conditions of the investigated NMC sample and on the investigated potential window.
Figure 6.6: Reversible specific charge vs. cycle from low voltage galvanostatic cycling measurements at 25 mAh g$^{-1}$ in 1M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte for different NMC samples.

Figure 6.6 plots the reversible specific charge from the low voltage galvanostatic cycling experiments, $Q_{\text{REV}}$, as function of the cycle number for different NMC samples. The NMC compound synthesized at 850°C with $x = 0$ shows the higher value of $Q_{\text{REV}}$ at each cycle. The fading of the performance is low; the difference between the first cycle and the 20$^{\text{th}}$ cycle is equal to 3.7%. The NMC compound synthesized at 850°C with $x = 0.1$ shows a smaller value of $Q_{\text{REV}}$ with respect to the NMC compound calcined at the same temperature and with $x = 0$. The difference between the first cycle and the 20$^{\text{th}}$ cycle is equal to 1.4%; the fading of the performance slightly decreases with increasing overlithiation degree. The NMC compound synthesized at 850°C with $x = 0.2$ has a very low reversible specific charge. The performance increases with the cycle number. The NMC compound synthesized at 700°C with $x = 0.1$ has a smaller $Q_{\text{REV}}$ and a higher fading of the performance with respect to the NMC compound calcined at 850°C with the same overlithiation degree. The difference
between the first cycle and the 20\textsuperscript{th} cycle is equal to 6.0\%. The NMC compounds synthesized at 1000\degree C show performances slightly lower than the analogous calcined at 850\degree C.

![Figure 6.7](image)

Figure 6.7: Reversible specific charge vs. cycle from high voltage galvanostatic cycling measurements at 25 mAh g\textsuperscript{-1} in 1M LiPF\textsubscript{6}, EC:DMC (1:1 by wt.) electrolyte for different NMC samples.

Figure 6.7 plots the reversible specific charge from the low voltage galvanostatic cycling experiments, \(Q_{REV}\), as function of the cycle number for different NMC samples. The NMC compound synthesized at 850\degree C with \(x = 0\) shows the higher value of \(Q_{REV}\) in the very first cycles, but the fading of the performance is very strong and the reversible specific charge decreases rapidly with the cycle number. The difference between the first cycle and the 15\textsuperscript{th} cycle is equal to 24.7\%. The NMC compound synthesized at 850\degree C with \(x = 0.1\) shows a smaller value of \(Q_{REV}\) in the very first cycles with respect to the NMC compound calcined at the same temperature and with \(x = 0\). After the 10\textsuperscript{th} cycle, the compound with \(x = 0.1\) has a higher \(Q_{REV}\) with respect to the NMC compound with \(x = 0\). The difference between the first cycle and the 15\textsuperscript{th} cycle is equal to 15.7\%; also in the high voltage experiments the fading of the performance decreases with increasing the overlithiation degree. The NMC compound
synthesized at 850°C with \( x = 0.2 \) has a very small reversible specific charge and it fails after very few cycles. The NMC compound synthesized at 700°C with \( x = 0.1 \) has the smallest reversible specific charge and a higher fading of the performance with respect to the NMC compound calcinated at 850°C with the same overlithiation degree. The difference between the first cycle and the 15\(^{th}\) is equal to 23.5%. Also in the high voltage experiments the NMC compounds synthesized at 1000°C show performance slightly lower than the analogous calcined at 850°C.

A comparison between the high voltage galvanostatic cycling experiments performed on the synthesized NMC compounds and the commercially available LiCoO\(_2\) was not possible, because the LiCoO\(_2\) failed after a few cycles. Based on the structural, morphological, and chemical analysis and on the standard electrochemical experiments, the NMC compounds synthesized at 850°C with overlithiation degree equal to 0 and 0.1 were selected as candidates for further analysis. The NMC compounds synthesized at 1000°C were discarded because they have lower performance with respect to the nominally same compounds synthesized at 850°C. The NMC compounds synthesized at 700°C have also lower performance with respect to the same nominally compounds synthesized at 850°C; moreover the structural analysis made by X-ray diffraction has not given a clear result as in the other cases (see figure 6.3). The NMC compounds with nominal overlithiation degree equal to 0.2 have also lower performance with respect to the compounds with lower overlithiation degree; moreover the chemical analysis made by iodometric titration has evidenced that the experimental overlithiation degree is equal to 0.167 (see table 6.1).

In the following text the NMC compound calcined at 850°C with \( x = 0 \) will be called stoichiometric compound, the NMC compound calcined at 850°C with \( x = 0.1 \) will be called overlithiated compound. The stoichiometric and overlithiated compounds were further analyzed by using the differential plot and performing cyclic voltammetry on the compounds. The differential plot is obtained from the derivative of the specific charge with respect to the potential of polarization; it plots \( dQ/dU_E \) vs. \( U_E \). The differential plot is very similar to the cyclic voltammogram. The differential plot of an intercalating compound consists of oxidative and reductive peaks, which represent the reversible and irreversible electrochemical processes occurring in the system. The differential plot was done for both high voltage and low voltage galvanostatic cycling experiments in the first cycle. The cyclic voltammetry was
performed on both stoichiometric and overlithiated compounds in the coin-type laboratory cell with scan rate equal to 0.05 and 0.02 mV s\(^{-1}\), respectively between 2.5 and 5.0 V (Li/Li\(^+\)). 1 M LiPF\(_6\) in EC:DMC (1:1 by wt.) was used as the electrolyte.

![Differential plot from the galvanostatic cycling experiments for the stoichiometric compound in the high voltage and low voltage experiment, respectively, during the first cycle at 25 mA g\(^{-1}\) in 1M LiPF\(_6\), EC:DMC (1:1 by wt.) electrolyte.](image)

**Figure 6.8:** Differential plot from the galvanostatic cycling experiments for the stoichiometric compound in the high voltage and low voltage experiment, respectively, during the first cycle at 25 mA g\(^{-1}\) in 1M LiPF\(_6\), EC:DMC (1:1 by wt.) electrolyte.

In figure 6.8 the differential plot of the high voltage (HV) and low voltage (LV) galvanostatic cycling experiments during the first cycle for the stoichiometric compound is represented. In the low voltage region the HV and LV differential curves coincide; the two electrodes based on the stoichiometric NMC are pristine and behave in the same way. A reversible oxidative peak is located at 3.8 V (Li/Li\(^+\)); this peak represents the de-intercalation process. After 4.3 V (Li/Li\(^+\)) the stoichiometric compound has a second oxidative peak, which is mostly irreversible. It is small and it is believed to be due to electrolyte oxidation [106]. The reductive peak located near 3.75 V (Li/Li\(^+\)) is due to the intercalation of the lithium ions back to the NMC compound. This peak has the same shape in both HV and LV experiments, thus indicating that the intercalation process is not changed. The intensity of the reductive
peak in the HV experiment is slightly smaller with respect to the intensity of the same peak in the LV experiment; also the potential of the reductive peak in the HV experiment is shifted to more cathodic values with respect to the same peak in the LV experiment. Both phenomena indicate an increase of the inner resistances of the system in the HV experiment.

In figure 6.9 the differential plot of the HV and LV galvanostatic cycling experiments during the first cycle for the overlithiated compound is represented. In the low voltage region a reversible oxidative peak located at 3.7 V (Li/Li$^+$) is observed; this peak represents the de-intercalation process. At potentials positive to 4.5 V (Li/Li$^+$), a very intense irreversible oxidative peak is observed. Structural changes were anticipated for the overlithiated NMC compound in this voltage region where CO$_2$ and O$_2$ development is likely. This question is investigated in details in the thesis of Fabio Rosciano (ETH Nr. 17847). The reductive peak located near 3.7 V (Li/Li$^+$) is due to the intercalation of the lithium ions. The shape and the location of this peak depend strongly on the type of the experiment. The lithium intercalation...
peak shifts to the cathodic direction in the HV experiments. The differential plot of the second cycle (not shown) suggests this to be a thermodynamic effect; if the shift would be due to the kinetics, the related oxidative (de-intercalation) peak would have to shift to more anodic values.

Figure 6.10: Differential plot from the galvanostatic cycling experiments for the overlithiated and stoichiometric compound in the high voltage experiment, respectively, during the first cycle at 25 mA g\(^{-1}\) in 1M LiPF\(_6\), EC:DMC(1:1 by wt.) electrolyte.

In figure 6.10 the differential plot of the HV galvanostatic cycling experiments during the first cycle for the stoichiometric and overlithiated compound are compared. The peak representing the de-intercalation process is smaller and located more cathodically for the overlithiated NMC compound; it indicates that the reversible specific charge in the LV experiments for the overlithiated NMC has to be smaller with respect to the stoichiometric compound. This is confirmed by the LV galvanostatic cycling experiments (see figure 6.7). At potentials positive to 4.5 V (Li/Li\(^+\)), the overlithiated phase has an intense irreversible oxidative peak. Dahn’s group suggested to explain the oxidative peak located at 4.5 V (Li/Li\(^+\))
with structural changes associated with oxygen loss from the oxide and a simultaneous Li$^+$ extraction [68]. In the same potential window, the stoichiometric NMC compound has a small peak located at 4.7 V (Li/Li$^+$). The relative position of the reversible peaks indicates that the overpotential in the system containing the overlithiated NMC is higher with respect to overpotential in the system containing the stoichiometric phase.

**Figure 6.11:** Cyclic voltammograms at 0.02 and 0.05 mV s$^{-1}$ in 1M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte for the stoichiometric NMC compound (1$^{st}$ cycle).

In figure 6.11 and 6.12 the cyclic voltammities at scan rate of 0.02 and 0.05 mV s$^{-1}$ for the stoichiometric and overlithiated NMC compound are respectively reported. Because the current is dependent on the scan rate, the ratio between the specific current, $i_m$, and the scan rate, $\nu$, is reported. The value $i_m\nu^{-1}$ is independent from the scan rate if the overpotential at the given scan rate and potential of polarization is negligible. As a general rule, by increasing the scan rate, a shift of the current peak to more anodic potentials should be observed for the oxidative half-cycle, and a shift of the current peak to more cathodic potentials should be observed for the reductive half cycle. For the stoichiometric compound the shift of the
potential is observed only in the oxidative half cycle and only in the potential window where de-intercalation is the main electrochemical process; it is also the potential range with the higher specific current. For the overlithiated compound the shift of the potential is observed in the oxidative half cycle, in both low and high voltage regions. In the reductive half cycle a reduction of the current peak is observed at higher scan rate.

![Graph](image)

**Figure 6.12:** Cyclic voltammograms at 0.02 and 0.05 mVs$^{-1}$ in 1M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte for the overlithiated NMC compound (1$^{st}$ cycle).

To summarize the results of the standard electrochemical measurements: all the synthesized NMC compounds were tested with galvanostatic cycling experiments, between them two samples were selected because they have shown good performances in the low voltage region (stoichiometric NMC compound) and in the high voltage region (overlithiated NMC compound); the overlithiated phase has shown a smaller fading of the performance with respect to the HV galvanostatic cycling experiments; the differential plot of the galvanostatic cycling experiments was used to study the differences in the electrochemical behavior between the two selected samples; the difference between the stoichiometric and overlithiated...
phases was observed in the high voltage region, above 4.5 V (Li/Li$^+$); the stoichiometric NMC compound has shown a lower overpotential (kinetic limitation) with respect to the overlithiated phase. The electrochemical process represented by the irreversible peak located in the high voltage region, at 4.7 V (Li/Li$^+$) for the stoichiometric NMC compound and at 4.5 V (Li/Li$^+$) for the overlithiated NMC compound, respectively seems to be the key for the stabilization of the overlithiated NMC phase in the HV galvanostatic cycling experiments (see figure 6.7).

6.4 DEMS Measurements

The DEMS technique analyzes on-line the electrochemically generated gases, giving the intensity of the mass signals ($m/z$) as a function of the electrode potential. The DEMS technique was used to verify the hypothesis of Dahn et al. [68], who explain the oxidative peak located at 4.5 V (Li/Li$^+$) in the overlithiated phases with structural changes associated with oxygen loss from the oxide. The DEMS experiments were performed in the DEMS cell. A cyclic voltammetry was performed on the active materials to investigate the gas development in the potential range 2.5 – 5.3 V (Li/Li$^+$). The scan rate of the cyclic voltammetry was 0.2 mV s$^{-1}$; the scan rate was selected based on the resolution of the mass spectrometer and the kinetic limitations of the system.

In figure 6.13 the comparative plot of the mass signal intensities, $I_m$, as measured reports the electrochemical development of O$_2$ and CO$_2$ for the stoichiometric and overlithiated NMC compounds. The value of the mass signal intensities is normalized for the mass of the sample. On the top the applied potential $U_E$ (Li/Li$^+$) is also given. The $m/z = 32$ signal was assigned to oxygen and $m/z = 44$ to CO$_2$, respectively.
Figure 6.13: Comparative plot of the mass signal intensities $I_m$ ($\mu A$ g$^{-1}$) as measured for the stoichiometric ($x = 0$) and overlithiated ($x = 0.1$) NMC compounds in 1M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.
Clearly, for the stoichiometric sample no oxygen evolution is detected while CO$_2$ is evolved during the first and further cycles in the high voltage region (only two cycles are shown in figure 6.13). The CO$_2$ evolution is due to the electrolyte oxidation, as evidenced for a number of electro-active oxides [106,119]. In contrast, for the overlithiated NMC oxide, both CO$_2$ and O$_2$ evolution is observed in the high voltage region but only during the first cycle. This result strongly supports the following hypothesis: during the first delithiation the overlithiated NMC compounds irreversibly lose oxygen at high potentials, as proposed by the Dahn’s group [120]; in the case of the overlithiated NMC materials, the oxidation of the electrolyte (evidenced by the CO$_2$ evolution) is somehow inhibited, in contrast to the stoichiometric material. A surface film composed of electrolyte oxidation products and/or changed surface properties of the NMC oxide due to the oxygen loss is believed to be the reason for the non-detection of the CO$_2$ development in the second cycle.

In figure 6.14 the comparative plot of the analyzed mass signal intensities, $J_m$, reports the electrochemical development of O$_2$ and CO$_2$ for the stoichiometric and overlithiated NMC compounds. The analyzed mass signal intensities $J_m$ are obtained with the analytical procedure described in paragraph 2.3. The intensity of the background line generated by the carrier gas and the vapors of DMC was subtracted from the measured data. The shape of the curves and the information obtained from figure 6.14 are the same of figure 6.13. The potential of polarization for the development of O$_2$ and CO$_2$ is better evidenced using the analyzed mass signal intensities.

Further comments rise from the detailed study of the analyzed mass signal intensities for the overlithiated NMC compound: the development of O$_2$ starts at potentials above the development of CO$_2$; the intensity of $m/z = 32$ shows a single peak located at 5 V (Li/Li$^+$); the intensity of $m/z = 44$ shows a doublet, the first peak is located at 5.3 V (Li/Li$^+$), the second one is located in the reductive half-cycle at 4.6 V (Li/Li$^+$). It has to be stressed that the amount of moles of gases developed by the overlithiated NMC compound is higher with respect to the amount of moles of gases developed by stoichiometric NMC phase (see figure 6.14). This implies a safety problem for the cycle life of a lithium-ion battery containing the overlithiated NMC phase as positive electrode. The safety problem is related to the increase of the pressure inside the battery, and a possible damage of the case of the battery.
Figure 6.14: Comparative plot of the analyzed mass signal intensities $J_m$ (nA g$^{-1}$) (see paragraph 2.3) for the stoichiometric and overlithiated NMC compounds in 1M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.
In figure 6.15 the mass signal cyclic voltammogram (MSCV) and the cyclic voltammogram (CV) for the stoichiometric NMC compound in the first cycle is shown. The specific current, $i_m$, is reported for the CV and the amount of moles of gas i generated in the unit time, $n(i)$, is reported for the MSCV. The amount of moles of gas i generated in the unit time is obtained by multiplying the total amount of moles in the gaseous phase flowing through the system and the molar fraction of the gas i in the flux. The molar fraction of the gas i in the flux is obtained by the ratio between the analyzed mass signal intensity $J_m$ and the sensibility factor of the gas i for the mass number m, $S_{i,m}$ (see paragraph 2.3). The value of $J_m$ was obtained with the procedure of calibration explained in paragraph 2.3.

![Figure 6.15](image.png)

**Figure 6.15**: First cycle CV and MSCV of O$_2$ and CO$_2$ at 0.2 mV s$^{-1}$ of the stoichiometric NMC compound in 1M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.

From the MSCV it is observed that the onset of the CO$_2$ evolution in the stoichiometric NMC compound is located at 4.35 V (Li/Li$^+$). The CO$_2$ evolution signal has two peaks: the first is located at 4.85 V (Li/Li$^+$) in the oxidative half cycle; the second peak is located at 4.85 V (Li/Li$^+$) in the reductive half cycle. The time delay between the generation of the gas in the cell and the detection in the mass spectrometer is equal to 16 seconds, which corresponds to a potential shift of circa 3 mV. A third peak is observed in the low potential
region of the reductive half cycle; the peak is located at 2.6 V (Li/Li⁺). The origin was not yet identified but it is believed to be due to release of CO₂ trapped in the pores of the electrode. The total amount of CO₂ produced in the first cycle is equal to 0.185 mmol per gram of active material. No oxygen is detected for the stoichiometric NMC compound.

Figure 6.16: First cycle CV and MSCV of O₂ and CO₂ at 0.2 mV s⁻¹ of the overlithiated NMC compound in 1M LiPF₆, EC:DMC (1:1 by wt.) electrolyte.

In figure 6.16 MSCV and CV for the overlithiated NMC compound in the first cycle is shown. From the MSCV it is observed that the onset of the CO₂ evolution in the overlithiated NMC compound is located at 4.35 V (Li/Li⁺); it corresponds to the onset of the CO₂ evolution in the stoichiometric NMC compound. The CO₂ evolution signal has two peaks: the first is located at 5.3 V (Li/Li⁺) in the oxidative half cycle; the second peak is located at 4.6 V (Li/Li⁺) in the reductive half cycle. Again, a third peak is observed in the low potential region of the reductive half cycle at 2.6 V (Li/Li⁺). The total amount of CO₂ produced in the first cycle is equal to 1.01 mmol per gram of overlithiated NMC compound.

The onset of the O₂ evolution in the overlithiated NMC phase is located at 4.7 V (Li/Li⁺); the generation of O₂ starts after the generation of CO₂. The O₂ evolution signal has a
single peak, than the signal drops to 0; the peak is located at 5.1 V (Li/Li\(^{+}\)) in the oxidative half cycle. The total amount of O\(_2\) produced in the first cycle is equal to 0.259 mmol per gram of active material.

6.5 On the Oxygen Evolution in NMC Compounds

The development of oxygen at high potential in the overlithiated NMC compound was expected. It was indirectly observed from Dahn et al. on an overlithiated mixed manganese / nickel oxide by post-mortem X-ray diffraction [68]. The release of oxygen from the structure of an overlithiated layered oxide is predicted by the balance of charge. The transition metal ions can be oxidized up to the oxidation state 4. The average oxidation state of the transition metals in the pristine overlithiated NMC compound is equal to 3.21; after the removal of 0.71 moles of Li\(^{+}\) per mole of overlithiated NMC compound, the transition metals cannot be oxidized further. The removal of the remaining 0.39 moles of Li\(^{+}\) can be done only by oxidation of the oxygen ions in the structure of the overlithiated NMC compound; 0.2 moles of O\(^{2-}\) have to be oxidized to compensate the charge flow due to 0.39 moles of Li\(^{+}\) removed from the structure of the active material. The oxygen radical formed at the interface active material / electrolyte can react with the electrolyte and generate CO\(_2\) or can react with another O radical and generate directly O\(_2\).

Kim et al. [121] have found that the nickel ions are oxidized in the low potential region, while the cobalt ions oxidation occurs in the potential window 3.9 – 4.7 V (Li/Li\(^{+}\)). The manganese ions in the structure are found in the oxidation state Mn\(^{4+}\). The cobalt ions are in oxidation state Co\(^{3+}\). In the overlithiated NMC compound synthesized during this PhD work, 63% of the nickel ions are in the oxidation state Ni\(^{3+}\), while 37% in the oxidation state Ni\(^{2+}\). The removal of 0.41 moles of Li\(^{+}\) is sufficient to oxidize all the nickel ions. The removal of remaining 0.69 moles of Li\(^{+}\) can be compensated by the oxidation of the cobalt ions or the oxygen ions. The number of moles of oxygen ions oxidized per mole of active material has to be included between 0.2 and 0.35.

The total amount of oxygen atoms contained in the gases detected during the DEMS experiments performed on the overlithiated NMC compound in the electrolyte 1 M LiPF\(_6\), EC:DMC (1:1 by wt.) was equal to 0.23 moles per mole of the active material. The real amount of oxygen ions oxidized in the structure of the overlithiated NMC and the amount of
oxygen atoms detected by the DEMS are not equal. The electrolyte contains oxygen atoms; a part of the oxygen contained in CO$_2$ could come from the electrolyte. The DEMS experiment on the overlithiated NMC compound was therefore repeated using 1 M LiPF$_6$ in acetonitrile (AcN) as electrolyte. Acetonitrile does not contain oxygen atoms; it is expected that the development of CO$_2$ is less than in EC:DMC (1:1 by wt.) electrolyte. The cyclic voltammetry was performed in the potential range 2.0 – 5.3 V (Li/Li$^+$). The scan rate of the cyclic voltammetry was 0.2 mV s$^{-1}$. Metallic lithium cannot be used in AcN, the counter and reference electrode were therefore made of de-intercalated LiFePO$_4$ ($U_{eq} = 3.4$ V vs. Li/Li$^+$). The LiFePO$_4$ was fully de-intercalated in 1 M LiPF$_6$, EC:DMC (1:1 by wt.) electrolyte.

**Figure 6.17:** Comparative plot of the generation of O$_2$ and CO$_2$, n(O$_2$) and n(CO$_2$) respectively (nmol s$^{-1}$ g$^{-1}$), for the overlithiated NMC compounds in 1 M LiPF$_6$, AcN electrolyte.

- 126 -
In figure 6.17 the comparative plot of O\textsubscript{2} and CO\textsubscript{2} is reported for the overlithiated NMC compound in 1 M LiPF\textsubscript{6}, AcN. The development of CO\textsubscript{2} and O\textsubscript{2} appears only in the first cycle. The O\textsubscript{2} signal shows a single peak located at 5.2 V (LI/Li\textsuperscript{+}). The development of CO\textsubscript{2} shows a doublet; first peak is in the oxidative half cycle at 5.25 V (LI/Li\textsuperscript{+}), the second peak is in the reductive half cycle at 4.7 V (Li/Li\textsuperscript{+}). A third peak in the CO\textsubscript{2} signal is observed in the oxidative half cycle at 4.0 V (Li/Li\textsuperscript{+}); in this potential window the electrolyte is normally considered stable. The third peak was never detected in the EC:DMC (1:1 by wt.) electrolyte.

In figure 6.18 the first cycle of the MSCV and the CV for the overlithiated NMC compound in 1 M LiPF\textsubscript{6}, AcN is shown. From the MSCV it is observed that the onset of the CO\textsubscript{2} evolution in the overlithiated NMC compound is located at 4.3 V (Li/Li\textsuperscript{+}); before this potential a peak is observed, it is very small and located at 4.0 V (Li/Li\textsuperscript{+}). The CO\textsubscript{2} evolution signal has two peaks: the first is located at 5.25 V (Li/Li\textsuperscript{+}) in the oxidative half cycle; the second peak is located at 4.7 V (Li/Li\textsuperscript{+}) in the reductive half cycle. The total amount of CO\textsubscript{2} produced in the first cycle is equal to 0.51 mmol per gram of overlithiated NMC compound; it is smaller than the total amount of CO\textsubscript{2} produced in EC:DMC (1:1 by wt.), as predicted.
The onset of the $O_2$ evolution in the overlithiated NMC phase is located at 4.7 V (Li/Li$^+$); the generation of $O_2$ starts after the generation of $CO_2$. The $O_2$ evolution signal has a single peak, than the signal drops to 0; the peak is located at 5.2 V (Li/Li$^+$) in the oxidative half cycle. The total amount of $O_2$ produced in the first cycle is equal to 0.282 mmol per gram of active material; it is very similar to the total amount of $O_2$ generated in EC:DMC (1:1 by wt.). The total amount of oxygen detected by the DEMS experiment in AcN is equal to 0.14 moles per mole of the active material.

The formation of $CO_2$ from acetonitrile is probably obtained by burning completely the molecule, with formation of $CO_2$, $H_2O$ and $NO_x$. A part of the oxygen released from the structure of the NMC compound could be not detected, and total amount of oxygen detected by the DEMS experiment is a conservative number; none the less 0.14 moles of O per mole of the active material is in the order of magnitude of the possible number of moles of oxygen ions oxidized. NO has mass number 30, and the development of other molecules with the same mass number from the system are not probable. The intensity of the mass signal 30 was monitored during the DEMS experiment of the overlithiated NMC compound in 1 M LiPF$_6$, AcN electrolyte and two peaks in $J_{30}$ were observed in the same potential window where $CO_2$ is formed; the complete burning of acetonitrile is confirmed by the experiment.

If the formation of 1.5 moles of $H_2O$ and 1 mole of NO for each 2 moles of $CO_2$ detected is considered, the total amount of oxygen released by the structure of the overlithiated NMC compound is equal to 0.20 moles per mole of active material. The oxidation of 0.20 moles of oxygen ions per mole of active material corresponds to an irreversible specific charge of circa 117 mAh g$^{-1}$. The irreversible specific charge in the first cycle of the HV galvanostatic cycling experiments for the overlithiated NMC compound is equal to 114 mAh g$^{-1}$. The irreversible specific charge in the overlithiated NMC compound is due to the oxidation of the oxygen ions in the structure and reaction of the oxygen radicals with the electrolyte.

The overlithiated NMC compound seems to release oxygen and to react with the electrolyte only in the first cycle; the oxidation of the electrolyte (evidenced by the $CO_2$ evolution) is somehow inhibited, in contrast to the stoichiometric material. A surface film composed of electrolyte oxidation products and/or changed surface properties of the NMC oxide due to the oxygen loss is believed to be the reason for the non-detection of the $CO_2$. 
development in the second cycle. The inhibition of the oxidation of the electrolyte after the first cycle seems to be independent from the electrolyte used; both AcN and EC:DMC have shown this characteristic. It is believed that a surface film based on nickel, manganese and cobalt oxide, formed during the release of oxygen radicals, is the reason for the inhibition of the oxidation of the electrolyte at high voltage in the following cycles.
Conclusions and Outlook

The main goal of this PhD thesis work was to develop the differential electrochemical mass spectrometry (DEMS) technique and the electrochemical impedance spectroscopy (EIS) technique further, for the study of the electro-catalytic properties of the active materials used in both positive and negative electrodes of lithium-ion batteries; in particular graphite and Li_{1+x}(Mn_{1/3}Ni_{1/3}Co_{1/3})_{1-x}O_2 compounds were deeply investigated as active materials for negative and positive electrodes, respectively.

During the PhD work, the sensitivity of the DEMS technique to gas evolution was enhanced thanks to the development of a new experimental setup, able to decrease the influence of the vapors of the electrolyte in the measurements, and of a mathematical tool for the subtraction of the background from the measured mass signals. A new cell was developed, with the implementation of a third electrode, which was used as reference electrode during the measurements. Several theoretical models were developed for describing the electrochemical processes occurring in the lithium-ion battery; in particular models describing porous electrodes, transport in pores, and the intercalation mechanisms were developed for understanding and fitting the EIS data. A new three-electrode symmetric cell was developed for the EIS measurements, to make the experimental setup nearer to the mathematical models. An analytical tool was developed for the Kramers-Kronig analysis of the EIS data.

Despite of the many advantages of graphite as active material for negative electrodes in lithium-ion batteries (high reversible specific charge, low cost, environmentally friendly), the graphite particles need the formation of a solid electrolyte interphase (SEI) to protect the graphite surface from exfoliation, a process which destroys the surface of graphite, lowering the cycle life and the performances of the lithium-ion battery. Moreover, the kinetic limitations of the electrodes based on graphite particles were investigated for different types of graphite, aiming to increase the specific power of the lithium-ion battery.

The DEMS technique was used to investigate the formation of the SEI on the graphite particles in a standard electrolyte, composed by 1 M LiPF_6, EC:DMC (1:1 by wt.). During the
formation of the SEI, the development of several gasses was observed. In particular, ethylene, hydrogen and CO$_2$ were observed. It was the first time CO$_2$ to be observable in DMC containing electrolyte, during the reductive SEI formation, even if its development was theoretically predicted before. The small amount of CO$_2$ developed was completely covered by the background noise, and it was observed thanks to both the increased resolution of the mass spectrometer and the subtraction of the background intensity in the mass signals.

The EIS technique was used to study the kinetic limitations of the electrodes based on graphite, with particular emphasis on the effects of porosity and electrolyte resistance. It was observed that the electrochemical process occurring at the surface of the graphite particles before the formation of the SEI is an adsorption process. Moreover, it looks like the standard adsorption model could not explain the EIS data for all the types of graphite. Other models were used to fit the impedance data. It was found out that the only plausible electrochemical process describing the EIS data for all types of graphite particles is an adsorption through surface states. It was also observed that the limitations due to the pore structure in electrodes based on graphite are dependent on the size of the particles; in particular, the smaller the graphite particle, the higher is the resistance of the pores.

During the PhD work, it was observed that the irreversible specific charge of the electrodes based on graphite particles is dependent on the areal density of the electrode. In particular, the higher the areal density, the smaller the irreversible specific charge. A new cell, called multiple-working-electrode (MWE) cell, was designed, for the study of the current density distribution along the thickness of the graphite electrode. Using the MWE cell, it was observed that the layer of graphite nearer to the counter electrode has the higher value of irreversible specific charge, and the value decreases in the farer layers. A hypothesis for explaining this behavior of the graphite electrodes was formulated. The hypothesis is based on the polarizability of the SEI layer when the graphite particle is fully charged with Li$^+$. When the SEI layer is polarized, the electrons can pass through it and reduce the electrolyte. The reduction of the electrolyte, being an irreversible process, causes the increase of the irreversible specific charge.

Among the active materials for positive electrodes in lithium-ion battery studied as possible substitutes of the LiCoO$_2$, the family of Li$_{1+x}$(Mn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$)$_{1-x}$O$_2$ compounds, called NMC compounds, seems to be one of the most promising. From the standard
electrochemical experiments, which include galvanostatic cycling and cyclic voltammetry, an irreversible oxidative process in the high voltage region, near 4.5 V (Li/Li\(^+\)) was observed. This irreversible process consumes more specific charge the higher the value of x in the NMC compound is. DEMS measurements in 1 M LiPF\(_6\), EC:DMC (1:1 by wt.) electrolyte have shown that for x = 0, CO\(_2\) is developed in the high voltage region in the first and subsequent cycles; for x = 0.1 CO\(_2\) and O\(_2\) were observed in the high voltage region, both produced only during the first cycle. Further DEMS experiments in 1 M LiPF\(_6\), AcN electrolyte for the x = 0.1 NMC compound have shown again the development of CO\(_2\) and O\(_2\) only in the first cycle. The experiments confirmed that the oxygen can come only from the structure of the NMC compound. Quantification of the amount of gas developed result in the loss of 0.2 moles of oxygen ions per mole of NMC compound, which can be also predicted theoretically from the NMC formula. The irreversible specific charge due to the oxygen loss and the irreversible specific charge observed in galvanostatic cycling experiments in the first cycle coincide within the 5% difference.

Suggestions for future work include the development of enhanced intercalation models which can consider the presence of the SEI and the energetical distribution of adsorption states and intercalation states in the active materials used in the electrodes of lithium-ion batteries. The development of a more sophisticated model for the transport of lithium in the active material is also suggested, for a better explanation of the low frequency behavior of the EIS data of intercalating electrodes. A better insight in the DEMS data acquired for graphite samples could help in the understanding of the SEI formation process. DEMS could also be used to prove the thickening of the SEI in the low potential region, which causes the increase of the irreversible specific charge in graphite electrodes. Even if the release of oxygen from the structure of NMC compounds was proven and quantified during this PhD work, for increasing the performances of the lithium-ion battery it could be interesting to verify if the oxygen ions are coming from the bulk structure or the surface of the NMC particles and if the oxygen release is related to the formation of another compound SEI-like at the surface of the NMC particle.
Bibliography


List of Symbols

\[ A_p \] cross sectional area of the pore [cm²]
\[ A_{p,m} \] cross sectional area of the m-th lateral pore [cm²]
\[ a \] characteristic length of the pore [cm]
\[ a_m \] characteristic length of the m-th lateral pore [cm]
\[ b_m \] distance between two lateral pores [cm]
\[ C_1 \] capacitance of the double layer in the outer Helmholtz plane [F cm²]
\[ C_2 \] capacitance of the double layer in the inner Helmholtz plane [F cm²]
\[ C_{dl} \] capacitance of the double layer at the interface [F cm²]
\[ C_{av,i} \] average concentration of species i in the cross section of the pore [mol cm⁻³]
\[ C_i \] concentration of species i in the electrolyte inside pores [mol cm⁻³]
\[ C_{S,i} \] concentration of species i in the bulk electrolyte [mol cm⁻³]
\[ C_{w,i} \] concentration of species i in at the wall of the pore [mol cm⁻³]
\[ C_e \] concentration of Li⁺ at the reacting interface [mol cm⁻³]
\[ D_i \] diffusion coefficient of species i [cm² s⁻¹]
\[ F \] Faraday constant [C mol⁻¹]
\[ G \] generation term of lithium in the solid phase [mol cm⁻³ s⁻¹]
\[ I \] current intensity of the electrochemical processes [A]
\[ I_{m} \] current intensity of the electrochemical processes inside the m-th lateral pore [A]
\[ I' \] current intensity in the electrolyte inside pores [A]
\[ I'_{T,m} \] total current intensity in the electrolyte inside the m-th lateral pore [A]
\[ I'' \] current intensity in the solid phase [A]
\[ I''_{T,m} \] total current intensity in the solid phase inside the m-th lateral pore [A]
\[ I_T \] total current intensity of the electrochemical processes [A]
\[ i \] current density due to electrochemical processes [A cm²]
\[ J_\beta \] transport of lithium in the solid phase [mol cm² s⁻¹]
\[ j \] imaginary unit, \( \sqrt{-1} \) [-]
k coefficient defined by eq. (3.47) [-]
k_{1,O} kinetic constant of the oxidation of the adsorption step (3.1) [s^{-1}]
k_{1,O,0} kinetic constant of the oxidation of the adsorption step at \Delta \phi_1 = 0 [s^{-1}]
k_{1,R} kinetic constant of the reduction of the adsorption step (3.1) [s^{-1}]
k_{1,R,0} kinetic constant of the reduction of the adsorption step at \Delta \phi_1 = 0 [s^{-1}]
k_{1,\theta} parameter defined by eq. (3.14) [A \text{ cm}^2]
k_{2,O} kinetic constant of the oxidation of the intercalation step (3.2) [s^{-1}]
k_{2,O,0} kinetic constant of the oxidation of the intercalation step at \Delta \phi_2 = 0 [s^{-1}]
k_{2,R} kinetic constant of the reduction of the intercalation step (3.2) [s^{-1}]
k_{2,R,0} kinetic constant of the reduction of the intercalation step at \Delta \phi_2 = 0 [s^{-1}]
k_{2,\theta} parameter defined by eq. (3.14) [A \text{ cm}^2]
K_\beta parameter defined by eq. (3.17) [A \text{ cm}^2]
k_\beta parameter defined by eq. (3.14) [A \text{ cm}^2]
K_\varepsilon parameter defined by eq. (3.17) [A \text{ cm} \text{ mol}^{-1}]
k_\varepsilon parameter defined by eq. (3.14) [A \text{ cm} \text{ mol}^{-1}]
L length of the pore [cm]
L_m length of the m-th lateral pore [cm]
N number of pores [-]
N_i number of adsorbing sites [mol cm^{-3}]
N_\sigma number of intercalating sites [mol cm^{-3}]
P_p perimeter of the cross section of the pore [cm]
R universal gas constant [J \text{ mol}^{-1} \text{ K}^{-1}]
R_1 resistance of the adsorbing step (3.1), defined by eq. (3.14) [\Omega \text{ cm}^2]
R_2 resistance of the intercalating step (3.2), defined by eq. (3.14) [\Omega \text{ cm}^2]
R_S electrolyte resistance outside the pores [\Omega]
R_U uncompensated resistance, defined by eq. (3.24) [\Omega]
r_1 rate of reaction of the adsorption step (3.1) [mol cm^{-3} s^{-1}]
r_2 rate of reaction of the intercalation step (3.2) [mol cm^{-3} s^{-1}]
T absolute temperature [K]
t time [s]
Z impedance of the reacting site [\Omega \text{ cm}^2]
$Z_{ad}$ impedance of the adsorption reaction $[\Omega \text{ cm}^2]$

$Z_I$ impedance of the intercalation reaction $[\Omega \text{ cm}^2]$

$Z_P$ impedance of the porous electrode $[\Omega]$

$\alpha$ parameter defined by eq. (3.37) [-]

$\beta$ occupancy of the intercalating sites [-]

$\beta_0$ occupancy of the intercalating sites at the interface [-]

$\beta_{av}$ average occupancy of the intercalating [-]

$\Gamma$ parameter defined as $\delta_1(1-\gamma)$ [-]

$\gamma$ parameter defined by eq. (3.9) [-]

$\gamma_i$ parameter defined by eq. (3.9) [-]

$\Delta\varphi$ potential drop at the interface electrode/electrolyte $[V]$

$\Delta\varphi'_{\text{ohm}}$ ohmic potential drop in the electrolyte $[V]$

$\Delta\varphi''_{\text{ohm}}$ ohmic potential drop in the solid phase $[V]$

$\Delta\varphi_m$ potential drop at the interface electrode/electrolyte $[V]$

inside the m-th lateral pore

$\Delta\varphi_1$ potential drop influencing the adsorption step (3.1) $[V]$

$\Delta\varphi_2$ potential drop influencing the intercalation step (3.2) $[V]$

$\Delta\varphi_i$ potential drop in the inner Helmholtz plane $[V]$

$\Delta\varphi_P$ total potential drop in the porous electrode $[V]$

$\Delta\varphi_T$ total potential drop at the interface $[V]$

$\delta_1$ average state of charge of the lithium in the inner Helmholtz layer [-]

$\delta_2$ average state of charge of the lithium in the solid phase [-]

$\theta$ occupancy of the adsorbing sites [-]

$\kappa$ function defined by eq. (3.37) [-]

$\kappa'$ function defined by eq. (3.38) [-]

$\lambda$ jumping distance $[\text{cm}]$

$\Xi_i$ coefficient defined by eq. (3.43) [-]

$\Xi'_i$ approximated value of $\Xi_i$ [-]

$\xi_i$ coefficient defined by eq. (3.44) [-]

$\xi'_i$ approximated value of $\Xi_i$ [-]
\( \rho \) resistivity defined by eq. (3.37) [\( \Omega \text{ cm} \)]

\( \rho_E \) average resistivity of the solid phase [\( \Omega \text{ cm} \)]

\( \rho_S \) resistivity of the electrolyte inside pores [\( \Omega \text{ cm} \)]

\( \tau \) time constant of the adsorption, defined by eq. (3.15) [s]

\( \tau_{D,i} \) time constant of diffusion of species \( i \) [s]

\( \omega \) angular frequency [s\(^{-1}\)]
Fabio La Mantia

Personal Information

Citizenship: Italian
Birthdate: August 25, 1980 – Brunico, Bolzano, Italy
Marital Status: Single
Languages: Italian (mother language), English (fluent), German (fluent)
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Education

Jun 2005 – Present
Paul Scherrer Institut and
Swiss Federal Institute of Technology
Villigen, Switzerland
Zürich, Switzerland
Doctoral work in electrochemistry laboratory.
(Prof. Dr. R. Nesper and PD Dr. P. Novák).

Sep 1999 – Nov 2004
Università degli Studi di Palermo
Palermo, Italy
Degree in Chemical Engineering (Majors in Materials Science) with marks 110/110 cum laude and award for thesis work and career, released from Chemical Engineering Department
Diploma Thesis: Characterization of Thin Amorphous Semiconducting Films by EIS and Differential Admittance
(Prof. Dr. F. Di Quarto and Dr. M. Santamaria).

Work Experience

Nov 2004 – May 2005
Chemical Engineering Department, UNIPA
Palermo, Italy
Laboratory Assistant
Study of the effect of thickness on the electronic properties of anodic valve metal oxides
Teaching Experience

Jun 2005 – Present  
Chemistry Department, ETHZ  
Zürich, Switzerland  
Teaching Assistant  
• Teaching assistant for course in Technical Electrochemistry, 5th semester.  
• Teaching assistant for laboratory training (water electrolysis).

Awards

15 Sep 2005  
Division of Electrochemistry, SCI  
Spoleto, Italy  
Award dedicated to the memory of prof. Bruno Mazza for diploma thesis: Characterization of Thin Amorphous Semiconducting Films by EIS and Differential Admittance

Extracurricular Activities

Sep 2002 – May 2005  
Hayashi ha Shitoryu Karate-do, Mitsuya-Kai  
Palermo, Italy  
Teaching Assistant  
• Teaching assistant for Karate-do children course

Hobbies include: modern literature, jogging, karate-do, and modeling.

References

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List of publications

Fabio La Mantia

Peer-reviewed publications


3. F. La Mantia, F. Rosciano, N. Tran, P. Novák, “Direct evidence of oxygen evolution from Li\textsubscript{i+x}(Ni\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3})\textsubscript{1-x}O\textsubscript{2} at high potentials”, *Journal of Applied Electrochemistry* **38**, 893-896 (2008).


Contributions to books

Conference talks

1. **F. La Mantia**, F. Rosciano, N. Tran, P. Novák, “Oxygen evolution from \( \text{Li}_{1+x} (\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x} \text{O}_2 \) at high potentials”, 213th ECS Meeting - Phoenix (Arizona) (2008).

2. **F. La Mantia**, F. Rosciano, N. Tran, P. Novák, “Direct evidence of oxygen evolution from \( \text{Li}_{1+x} (\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x} \text{O}_2 \) at high potentials”, GEI ERA 2007 - Cagliari (Italy) (2007).

Posters

1. S. H. Ng, **F. La Mantia**, W. Maerkle, M. E. Spahr, C. Vix-Guterl, P. Novák, “The influence of electrode density on the electrochemical performance of highly crystalline graphites in Li-ion batteries”, CARBON’08, Nagano (Japan) (2008).

2. F. Rosciano, **F. La Mantia**, N. Tran, P. Novák, “An in situ study of the origin of the irreversible plateau observed at high potentials for the \( \text{Li}_{1+x} (\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x} \text{O}_2 \) system”, 11th EuroConference on Science and Technology of Ionics, Batz sur Mer (France) (2007).


4. **F. La Mantia**, J. Vetter, P. Novák, “Characterization of materials for lithium-ion batteries with EIS, studied through a coupled partial ion-transfer model”, 1st Symposium Impedanzspektroskopie, Essen (Germany) (2006).

5. L. Hardwick, **F. La Mantia**, F. Rosciano, A. Wokaun, P. Novák, “Analytical methods for lithium-ion battery characterisation”, 1st EMPA PhD Symposium, Dübendorf (Switzerland) (2005).