

High Capacity Materials for Next Generation Li-Ion Batteries



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Ad Anna e Daniele,

*"... Non vogliate negar l'esperienza
di retro al sol, del mondo senza gente.*

*Considerate la vostra semenza
fatti non foste a viver come bruti
ma per seguir virtute e canoscenza"*

(Dante Alighieri, Divina Commedia, Inferno, canto XXVI, 116-120)

Declaration of Originality

I, Niccolò Guerrini, hereby declare that all work presented in this doctoral thesis, which is approximately 40,000 words in length, is original and where the work of others has been included it has been clearly referenced and acknowledged. This thesis is an account of work carried out at the School of Chemistry, University of St Andrews between November 2013 and November 2014 and the Department of Materials, University of Oxford between November 2014 and December 2017, under the supervision of Prof. Peter G. Bruce. No part of this thesis has been submitted towards another degree at the University of Oxford or elsewhere.

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A big “grazie” to my family: to my parents for having been the corner stones of my life, constantly surrounding me with love and kindness, always ready to lend their hands every time I fall. To my sister for being a bright, beautiful and fun young woman always standing by my side.

Finally, thank you to my love Yara for being the joyful, marvellous woman that she is, alleviating with her smile the difficult moments of this great journey.

Abstract

With the staggering growth in the recent years of the Lithium Ion Batteries market and the large number of different applications, in which these devices are currently employed, a change of paradigm in terms of the active materials composing the electrodes in these batteries is required. To meet the market needs in terms of performance (energy density and power), safety and respect of the environment, non-toxic light materials with high capacities are highly sought after.

The main goal of this work was to provide an insight into the mechanisms which limit the application of the Li-Rich based cathodes and hard carbon and silicon anodes. These high capacity materials would be ideal candidates to combine into a full cell for next generation batteries with enhanced energy densities.

The mechanisms underpinning the electrochemical behaviour of a family of cobalt-free lithium-rich layered oxide cathodes, with general formula $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$ ($0 \leq x \leq 0.3$), has been unravelled. Initially, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ was synthesized via a one-pot synthetic route and studied to understand the origin of the high potential plateau appearing over the first charge. Thanks to a careful structural and electrochemical characterization and powerful spectroscopic techniques (XANES, SXAS, RIXS) the presence of reversible anionic redox activity has been demonstrated. Subsequently the focus of the work has moved on to unravelling the role of the nickel substitution in favouring the oxygen redox activity over the oxygen loss phenomenon for this family of materials.

In parallel, a study on the improvement of the cyclability and efficiency of high capacity silicon-based anodes has been carried out using new polymeric binders, some of which, have been shown to guarantee more stable cycling and higher capacities with respect to the established binder sodium carboxymethylcellulose (Na-CMC). Additionally, in the attempt to address the issue concerning the First cycle Irreversible Capacity (FIC) of the silicon anodes, a highly reducing pre-treatment has been performed on the electrodes. As well, the treatment has been tested on hard carbon anodes that, despite being promising materials for Lithium and also Sodium Ion Batteries, are usually plagued by large FIC. An important improvement in terms of coulombic efficiency at the beginning of cycling has been observed in all the tested materials without any sign of detrimental effects on the electrodes overall performance.

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1 Introduction

1.1 Background

The handling and storage of energy has been of paramount importance to mankind in order to guarantee its technological development and still constitutes one of the biggest research areas in science.

Chemical species can be used to store energy. These chemical species can then be reacted together to release energy. In the example of a car the internal combustion engine acts as a transducer which transforms the chemical energy stored in gasoline to the mechanical energy needed to move a car.

Among these transducers one of the most important is the galvanic cell, commonly denominated “battery” that transduces chemical energy into electrical energy thanks to a spontaneous electrochemical process in which one chemical species is oxidized in order to reduce another. One of the main reasons why batteries have become so important since their invention (A. Volta, 1799, Figure 1.1) is that their working principle (electrochemical transduction of energy) can operate isothermally and avoid the thermodynamic limitations imposed by Carnot’s cycle. This implies that batteries can reach much higher efficiencies of energy conversion with respect to conventional combustion engines.

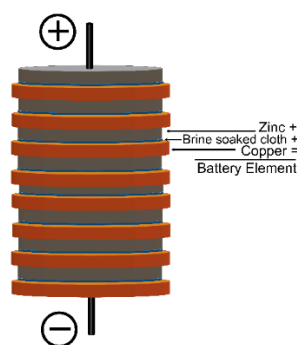


Figure 1.1 Scheme of a voltaic pile.

Since the advent of the voltaic pile an endless number of battery designs and materials have been investigated to get higher energy densities and power.

A first distinction has to be made between “primary” (i.e. non rechargeable) cells and “secondary” (i.e. rechargeable) cells.

Primary cells are the main type of commercially available batteries and are used to power a variety of small devices.

The Zinc-air cell, Li-I₂ cell and the Zn/MnO₂ alkaline cell are a few examples of the most important primary cells¹.

Secondary cells or rechargeable cells, invented not long after Volta’s pile (G. Plante’ 1859, Lead-acid cell), have the advantage that the spontaneous electrochemical process happening during the discharge can be reversed by passing through the cell a current of the opposite sign, therefore, allowing for multiple usages.

Lead-acid and nickel-cadmium cells dominated the market for rechargeable cells over the whole 20th century and, especially lead-acid batteries, are still the technology of choice for several applications (i.e. cars’ engines). These types of cells started to be challenged in the late 70’s and 80’s, when other types of cells such as the nickel metal hydride and the lithium-ion became available.

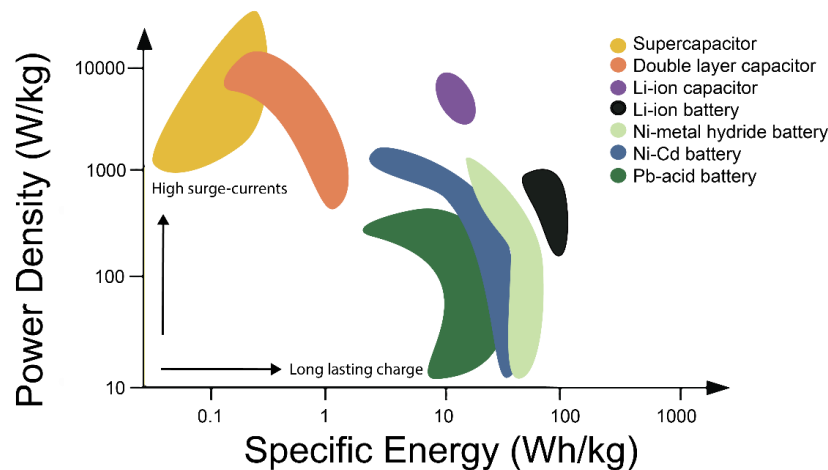


Figure 1.2 Ragone plot in which the power density of energy storage devices, expressed in W/kg is reported vs. the energy density expressed in Wh/kg. This kind of plot, invented by David V. Ragone, allows for a simple and straightforward comparison of energy storage systems.

Lithium ion batteries (LIBs) turned out to be a real breakthrough in battery technology due to their unique characteristics.

In Figure 1.2 a Ragone plot² is shown, in which the gravimetric energy density (also known as specific energy) expressed in Wh/kg is plotted against the power density also known as specific power) expressed in W/kg. The value of the specific energy indicates how much energy can be stored per unit mass of material whilst the specific power how quickly the energy can be released. This kind of plot allows an easy comparison of the characteristics of different energy storage devices to be made. It is clear from Figure 1.2 that LIBs present the highest specific energy (~160 Wh/kg) and specific power (~600 W/kg) with respect to other secondary batteries such as Ni-metal hydride, Ni-Cd or Pb-acid.

Thanks to their superior characteristics the number of Li-ion batteries employed to power all portable electronics, from smartphones to PCs, is increased with a steep production rate in the last two decades. In the recent years, LIBs have also been employed to power several kinds of Hybrid Electric Vehicles (HEVs)³ and Electric Vehicles (EVs)⁴ by many car manufacturers (e.g. Tesla⁵, Toyota⁶, Volvo⁷) and have found use to balance the

supply and demand in the electric grids where often they have been coupled with intermittent source of energy such as solar panels or wind turbines.

With the market share of LIBs explosion, a great deal of funds have been invested in scientific research to keep up with the increasing demand of higher specific energy and power for these devices. The number of scientific works related to Li-ion batteries has increased exponentially and the performance of a wide variety of materials, some of which will be detailed in this chapter, have been investigated as components of the batteries.

Despite the great scientific efforts and the pressing demand of the market there are still great challenges that need to be overcome to allow LIBs to stay competitive as the main energy supply devices in portable electronics, EVs and HEVs. The safety and performance (higher specific capacity and rate capability [these terms will be detailed in Chapter 2]) must be increased and the weight and volumes of the cells decreased, leaving yet unanswered questions to challenge both researchers and engineers.

1.2 Li-ion Battery, How It Works

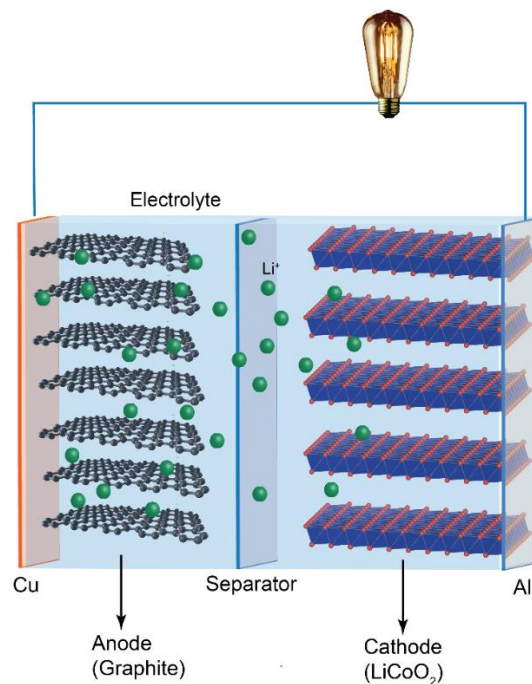


Figure 1.3 Schematic representation of a Lithium Ion Battery with a lithium cobalt oxide cathode and a graphite anode.

As already mentioned in the previous paragraphs the purpose of a battery is to transduce chemical energy into electrical energy and in the case of secondary batteries this process has to be reversible.

The lithium ion battery is an electrochemical cell made up of three main components:

- Cathode or positive electrode: is where the reduction reaction is happening during the cell discharge (i.e. spontaneous process)
- Anode or negative electrode: is where the oxidation reaction is happening during the cell discharge (i.e. spontaneous process)
- Electrolyte

Figure 1.3 schematically represents the most common kind of commercial lithium ion electrochemical cell in which the anode's active material is graphite and the cathode's active materials is the layered transition metal oxide LiCoO_2 (see following paragraphs). The electrodes are physically separated by a polymeric (i.e. polyethylene) separator

soaked in the third fundamental component of the battery, the electrolyte, that usually is a mixture of organic carbonates in which is dissolved a high concentration (1 M) of a salt of lithium (usually LiPF_6). The salt allows for the ionic conductivity of lithium ions between the two electrodes during the cycling of the cell whilst it is fundamental that the solvent does not conduct electrons to avoid short-circuits.

The working principle of a battery is based on the separation of an electrochemical reaction into two half-cell reactions, happening at the anode and cathode respectively, as exemplified below:

- $\text{LiCoO}_2 + \text{C} \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}$ Overall redox reaction
- $\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^-$ Positive electrode / cathode
- $\text{C} + x\text{Li}^+ + x\text{e}^- \rightleftharpoons \text{Li}_x\text{C}$ Negative electrode / anode

Each half cell reaction happens at a reduction potential E that is characteristic of the reacting active material in the electrode and the potential difference ΔE (defined as $\Delta E = E_{\text{cathode}} - E_{\text{anode}}$) between cathode and anode in a lithium ion battery is typically around 3.5-4 V vs. Li^+/Li .

During the discharge, which is a spontaneous thermodynamically driven process, the oxidation reaction takes place at the anode with lithium ions released in the electrolyte and electrons collected at the current collector (Figure 1.3). Driven by the potential difference between the electrodes, the electrons migrate through an external wiring from the anode to the cathode where the reduction reaction takes place. Simultaneously the lithium ions diffuse through the bulk of the electrolyte to the cathode/electrolyte interface where they are inserted in the cathode host structure to balance the negative charge resulting from the reduction process. The opposite mechanism happens during the charge of the battery when an external potential difference equal and opposite to ΔE is applied to the electrodes forcing the spontaneous electrochemical reaction to go backwards.

Thanks to the spontaneous current flowing in the external circuit during the cell discharge it is possible to power electronic devices or electric engines.

1.3 Lithium Ion Batteries, History

The first lithium ion battery was launched on the market by Sony^{8,9} corporations in 1991. Until then, there had been a great industrial interest towards LIBs, thanks their high energy densities and large operating voltage window, and several companies had been trying to develop a stable lithium metal battery, with a lithium metal anode and a MnO_2 cathode^{10,11}, facing major safety issues due to the formation of lithium metal dendrites during cycling that would have induced a short-circuit of the cell and, given the flammability of the electrolyte components, a risk of explosion. Other attempts had been made by Exxon, Bell laboratory and Moli Energy with a Li/TiS_2 and a Li/NbSe_3 cells^{12–15} that were also plagued by safety issues due to the extreme shock-sensitivity of LiClO_4 used as salt^{16,17} in the electrolyte mixture. Although very unsuccessful, these first prototypes of LIBs allowed to understand the dynamics of the electrochemical processes during cycling and the requirements needed to obtain a safe product.

Despite Sony was the first manufacturer to launch a commercial LIB, a great deal of scientific studies preluded the success of Li-ion secondary cells. Lithium metal had attracted scientists as a possible anode material thanks to its low redox potential¹⁸ (-3.04 V vs. Standard Hydrogen Electrode) and its lightness (6.94 g mol^{-1}). The idea of a secondary battery in which lithium ions could reversibly move between two electrodes (usually denominated 'rocking chair' system) to be intercalated/de-intercalated during the charge/discharge process had been already explored in 1970's by Whittingham^{19,20} and Armand²¹ in different works. The idea was subsequently picked up by Lazzari and Scrosati that employed a lithiated tungsten oxide as cathode and titanium disulphide as anode²². Although the potential window of Scrosati's cell was very narrow the battery cycled for over 50 cycles proving the concept of the rocking-chair motion of lithium ions in the battery.

A crucial discovery for cathode materials came from Goodenough research group in 1980, when they discovered the ability of transition metal oxides²³ with the α -NaFeO₂ structure to reversibly intercalate lithium ions at high potential values. In particular the cobalt-based member of the family, LiCoO₂, turned out to be the material of choice for the first commercial Sony cell and is still today the active material in many commercial²⁴ LIBs.

On the anode side graphite^{25,26} had been known to intercalate lithium although heavily affected by the co-intercalation of solvents molecules from the electrolyte that were reduced and lead to a progressive delamination^{27,28} of the electrode. A step forward was made by Dahn and co-workers²⁹ that reported the good resistance of petroleum coke to solvent intercalation and the beneficial effect of ethylene carbonate as additive³⁰ in the propylene carbonate electrolyte with both graphite and petroleum coke.

Also Yoshino et al. from the company Asahi Kasei had reported in a previous patent³¹ the advantages of using low temperature carbons such as petroleum coke and proposed as well the use of LiPF₆ and LiClO₄ as salts for the electrolyte instead of the highly toxic LiAsF₆ used by Dahn et al.³²

Despite these initial and fundamental improvements, restless research of new candidates as electrode's material has continued for almost three decades now in the attempt to better understand the complex chemistry underpinning the working mechanisms of the known electrode active materials but also trying to synthesize new materials with higher energy densities and power.

Among the materials that have raised more attention in the last decade there is the family of so-called "lithium rich" layered³³ transition metal oxides for the cathodes whilst for the anodes a great deal of interest has been devoted to the study of silicon nanoparticles and the family of hard carbons.

The investigation of lithium-rich transition metal oxides, silicon nanoparticles and hard carbon respectively employed the first as cathodes and the last two as anodes active materials are the focus of this thesis.

1.4 Cathodes

The majority of active materials employed as cathodes³⁴ (positive electrodes) in secondary LIBs are transition metal oxides, able to reversibly intercalate lithium ions, in which the insertion/extraction of lithium is accompanied by the reduction/oxidation of the transition metal (TM) centres to maintain charge neutrality.

Whilst the change in the TM oxidation number can account for the charge neutrality, the large compositional variations due to the insertion/extraction of lithium ions often lead to phase transitions in the cathode's lattice during cycling and for this reason it is crucial for a good cathode material to possess a stable crystal structure over wide compositional ranges. Another important aspect concerns the ionic and electronic conductivities across the crystalline host structure that have to match the current rates employed during the battery electrochemical cycling.

Additionally, an operation potential within the stability window of the electrolyte, together with a low molar and formula weights are highly desirable characteristics to guarantee high specific energy (per unit mass) and energy density (per unit volume) of the material.

It follows an overview on the most relevant active materials for LIBs cathodes.

1.4.1 Spinels

Spinels materials are a wide and well known family of materials with generic formula AB_2O_4 that present a structure with $Fd\bar{3}m$ symmetry constituted by a cubic close-packed (ccp) array of oxygens (ABCABC) where the cations A and B occupy one eighth of the tetrahedral sites and one half of the octahedral sites respectively³⁵ (Figure 1.4).

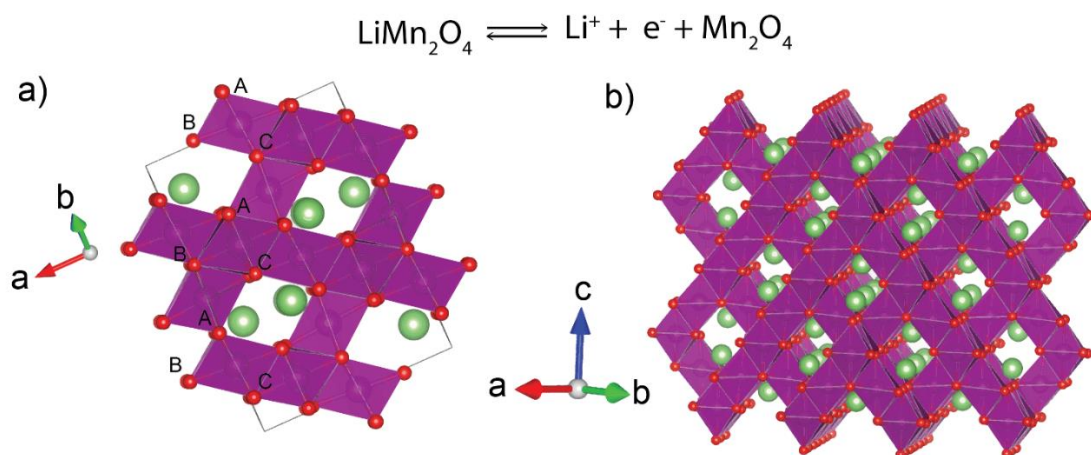


Figure 1.4 Redox reaction associated with the extraction/insertion of lithium ions and schematic representation of a spinel LiMn_2O_4 structure characterised by the $\text{Fd}\bar{3}\text{m}$ cubic symmetry (b). The lithium ions are represented by green spheres and the MnO_6 octahedra are in purple with the red oxygens spheres sitting on the corners. In a) is possible to observe the cubic close packed array of oxygen layers stacked with the characteristic ABC fashion.

In spinels employed as cathode materials lithium occupies the A sites and one or more transition metals species the B sites.

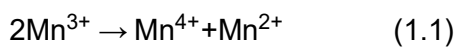
The best renown member³⁶ of the spinel family is LiMn_2O_4 in which the edge-sharing MnO_6 octahedra form a 3-dimensional network percolated by channels made of tetrahedral sites, one-eighth of which are occupied by lithium ions, that allow for a fast and reversible motion of the alkali metal ions during the material electrochemical cycling. Manganese is half in +3 and half in +4 oxidation number in the pristine and the material intercalates/de-intercalates lithium through the electrochemical reaction indicated in Figure 1.4 at a potential³⁷ of ~ 4 V vs. Li^+/Li .

The theoretical capacity for the extraction of the whole lithium of LiMn_2O_4 is 148 mAhg^{-1} although it is possible to increase the amount of intercalated lithium in the lattice by an insertion process happening at a potential of ~ 3 V vs. Li^+/Li in the empty interstitial octahedral sites.

The insertion of lithium beyond 1 mole per formula unit, yielding $\text{Li}_x\text{Mn}_2\text{O}_4$ with $1 \leq x \leq 2$, reduces Mn^{4+} to Mn^{3+} and up to $x = 1.1$ the product obtained is a solid solution. Beyond x

= 1.1 the concentration of the Jahn-Teller distorted Mn^{3+} becomes large enough to distort the lattice reducing the symmetry of the crystal structure from cubic to tetragonal with anisotropic expansion of the unit cell. The symmetry mismatch leads to a phase separation of the two distinct phases LiMn_2O_4 and $\text{Li}_2\text{Mn}_2\text{O}_4$ as lithium is inserted with the second growing at the expense of the first.

Despite the possibility to achieve higher capacities thanks to the 3 V insertion process, the performance of LiMn_2O_4 quickly fades during cycling. The reasons of such a loss in performance has been attributed partially to the phase changes illustrated above and partially to the possibility of a disproportionation reaction of Mn^{3+} at potentials above 4 V vs. Li^+/Li with formation of soluble Mn^{2+} ,



The loss of manganese would then lead to a progressive decrease in the amount of lithium that can be extracted/inserted in the material.

In order to stem this phenomenon and stabilise the material, the substitution of manganese with other TM elements such as Ni, Co, Cr, Al, Fe and others^{38,39} has been proposed. Among these materials $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been one of the most successful^{40,41} with a theoretical capacity around 147 mAhg^{-1} and a working potential close to 5 V vs. Li^+/Li .

Thanks to their low costs and easy synthetic procedures, spinel materials have successfully employed as cathode active materials in EVs such as the *Nissan Leaf*.

1.4.2 Olivines

Olivines with generic formula B_2AO_4 constitute the hexagonal analogue of the spinel materials in which the B atoms occupy one half of the octahedral sites and atoms A one eighth of the tetrahedral sites available in a hexagonal close packed (hcp) array of oxygen atoms (ABABAB).

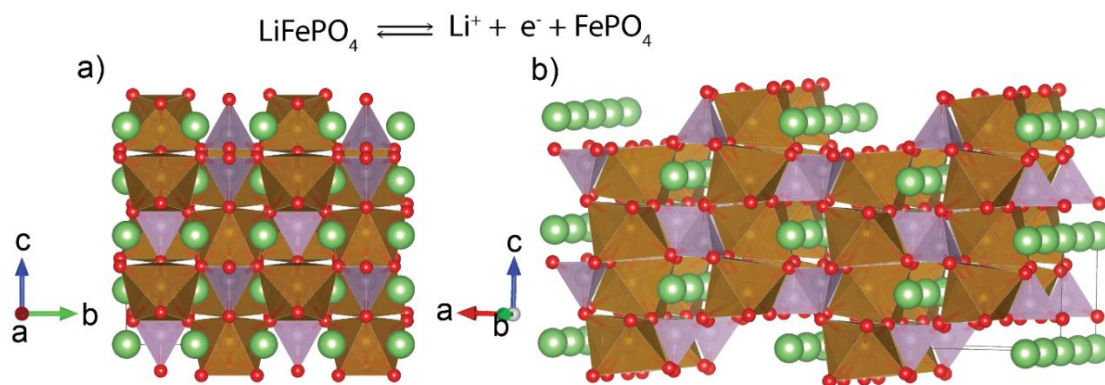


Figure 1.5 Redox reaction associated with the extraction/insertion of lithium ions and schematic representation of an olivine LiFePO_4 structure characterised by the Pnma orthorhombic symmetry. The lithium ions are represented by green spheres, the PO_4 tetrahedra are in light violet and the FeO_6 octahedra are in olive-green with the red oxygens spheres sitting on the corners.

These materials present a crystal structure belonging to the Pnma symmetry group and were proposed as good candidates for LIBs batteries in 1997 by Padhi et al⁴². The most famous member of this family is LiFePO_4 where P occupies A sites and Fe with Li occupy B sites. In the olivine structure the octahedral sites occupied by lithium run in edge sharing chains along the c-axis whilst the octahedral sites occupied by iron form zig-zag shaped chains running parallel to the lithium sites chains. Each of the tetrahedral anions PO_4^{3-} shares one edge and one vertex with the FeO_6 octahedra (Figure 1.5).

LiFePO_4 de-intercalates/intercalates lithium at a constant potential of 3.5 V vs. Li^+/Li via a two-phase $\text{LiFePO}_4/\text{FePO}_4$ process (Figure 1.5) reaching reversible capacities close to the theoretical value of 175 mAhg^{-1} for several hundredths of cycles. It is worth noticing that the redox active couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ would be active at lower potential than 3.5 V vs. Li^+/Li but thanks to the highly polarized P-O bond the iron redox couple is stabilized via inductive effect hence its redox potential is raised.

Thanks to the very reversible electrochemistry, good capacities, low production cost and high safety guaranteed by the lattice stability, olivines have been immediately regarded as good cathode materials for commercial LIBs and have been employed to partially substitute the more expensive and toxic NiMH cells. Despite the good properties though olivines suffer of poor rate capabilities and are not suitable materials for high rate cycling.

This is mostly due to the lithium diffusion rate⁴³ limitation across the $\text{LiFePO}_4/\text{FePO}_4$ interphase and to the poor electronic conductivity of the material (10^{-9} Scm^{-1}). Several strategies have been adopted to improve the rate capability such as the synthesis of nanosized^{44–47} particles to reduce the length of the lithium ions solid state diffusion path and the use of carbon coating to improve the electronic conductivity.

Isostructural materials to LiFePO_4 have been synthesized with other TM species^{48–51} replacing Fe like Mn, Co and Ni although due to higher cost of the raw materials and poorer performance have not raised the same interest as their Fe counterpart.

1.4.3 Silicates

Silicates form another large family of polyanion-based materials that have been synthesized and investigated for lithium ion battery applications^{52–55} in the early 2000's. These materials present the general formula Li_2MSiO_4 where $\text{M} = \text{Fe}$, Mn and Co in their stoichiometric formulation. As for the olivines the silicate lattice⁵⁶ is very stable and resistant to high temperature degradation thanks to the strong Si-O covalent bond of the SiO_4^{3-} anions. The silicates lattice is constituted^{56,57} by a distorted hexagonal close packed array of oxygens in which the cations occupy half of the tetrahedral sites.

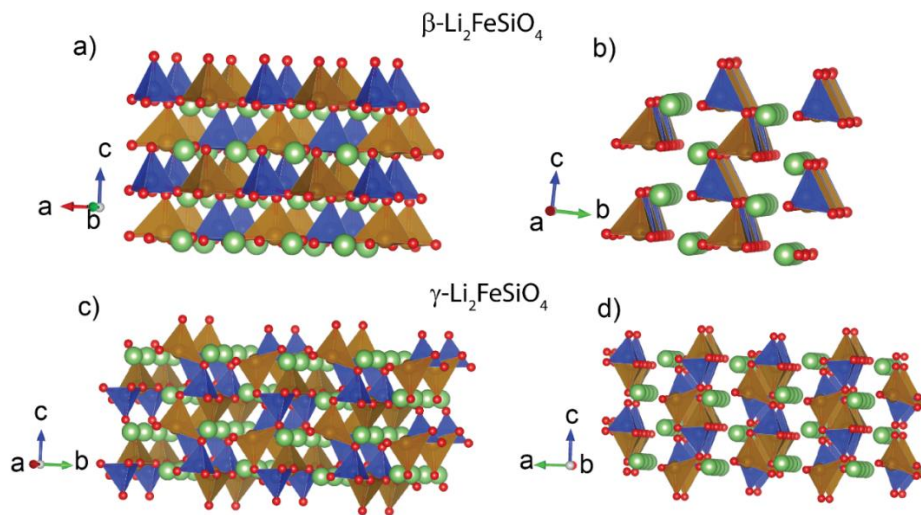
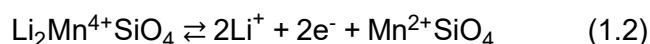


Figure 1.6 Schematic representation of a silicate $\text{Li}_2\text{FeSiO}_4$ structure. In a) and b) is shown the β -polymorph possessing $\text{Pmn}2$ orthorhombic symmetry, whilst in c) and d) the

γ -polymorph is reported presenting a Pmna orthorhombic symmetry. The lithium ions are represented by green spheres, the SiO_4 tetrahedra are in blue and the FeO_4 tetrahedra are in olive-green with the red oxygens spheres sitting on the corners.

Many are the possible polymorphs^{57,58} for these materials although the two most relevant ones are denominated β and γ (corresponding to the low and high temperature forms respectively) that differ in the orientation of the MO_4 tetrahedra (Figure 1.6)

In the β polymorph all tetrahedra point in the same direction, perpendicular to the oxygen close packing planes, sharing only corners with each other, whereas for the γ type the direction of half of the tetrahedra is inverted (Figure 1.6-c and -d). Several kinds of β and γ polymorphs exist with different degrees of distortions of the parent compounds structures. Interestingly each different polymorph of the same kind of silicate presents characteristic electrochemistry and cycling performance⁵⁹. The theoretical capacities of silicates are attractive with values above 300 mAhg^{-1} for the manganese^{60,61} silicate $\text{Li}_2\text{MnSiO}_4$ in which is possible to extract all the lithium thanks to the activation of both redox couples $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Mn}^{4+}/\text{Mn}^{3+}$ as illustrated in Equation (1.2).



Despite the interesting electrochemical properties silicates are affected by very poor electronic (10^{-14} - $10^{-18} \text{ Scm}^{-1}$) and ionic conductivities^{52,62}. Similarly, strategies to the ones adopted for LiFePO_4 have been attempted with reduction of the particles⁵⁹ dimensions and the use of graphitic carbon coating with partial improvements in rate performance. As well, Billaud et al. proposed a new strategy to increase the ion transport rates by synthesizing Li-rich silicates⁶³ with formula $\text{Li}_{2+2x}\text{M}_{1-x}\text{SiO}_4$ (with $0 \leq x \leq 0.3$) achieving an increase in the ionic conductivities of more than two orders of magnitude.

1.4.4 Layered transition metal oxides

The so-called layered transition metal oxides⁶⁴ thanks to their attractive structures and promising theoretical specific capacities constitute the largest and most investigated family of active materials for lithium ion battery cathodes.

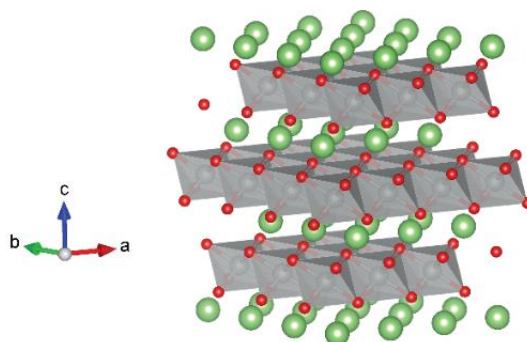


Figure 1.7 Layered structure of a generic TM oxide, formula LiMO_2 , with the alternating layers of lithium ions (green spheres) and edge-sharing MO_6 (grey) octahedra piled-up to form the crystal structure.

Although layered compounds of heavy alkali metals with oxides of cobalt, manganese and chromium had been already widely investigated in the 1970's by Delmas⁶⁵, there was essentially no deep study of the lithium compounds, until in the early 1980s Goodenough et al. recognised the possibility of electrochemically de-lithiating the layered LiCoO_2 effectively opening a new era for the energy storage technologies.

The structure of the layered oxides, general formula $\text{A}_x\text{M}_y\text{O}_2$, is made of a close packed⁶⁶ oxygen array in which the transition metals (M) are bound into either octahedral or trigonal prismatic sites to six oxygens (Figure 1.7) forming 2D MO_2 piled slabs. Each slab interacts with its neighbouring ones via weak Van der Waals interactions so that alkali metal ions (A) can be hosted between the layers to guarantee the charge balance. Depending on the alkali metals dimensions, the MO_2 layers can pack in different ways to form the right geometry to host the alkali metal ions (e.g. lithium is hosted in octahedral sites whilst the bigger sodium goes into trigonal prismatic sites), although the most stable configuration is achieved when the condition $M_{\text{radius}}/A_{\text{radius}} < 0.9$ is fulfilled⁶⁷.

Two are the main types of nomenclatures adopted for these compounds: the first one is the classic ABC notation (Figure 1.4-a) whilst the second, proposed by Claude Delmas⁶⁸, is made of a letter and a number (e.g. O3) where the letter indicates the geometry of the interstices in which the alkali metal ions are hosted (O = octahedral, P = trigonal

prismatic, T = tetrahedral) and the number refers to the number of MO_2 sheets in the unit cell (Figure 1.8).

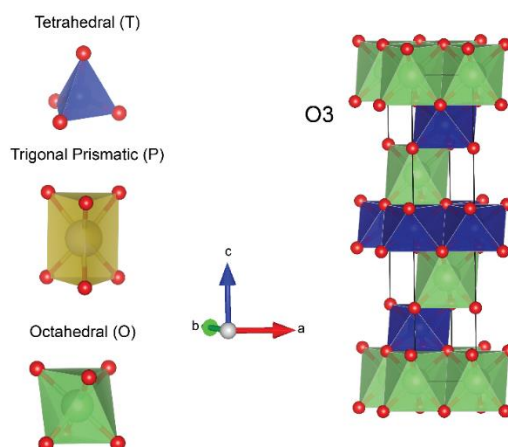


Figure 1.8 Coordination geometries for the alkali metal ions (left) in the Delmas notation⁶⁸ for layered oxides and schematic representation for the unit cell of an O3 type structure (e.g. LiCoO_2) in which the LiO_6 octahedra are in green.

Stoichiometric layered oxides

This class of layered oxides is characterised by the presence of alkali metal ions only in the alkali metal layers. The most famous member of this family is surely LiCoO_2 , employed by Sony in 1991 as cathode^{8,9,23} for the first commercial LIB, is still one of the material of choice for commercial LIBs. It is made by superimposed layers of lithium ions, hosted in octahedral interstices, and edge-sharing CoO_6 octahedra (Figure 1.9) characterised by a cubic close packed lattice of oxygen atoms with an O3 structure (as described above) and an $R\bar{3}m$ cell symmetry. lithium ions can reversibly extracted/inserted for several hundreds of cycles at an average working potential of 3.7 V vs. Li^+/Li following the electrochemical reaction reported in Figure 1.9. Despite presenting a theoretical capacity of about 275 mAhg^{-1} only half of it can actually be exploited due to the structural instability arising when more than 0.5 lithium per formula unit are extracted⁶⁹.

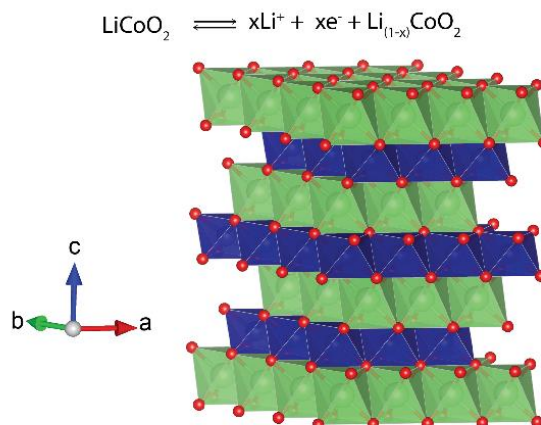


Figure 1.9 Redox reaction associated with the extraction/insertion of lithium ions and schematic representation of LiCoO_2 structure possessing $R\bar{3}m$ trigonal symmetry. The LiO_6 octahedra are represented in green, the CoO_6 octahedra are in blue and the oxygens (red spheres) sit on the corners.

Beside LiCoO_2 other two materials such as LiNiO_2 and LiMnO_2 have been intensively investigated. LiNiO_2 presents identical structure to the cobalt oxide although the synthesis of this materials is more challenging due to the presence of a high number of defects such as stacking faults.

The working potential of the stoichiometric layered nickel oxide⁷⁰⁷¹ is slightly lower than the cobalt one, ~ 3.6 V vs. Li^+/Li , due to the higher energy of the nickel t_{2g} orbitals and, as seen in LiCoO_2 , only 140 mAhg^{-1} , over 270 mAhg^{-1} of theoretical capacity, are exploitable without any structural degradation that in this case is highly exothermic representing a real safety hazard.

On the other hand, the manganese equivalent of the layered oxides described above, LiMnO_2 , has been widely investigated thanks to the much cheaper reagents compared to Ni and Co, the minimal toxicity and high theoretical capacity of 285 mAhg^{-1} . Unfortunately, LiMnO_2 is difficult to be readily synthesized due to the preferential formation of the more stable spinel LiMn_2O_4 . It can be prepared via ionic substitution⁷² at low temperature starting from the P3 structure of $\alpha\text{-NaMnO}_2$, although Tabuchi et al. attained the material via direct hydrothermal reaction⁷³. The process yields the kinetically stable,

thermodynamically unstable, O3 LiMnO_2 that presents⁷⁴ a lower crystal symmetry C2/m with respect to the cobalt and nickel compounds due to the presence of the Jahn-Teller active Mn^{3+} . The instability of the compound is manifested during the electrochemical cycling that is characterized by a quick fade in capacity for this material with simultaneous structural rearrangement to form the stable spinel lattice.

In the attempt to stabilize LiMnO_2 , doping strategies with other cations such as Co, Ni, Al and Cr have been attempted by several groups^{75–77}. Among these materials the mixed layered oxide $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (denominated NMC) has been the most successful and a very promising material for commercial use presenting enhanced stability and improved performance^{78–81}.

Lithium-rich layered oxides

Lithium rich layered oxides are characterized by the presence of lithium within the transition metal layer. The first member of this family, $\text{Li}_{1.09}\text{Mn}_{0.91}\text{O}_2$, was synthesized⁸² by Thackeray et al. via acid treatment followed by lithiation of Li_2MnO_3 . These materials can be thought as the solid solution^{33,83} $x\text{Li}_2\text{MnO}_3(1-x)\text{LiMO}_2$, where M= Ni, Co, Al, Cr, Fe, Ti or a mixture of them^{84–86}, present an O3 structure with a cubic close packed array of oxygens and the cations hosted in the octahedral sites as analogous to the stoichiometric LiCoO_2 although the symmetry for the lithium rich materials is lowered from rhombohedral $R\bar{3}m$ to the monoclinic C2/m due to the ordering of the manganese and lithium ions in the transition metal layer⁸³.

Depending on the synthetic conditions and the redox active transition metals the lithium rich materials show a wide range of performance⁸⁴ and working potentials.

Interestingly, most of these compounds present reversible capacities well beyond the transition metals redox activity that might be explained with the presence of oxygen redox activity^{87–90}. The end member of the solid solution Li_2MnO_3 shows to be electrochemically active, although the formal oxidation number on manganese in this compound is 4+. This

activity has been attributed to the oxidation of oxygen in the lattice that would lead to the extraction of lithium and concomitant loss of molecular oxygen upon charge^{91,92}.

Among the most famous and commercially attractive lithium rich layered compounds there are the $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and the lithium rich NMC compounds with formula^{85,93,94} $x\text{Li}_2\text{MnO}_3(1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with $0 < x < 1$. These compounds show reversible capacities higher than 200 mAhg^{-1} for several tenths of cycles but the progressive voltage fade during cycling, together with low rate capabilities, partially related to the insulating nature of Mn^{4+} , have so far hindered the launch on the market of these materials. A great deal of work has been carried out in the recent years by several groups to address these problems by unravelling the mechanisms underpinning the chemistry of lithium rich cathodes through the study of the local structure (e.g. the influence of synthetic routes and conditions on the local ordering of cations in the transition metal layer)^{95,96}.

Due to the complexity of the systems involved many aspects are still partially unresolved or matter of intense debate in the academic community making this class of materials one of the most intriguing to study.

1.5 Anodes

As already mentioned, the first prototypes of secondary LIBs employed a foil of metallic lithium as anode (negative electrode). This was due to the unique chemical-physical properties of elemental lithium such as the low reduction potential (-3.04 V vs. SHE) and the lightness of this element (6.94 gcm^{-3}), that still today make it the Holy Grail material for anodes in terms of energy density^{97,98}.

Despite its great properties though, lithium is a very reactive and air sensitive element that when repeatedly cycled in a secondary battery presents important safety issues.

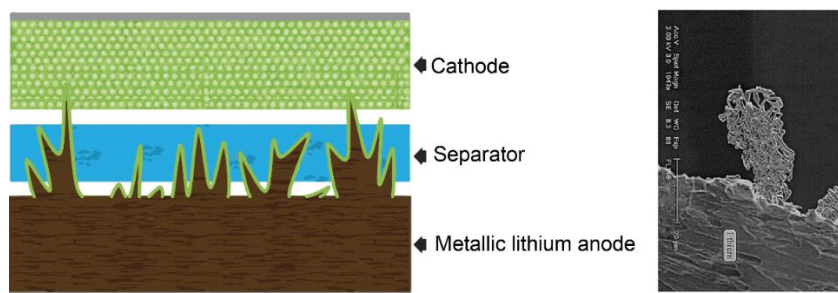


Figure 1.10 Representation of the lithium dendrites growing from the anode surface and piercing through the separator until reaching the cathode leading to short circuiting (left). SEM picture of a lithium dendrite (right, reproduced from Kim et al.⁹⁸).

The biggest danger is related to the formation of metallic dendrites (Figure 1.10) on the anode surface that upon repeated cycling could grow long enough to pierce through the separator and reach the cathode short-circuiting⁹⁹ the cell. If that happens, a very high current density would flow through the nanometric diameter of the dendrite overheating it and consequently generating a spark that would ignite the electrolyte leading to the cell explosion.

To avoid the safety risks, metallic lithium has been replaced by other materials able to intercalate lithium ions at potential values close to that of the Li^+/Li redox couple that will be detailed in the following paragraphs.

Despite the improved safety in terms of lithium dendrites formation, a working potential close to -3.0 V vs. SHE still represents a risk in terms of performance stability. This is because at the anode working potential, the electrons in the active material have an electrochemical potential ($\bar{\mu}_e$) that is higher in energy than the LUMO of most of the electrolytes organic solvents¹⁰⁰ (Figure 1.11).

electrolyte additives to yield the most stable SEI possible. Currently the standard electrolytes for LIBs are based on a mixture of organic carbonates (e.g. ethylene carbonate, dimethyl carbonate, propylene carbonate) in different weight ratios.

It is fundamental for the SEI layer to be a good ionic conductor to guarantee the transport of lithium ions during the insertion/extraction process occurring when the electrode is cycling.

The dimensional stability of the anode during cycling can affect the SEI conductivity as it is important to avoid excessive expansion and contraction of the electrode over lithiation/de-lithiation that could lead to a damage of the SEI exposing fresh electrolyte to the anode surface that would lead to further reduction and consumption of it with simultaneous thickening of the SEI (longer path to cover for the conduction of lithium ions when moving from/to the electrode bulk to/from the electrolyte, resulting in lower ionic conductivity). Despite its essential role in guaranteeing the stability of the electrode, the formation of the SEI layer during the first cycle irreversibly consumes¹⁰⁶ part of the charge. This phenomenon is known as First cycle Irreversible Capacity (FIC) and will be detailed in Chapter 6.

The following section is an overview on the most relevant active materials for LIBs anodes

1.5.1 Graphite

Graphite is still the most used active material in commercial LIBs, thanks to its relatively good specific capacity, 372 mAhg^{-1} , and its working reduction potential^{107,108} close to 0 V vs. Li^+/Li .

The structure of graphite (Figure 1.13) is made of a perfect stacking of graphene layers that can reversibly intercalate up to one lithium per six carbons²¹ (corresponding to a capacity of 372 mAhg^{-1}) following the reaction shown in Figure 1.13

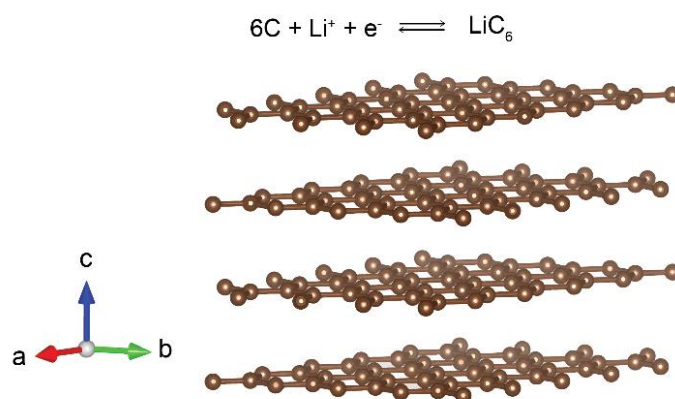


Figure 1.13 Schematic representation of the graphite layered structure

Due to the working potential very close to that of the Li^+/Li couple the stability of the SEI is extremely important for graphite anodes to avoid the plating of metallic lithium with consequent growth of dangerous dendrites.

Graphite is the most crystalline ordered member of a wide family of carbonaceous materials with graphitic structures in which different degrees of defects are presented that are capable of reversibly intercalating lithium ions at low voltages¹⁰⁹.

1.5.2 Hard Carbons

From the pyrolysis of epoxy resins and natural hydrocarbons^{110–112} such as sugars or cellulose, under inert atmosphere or vacuum, it is possible to obtain another family of carbonaceous materials known as hard carbons. These materials present a disordered structure^{112–114} in which small domains of graphene layers are stacked as in a graphite-like fashion but with randomly distributed covalent bonds connecting the planes. These ordered domains are immersed in an amorphous and porous carbon matrix. Depending on the precursors and synthetic conditions it is possible to tune the particle dimensions and crystallinity of the final product.^{114,115}

Hard carbons are able to reversibly intercalate lithium¹¹² as well as sodium^{113,116} ions not only within the layered domains but also in the pores of the amorphous matrix allowing these materials to have a wide range of performance (up to 600 mAhg^{-1} of reversible

capacity for lithium ions)¹¹² that can vary depending on the porosity and the particle dimensions. These characteristics make hard carbons a very attractive system to be employed not only in LIBs but also in the realising sodium ion battery (NIBs) technologies. The dimensional stability¹⁰⁹ for hard carbons is not as good as the graphite one meaning a larger volume expansion and contraction over lithiation/de-lithiation that makes the SEI layer less stable. This implies that the irreversible capacities in the first cycles for hard carbons are much larger¹¹⁴ (40-50% of the inserted charge) than for graphite. Despite their attractive high capacity, the ability to intercalate Li but also Na ions and the low working potentials close to the Li^+/Li and Na^+/Na^0 couples, the problem related to the SEI instability and high irreversibility in the performance have so far hindered hard carbon in finding commercial application. Further investigation on the origins of the irreversibility and the investigation of possible ways to address the problem will be detailed in chapter 6.

1.5.3 Lithium Titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (abbreviated LTO) is the best-known member of a family of transition metal oxides (e.g. WO_2 , MoO_2 , Fe_3O_4)^{117–120} able to reversibly intercalate lithium ions at relatively low potential (1.5-2 V vs. Li^+/Li).

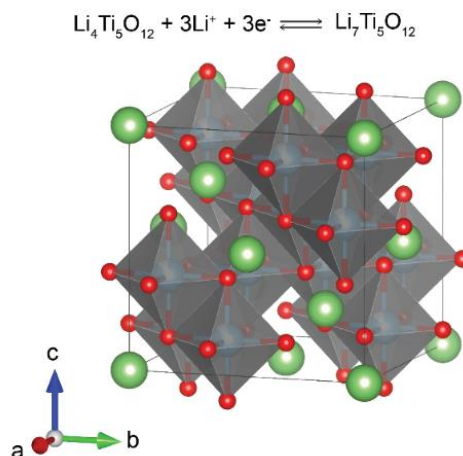


Figure 1.14 Redox reaction associated with the insertion/extraction of lithium ions and schematic representation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ possessing a defect spinel cubic structure. The

lithium ions are represented as green spheres whilst the TiO_6 octahedra are in dark-grey with the oxygens (red spheres) sitting on the corners.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ presents a defect spinel structure^{121,122} (Figure 1.14) that is able to intercalate 3 lithium ions at a voltage of 1.5 V vs. Li^+/Li , corresponding to a specific capacity of 175 mAhg^{-1} . Thanks to its working potential, most of the carbonates employed in the electrolyte mixture do not decompose on the anode surface during cycling to form an SEI layer. This allows for a much faster insertion and extraction rate of lithium ions in the structure making of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ a suitable anode material for cells in which high power is required and a safer material compared to carbons with no risks of dendrites formation.

The biggest drawback in employing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for commercial purposes is its low energy density due to the relatively low capacity and working potential.

1.5.4 Lithium Alloys

The lithium alloy materials comprise a group of elements able to alloy with lithium at potential values close to that of the Li^+/Li redox couple. These materials have received much attention in the last two decades thanks to their high capacities and low working potential. Table 1.1 reports the most important of these elements and their properties are compared with those of metallic lithium, graphite and LTO.

Table 1.1 Comparison of the diverse properties of different anodes active materials for Li-ion batteries¹²³. The colour shading indicates the mechanism through which lithium is stored: orange for plating, green for intercalation and red for alloying.

Materials	Li	C	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	Si	Sn	Sb	Al	Mg	Bi
Density (gcm^{-3})	0.53	2.25	3.5	2.33	7.29	6.7	2.7	1.3	9.78
Lithiated phase	Li	LiC_6	$\text{Li}_7\text{Ti}_5\text{O}_{12}$	$\text{Li}_{4.4}\text{Si}$	$\text{Li}_{4.4}\text{Sn}$	Li_3Sb	LiAl	Li_3Mg	Li_3Bi
Theoretical specific capacity (mAhg^{-1})	3862	372	175	4200	994	660	993	3350	385
Theoretical charge density (mAhcm^{-3})	2047	837	613	9786	7246	4422	2681	4355	3765
Volume change (%)	100	12	1	320	260	200	96	100	215
Potential (V vs. Li^+/Li^0)	0	0.05	1.6	0.4	0.6	0.9	0.3	0.1	0.8

From Table 1.1 it appears clear that there is a wide range of materials able to store lithium through different mechanisms at low voltage values, presenting a wide variety of properties. For example, due to its capacity to alloy with lithium around 0.3 V vs. Li^+/Li , aluminium cannot be the current collector of choice, as it happens for cathodes, in the case of Li-ion battery anodes. Instead the much heavier and more expensive copper is necessarily employed. Among the materials reported above, silicon has been regarded as the best candidate for high energy density anodes in LIBs over the last decade.

1.5.5 Silicon

Silicon has attracted much attention thanks to its high theoretical capacity, ten times higher than graphite (4200 mAhg^{-1})¹²⁴, and its low cost. This anode material has an intercalation potential of 0.3-0.4 V vs. Li^+/Li which makes it safer than graphite (0.05 V vs. Li^+/Li) averting deposition of metallic lithium and avoids important loss in energy (e.g. lithium titanate anodes: 1.5 V vs. Li^+/Li)¹²². Nevertheless, some challenging problems still have to be overcome to gain a good implementation of silicon alloy anodes in commercial LIB. This includes the large volume change¹²⁵ (up to 300 %) of the alloy material during the lithium ion insertion/extraction process and the important energy loss due to the First cycle Irreversible Capacity (FIC).

The alloying mechanism

The alloying mechanism of lithium with silicon has been widely investigated and proven to be highly sensitive to the experimental conditions such as the average silicon particles dimensions, cycling cut-off voltage and temperature.

In an early study it was shown by Wen and Huggins¹²⁶ that at 415 °C the electrochemical process of lithium alloying with silicon follows the Li-Si phase diagram that produces the four different products Li_2Si_7 , Li_7Si_3 , $\text{Li}_{13}\text{Si}_4$ and $\text{Li}_{22}\text{Si}_5$ with the onset potentials of 332, 288, 158, and 44 mV, respectively (Figure 1.15).

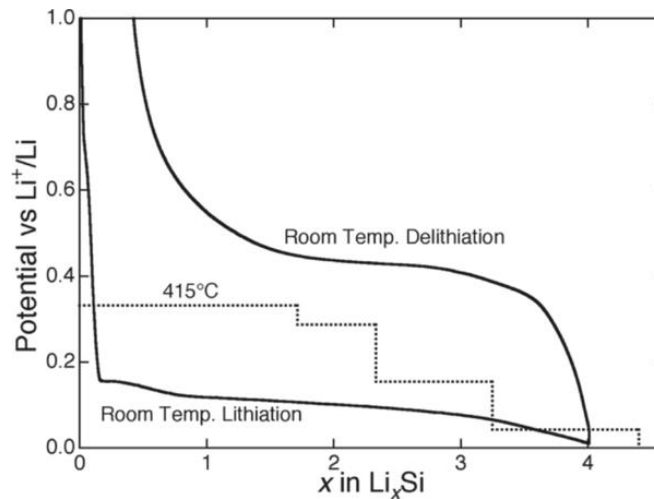


Figure 1.15 Comparison of the coulometric titration of the Li-Si system at 415 °C with the galvanostatic load curve of a silicon-based electrode at room temperature. The presence of several steps in the titration curve indicates the presence of multiple two-phase processes happening at high temperature. In contrast the room temperature galvanostatic curve shows the presence of a unique sloped region during the alloying process. Reproduced from McDowell et al.¹²⁷.

At room temperature though the reaction of lithium with micrometric sized silicon deviates from the equilibrium predictions with the first cycle alloying process presenting a plateau region centred around 0.1 V vs. Li^+/Li hence indicating the presence of a two phase process (figure solid line). Thanks to detailed XRD studies it has been shown that the two phases resulting in the flat plateau during the first cycle alloying process were an amorphous lithiated silicon phase and a crystalline pristine silicon phase. The two-phase alloying process is related to the large activation energy required to break the crystalline silicon lattice.

The lithiated micrometric-sized silicon phase stays amorphous above 50 mV vs. Li^+/Li whilst below the 50 mV potential a highly crystalline phase with composition $\text{Li}_{15}\text{Si}_4$ is formed determining the presence of a plateau in the curve for the de-alloying process (figure).

Additionally, the silicon particle size plays a crucial role in determining the voltage profiles shape during the cycling. The size effect becomes evident in the case of nanosized silicon particles for which the alloying/de-alloying voltage profiles do not appear to be

affected by the lower voltage cut-off even when discharged to 0 V vs. Li^+/Li as reported for the micrometric silicon (Figure 1.16).

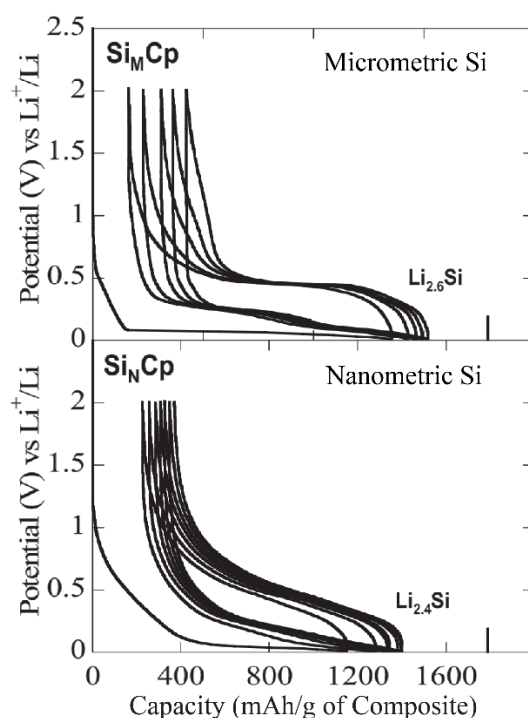


Figure 1.16 Comparison of the load curves shape for silicon-based electrodes galvanostatically cycled between 0 and 2V vs. Li^+/Li . Micrometric silicon was employed in the top panel whilst silicon nanoparticles were used in the bottom panel. Reproduced from Saint et al.¹²⁸, with permission from Wiley-VCH.

Problems affecting silicon and strategies to solve them

For pure crystalline silicon powder deposited on a copper current collector the lithium insertion/extraction volume effect and the first cycle irreversible capacity are responsible for a dramatic decrease in performance for this material reducing the cycling efficiency to 35-60% and the overall capacity to less than 1000 mAhg^{-1} after only one cycle of charge/discharge. This is observed in Figure 1.17 in which are shown an initial irreversible capacity of more than 2600 mAhg^{-1} and a coulombic efficiency lower than 30%.

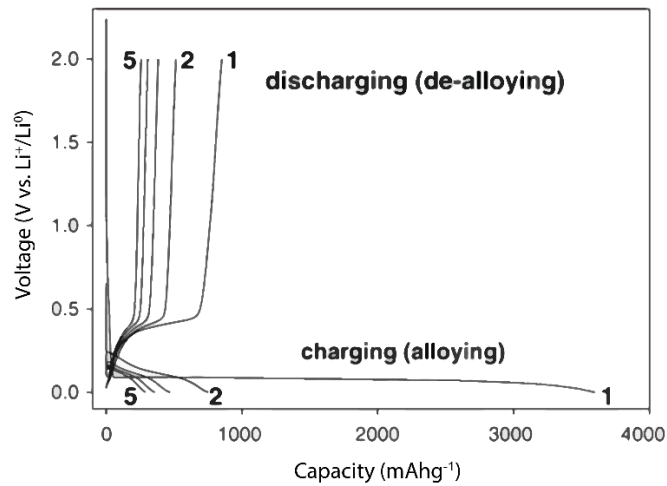


Figure 1.17 Voltage profiles for the alloying/de-alloying process of lithium with a pure silicon electrode. Large irreversibility is observed for the first cycle. Reproduced from Kim et al.¹²⁹ with permission from J. Power Sources.

The origins of such a large loss in capacity during the electrode cycling can be summarized in 4 main reasons:

- 1) Loss of active material: this phenomenon is due to the large volume change of the silicon particles upon cycling which leads to a detachment of the particles from the current collector, as a result of pulverisation and cracking of the electrode material¹³⁰.

During the lithiation process both the carbon matrix and the silicon particles undergo a compressive stress as a result of the volume expansion. In the subsequent de-lithiation process, the particles are subjected to a strong tensile stress due to the material contraction leading to the electrode cracking¹³¹. A schematic representation of this phenomenon is reported in Figure 1.18

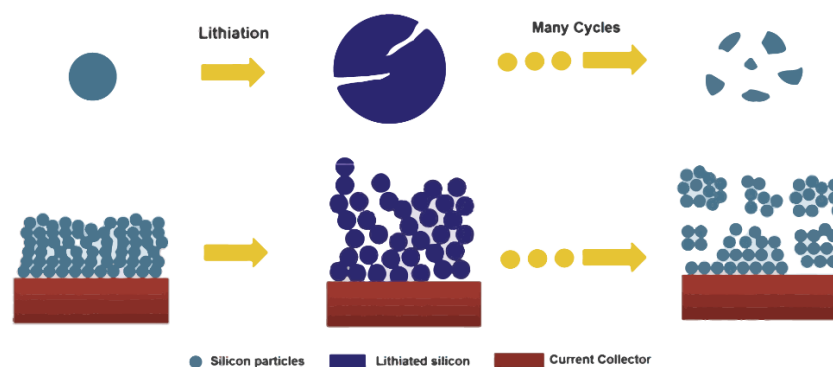


Figure 1.18 Schematic representation of the silicon electrode failure mechanism due to the large volume expansion and contraction, over lithiation/de-lithiation, leading to the electrode delamination and loss of active material. Figure edited from Wu et al.¹³⁰

- 2) Formation of Solid Electrolyte Interphase (SEI) : as for all anode systems also in silicon there is the formation of a passivating film^{103,104,132} on the particles deriving from the decomposition of the electrolyte at anode's surface potential values (Figure 1.12).

The SEI layer is usually composed of various lithium alkylcarbonates, Li_2O_2 , LiF and Li_2CO_3 . Differently from graphite, where a stable SEI is developed at 0.5-1 V vs. Li^+/Li during the first cycle^{102,105}, SEI formation in Si anodes is a dynamic process due to the constant volume changes of the particles during the insertion/extraction process of lithium. The volume variation generates cracks in the SEI formed in previous charge/discharge cycles, exposing fresh Si surface to the electrolyte and thus leads to continuous SEI growth with related consumption¹⁰⁶ of lithium ions (i.e. loss of charge) continued in the electrolyte.

- 3) Lithium Trapping: sometimes lithium ions get irreversibly trapped in the silicon structure¹³³. Trapping is mainly due to slow ion release kinetics or to the formation of highly stable lithiated compounds with impurities of S, P and O present in the material. Even the presence of a high density of structural defects¹³⁴, especially at the surface boundaries of silicon particles is expected to contribute to this phenomenon.

- 4) Aggregation of silicon particles: the particles undergo agglomeration during cycling due to the welding effect caused by the pressure, as a result of the strong expansion of silicon particles upon the lithiation process. Bigger agglomerated particles means longer diffusion lengths for lithium ions, which lead to slower release kinetics.

Different strategies have been developed attempting to reduce the detrimental effect of large volume changes and electrolyte side reactions on cycle life, capacity fade and first cycle irreversible capacity values of silicon anodes such as the use of composite anodes^{135–137}, the control of silicon particles dimensions and morphology^{138–140}, the control of the voltage window¹²⁵ and the investigation of suitable binders to counteract the volume change.^{141,142}

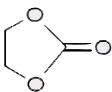
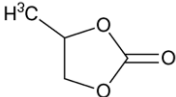
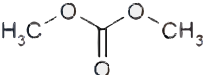
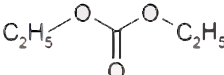
1.6 Electrolytes

Electrolytes¹⁴³ play the crucial role of guaranteeing the ionic conduction of the alkali metal ions from one electrode to the other during the battery cycling. Hence it is fundamental that the electrolyte possess a high ionic conductivity ($>10^{-3} \text{ Scm}^{-1}$). Liquids are usually preferred to solids mainly because of the superior conductivities and contact with the electrode at the interface at room temperature.

Additionally, due to the high operational voltage of Li-ion batteries (typically $>3 \text{ V}$ vs. Li^+/Li) water-based electrolytes have to be discarded in favour of more stable mixtures of organic carbonates and ethers.

Carbonates solvents are usually preferred to ethers due to their good cycling performance and the main representatives are shown in the table below.

Table 1.2 List of the principal solvents employed in Lithium Ion Batteries.

Name	Structure	Melting point (°C)	Boiling point (°C)	Relative permittivity ϵ_r
Ethylene Carbonate (EC)		40	248	89.6
Propylene Carbonate (PC)		-49	240	64.4
Dimethyl Carbonate (DMC)		4.6	91	3.1
Diethyl Carbonate (DEC)		-43	126	2.8

Propylene carbonate has been one of the first solvents employed in LIBs electrolytes although it was soon demonstrated that it determines the exfoliation of graphite electrodes being co-intercalated with lithium ions at potentials lower than 1 V vs Li^+/Li . This problem was solved employing a mixture of PC with EC that partially decomposes on the anode surface around 1.5 V to form a protective SEI layer. High concentrations of lithium salts¹⁷ are dissolved in the organic solvent mixtures to ensure the ionic conductivity across the electrolyte bulk, with LiPF_6 and LiClO_4 being the most commonly employed, although the use of the perchlorate has been progressively reduced because of its high instability and new salts such as the imide LiFSI ¹⁴⁴ have shown better stability to hydrolysis and better ionic conductivities than LiPF_6 .

As well a great deal of research has been devoted to investigate electrolyte additives able to form a more stable and fast lithium conducting SEI on the anode at low voltage values^{30,145} hence increasing the coulombic efficiency and the cycle life of the cell..

Due to the flammable nature of the solvents other kinds of electrolyte systems for LIBs have been recently investigated to achieve higher safety. In particular a great deal of

research has gone into the study of polymer electrolytes and ionic liquids. Both have the advantage of being more stable than liquid electrolytes over a wide range of temperatures and potentials although the conductivities achieved are so far too low to compete with their liquid counterparts.

1.7 Thesis Contents and Target

The achievement of high performance LIBs with improved specific and volumetric energy densities, requires a painstaking and thorough investigation of new materials that are capable to match the market demands.

The target of this work is the investigation and improvement of high performance materials for both anodes and cathodes that could be employed to make up a high energy density battery. To do so, three classes of high capacity materials were chosen and investigated: the lithium-rich nickel substituted layered oxides for the cathodes; the silicon nanoparticles and the hard carbons for the anodes. These materials, despite being affected by relatively large coulombic inefficiencies at the beginning of cycling, show larger reversible capacities (particularly Li-rich oxides and silicon) with respect to materials commonly employed in commercial cells such as graphite and LiCoO_2 . Once optimized, these materials would make up an appealing full cell able to deliver superior performance in terms of specific and volumetric energy density respect to the Li-ion cells currently available on the market. The higher energy densities could be achieved thanks to the large capacities displayed by the materials under study during cycling and the high operational potential of Li-rich oxides with respect to silicon and hard carbon (being energy density the product of the cell capacity and the potential difference between the electrodes).

To achieve the main goal a series of secondary targets are addressed in the thesis that is divided in two main thematic areas, cathodes and anodes:

For the cathodes part, the work is focused on the comprehension of the working mechanisms behind the electrochemical performance of the well-known family $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$ of layered transition metal oxides with two main chapters presented, whose aims are:

For the cathodes:

- 1- To prepare the $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ layered oxide and to fully characterise the unexplained charge compensation mechanisms using several spectroscopic and electrochemical techniques.
- 2- To investigate the curious effect of Ni substitution in $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$ trying to understand its role on the fine balance between the oxygen loss and the oxygen redox processes.

For the anodes:

- 1- To fabricate, characterise and improve the cycling stability and electrochemical performance of silicon-based anodes employing new conducting binders never used before for this material.
- 2- To reduce the impact of First cycle Irreversible Capacity in silicon and hard carbon anodes employing an innovative, fast and scalable pre-treatment of the anodes, studying the effect of the treatment on the electrodes' surface.

1.8 References

- 1 List of battery types - Wikipedia, https://en.wikipedia.org/wiki/List_of_battery_types, (accessed 15 December 2017).
- 2 T. Christen and M. W. Carlen, *J. Power Sources*, 2000, **91**, 210–216.
- 3 Hybrid vehicle, https://en.wikipedia.org/wiki/Hybrid_vehicle, (accessed 10 December 2017).
- 4 Electric vehicle, https://en.wikipedia.org/wiki/Electric_vehicle, (accessed 10 December 2017).
- 5 Model S | Tesla UK, https://www.tesla.com/en_GB/models, (accessed 21 December 2017).
- 6 Toyota Global Site | EV Electric Vehicle, http://www.toyota-global.com/innovation/environmental_technology/electric_vehicle/, (accessed 21 December 2017).
- 7 Twin Engine | Volvo Cars UK Ltd, <https://www.volvocars.com/uk/about/our-innovations/drive-e/twin-engine>, (accessed 21 December 2017).
- 8 K. Nagaura, T. Tozawa, *Prog. Batter. Sol. cells*, 1990, **9**, 209.
- 9 K. Ozawa, *Solid State Ionics*, 1994, **69**, 212–221.
- 10 J. C. Hunter, *J. Solid State Chem.*, 1981, **39**, 142–147.
- 11 J. C. Hunter, *U.S. Pat. US4246253 A*.
- 12 G. L. Holleck and J. R. Driscoll, *Electrochim. Acta*, 1977, **22**, 647–655.
- 13 D. W. Murphy and F. a Trumbore, *J. Electrochem. Soc.*, 1976, **123**, 960–964.
- 14 D. Fouchard and J. B. Taylor, *J. Power Sources*, 1987, **21**, 195–205.
- 15 K. Brandt and F. C. Laman, *J. Power Sources*, 1989, **25**, 265–276.
- 16 R. Marom, O. Haik, D. Aurbach and I. C. Halalay, *J. Electrochem. Soc.*, 2010, **157**, A972.
- 17 R. Younesi, G. M. Veith, P. Johansson, K. Edström and T. Vegge, *Energy Environ. Sci.*, 2015, **8**, 1905–1922.
- 18 R. A. Huggins, *Advanced batteries: Materials science aspects*, Springer US, Boston, MA, 2009.
- 19 M. S. Whittingham and R. R. Chianelli, *J. Chem. Educ.*, 1980, **57**, 569.
- 20 M. S. Whittingham, *Science (80-.)*, 1976, **192**, 1126–1127.
- 21 M. Armand and P. Touzain, *Mater. Sci. Eng.*, 1977, **31**, 319–329.
- 22 M. Lazzari, *J. Electrochem. Soc.*, 1980, **127**, 773.
- 23 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, 1980, **15**, 783–789.
- 24 B. Scrosati, *Electrochim. Acta*, 2000, **45**, 2461–2466.
- 25 R. Yazami and P. Touzain, *J. Power Sources*, 1983, **9**, 365–371.
- 26 T. Ohzuku, Y. Iwakoshi and K. Sawai, *J. Electrochem. Soc.*, 1993, **140**, 2490.
- 27 Y. Ein-Eli, B. Markovsky, D. Aurbach, Y. Carmeli, H. Yamin and S. Lusk, *Electrochim. Acta*, 1994, **39**, 2559–2569.

- 28 A. N. Dey and B. P. Sullivan, *J. Electrochem. Soc.*, 1970, **117**, 222.
- 29 R. Fong, S. Ulrich and J. . Dahn, *J. Electrochem. Soc.*, 1990, **137**, 2009.
- 30 S. S. Zhang, *J. Power Sources*, 2006, **162**, 1379–1394.
- 31 A. Yoshino, K. Sanekata and T. Nakajima, *US Pat. US4668595 A*, 1989, 1–9.
- 32 J. R. Dahn, R. Fong and M. J. Spoon, *Phys. Rev. B*, 1990, **42**, 6424–6432.
- 33 C. S. Johnson, N. Li, C. Lefief, J. T. Vaughey and M. M. Thackeray, *Chem. Mater.*, 2008, **20**, 6095–6106.
- 34 J. W. Fergus, *J. Power Sources*, 2010, 195, 939–954.
- 35 M. Thackeray, A. de Kock and W. I. F. David, *Mater. Res. Bull.*, 1993, **28**, 1041–1049.
- 36 M. M. Thackeray, A. de Kock, H. Rossouw and D. Liles, *J. Electrochem. Soc.*, 1992, **139**, 363.
- 37 H. Huang and P. G. Bruce, *J. Electrochem. Soc.*, 1994, **141**, L106.
- 38 H. Lourdes, J. Morales, L. Sanchez and J. Santos, *Solid State Ionics*, 1999, **118**, 179–185.
- 39 M. Okada, Y.-S. Lee and M. Yoshio, *J. Power Sources*, 2000, **96**, 196–200.
- 40 S. Patoux, L. Daniel, C. Bourbon, H. Lignier, C. Pagano, F. Le Cras, S. Jouanneau and S. Martinet, *J. Power Sources*, 2009, **189**, 344–352.
- 41 G. Q. Liu, L. Wen and Y. M. Liu, *J. Solid State Electrochem.*, 2010, 14, 2191–2202.
- 42 A. K. Padhi, *J. Electrochem. Soc.*, 1997, **144**, 1188.
- 43 J. Come, P.-L. Taberna, S. Hamelet, C. Masquelier and P. Simon, *J. Electrochem. Soc.*, 2011, **158**, A1090.
- 44 K.-F. Hsu, S.-Y. Tsay and B.-J. Hwang, *J. Mater. Chem.*, 2004, **14**, 2690–2695.
- 45 L. Wang, Y. Huang, R. Jiang and D. Jia, *Electrochim. Acta*, 2007, **52**, 6778–6783.
- 46 S.-L. Chou, J.-Z. Wang, M. Choucair, H.-K. Liu, J. a. Stride and S.-X. Dou, *Electrochem. commun.*, 2010, **12**, 303–306.
- 47 Y. Wang, Y. Wang, E. Hosono, K. Wang and H. Zhou, *Angew. Chemie - Int. Ed.*, 2008, **47**, 7461–7465.
- 48 S. Y. Chung, J. T. Bloking and Y. M. Chiang, *Nat. Mater.*, 2002, **1**, 123–128.
- 49 F. Zhou, M. Cococcioni, K. Kang and G. Ceder, *Electrochem. commun.*, 2004, **6**, 1144–1148.
- 50 C. A. J. Fisher, V. M. Hart Prieto and M. S. Islam, *Chem. Mater.*, 2008, **20**, 5907–5915.
- 51 M. M. Galceran, M. Casas-Cabanas, A. Guerfi, M. Armand, T. Rojo, K. Zaghib and A. Paolella, 2017.
- 52 A. Nytén, S. Kamali, L. Häggström, T. Gustafsson and J. O. Thomas, *J. Mater. Chem.*, 2006, **16**, 2266–2272.
- 53 A. Nytén, A. Abouimrane, M. Armand, T. Gustafsson and J. O. Thomas, *Electrochem. commun.*, 2005, **7**, 156–160.
- 54 R. Dominko, M. Bele, M. Gabersček, A. Meden, M. Remškar and J. Jamnik, *Electrochem. commun.*, 2006, **8**, 217–222.
- 55 T. Muraliganth, K. R. Stroukoff and A. Manthiram, *Chem. Mater.*, 2010, **22**, 5754–

5761.

- 56 S. I. Nishimura, S. Hayase, R. Kanno, M. Yashima, N. Nakayama and A. Yamada, *J. Am. Chem. Soc.*, 2008, **130**, 13212–13213.
- 57 M. S. Islam, R. Dominko, C. Masquelier, C. Sirisopanaporn, A. R. Armstrong and P. G. Bruce, *J. Mater. Chem.*, 2011, **21**, 9811.
- 58 C. Eames, A. R. Armstrong, P. G. Bruce and M. S. Islam, *Chem. Mater.*, 2012, **24**, 2155–2161.
- 59 R. Dominko, D. E. Conte, D. Hanzel, M. Gaberscek and J. Jamnik, *J. Power Sources*, 2008, **178**, 842–847.
- 60 R. Dominko, *J. Power Sources*, 2008, **184**, 462–468.
- 61 R. J. Gummow and Y. He, *J. Power Sources*, 2014, 253, 315–331.
- 62 a R. Armstrong, C. Lyness, P. M. Panchmatia, M. S. Islam and P. G. Bruce, *Nat. Mater.*, 2011, **10**, 223–9.
- 63 J. Billaud, C. Eames, N. Tapia-Ruiz, M. R. Roberts, A. J. Naylor, A. R. Armstrong, M. S. Islam and P. G. Bruce, *Adv. Energy Mater.*, 2017, **7**, 1601043.
- 64 T. Ohzuku and A. Ueda, *Solid State Ionics*, 1994, **69**, 201–211.
- 65 C. Fouassier, C. Delmas and P. Hagenmuller, *Mater. Res. Bull.*, 1975, **10**, 443–449.
- 66 P. He, H. Yu, D. Li and H. Zhou, *J. Mater. Chem.*, 2012, **22**, 3680.
- 67 E. Wu, P. Tepesch and G. Ceder, *Philos. Mag. B*, 1998, **77**, 1039–1047.
- 68 C. Delmas, C. Fouassier and P. Hagenmuller, *Phys. B+C*, 1980, **99**, 81–85.
- 69 M. M. Thackeray, *J. Electrochem. Soc.*, 1995, **142**, 2558.
- 70 J. R. Dahn, U. von Sacken, M. W. Juzkow and H. Aljanaby, *J. Electrochem. Soc.*, 1991, **138**, 2207–2211.
- 71 A. Rougier, *J. Electrochem. Soc.*, 1996, **143**, 1168.
- 72 A. R. Armstrong and P. G. Bruce, *Nature*, 1996, **381**, 499–500.
- 73 M. Tabuchi, K. Ado, H. Kobayashi, H. Kageyama, C. Masquelier, A. Kondo and R. Kanno, *J. Electrochem. Soc.*, 1998, **145**, L49–L52.
- 74 P. G. Bruce, A. R. Armstrong and R. L. Gitzendanner, *J. Mater. Chem.*, 1999, **9**, 193–198.
- 75 Y.-I. Jang, B. Huang, Y. Chiang and D. R. Sadoway, *Electrochem. Solid-State Lett.*, 1998, **1**, 13–16.
- 76 A. R. Armstrong, A. D. Robertson, R. Gitzendanner and P. G. Bruce, *J. Solid State Chem.*, 1999, **145**, 549–556.
- 77 I. . Davidson, R. . McMillan, H. Sleg, B. Luan, I. Kargina, J. . Murray and I. . Swainson, *J. Power Sources*, 1999, **81–82**, 406–411.
- 78 Y. Ding, P. Zhang, Z. Long, Y. Jiang and D. Gao, *J. Alloys Compd.*, 2008, **462**, 340–342.
- 79 S. Lee and S. S. Park, *J. Phys. Chem. C*, 2012, **116**, 6484–6489.
- 80 P. Gao, Y. Li, H. Liu, J. Pinto, X. Jiang and G. Yang, *J. Electrochem. Soc.*, 2012, **159**, A506.
- 81 K. M. Shaju and P. G. Bruce, *Adv. Mater.*, 2006, **18**, 2330–2334.

- 82 M. H. Rossouw, D. C. Liles and M. M. Thackeray, *J. Solid State Chem.*, 1993, **104**, 464–466.
- 83 M. M. Thackeray, S. H. Kang, C. S. Johnson, J. T. Vaughey and S. A. Hackney, *Electrochem. commun.*, 2006, **8**, 1531–1538.
- 84 Y. M. Todorov and K. Numata, in *Electrochimica Acta*, Pergamon, 2004, vol. 50, pp. 495–499.
- 85 Z. Lu, D. D. MacNeil and J. R. Dahn, *Electrochem. Solid-State Lett.*, 2001, **4**, A200.
- 86 T. Zhao, L. Li, S. Chen, R. Chen, X. Zhang, J. Lu, F. Wu and K. Amine, *J. Power Sources*, 2014, **245**, 898–907.
- 87 K. Luo, M. R. Roberts, R. Hao, N. Guerrini, D. M. Pickup, Y.-S. Liu, K. Edström, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *Nat. Chem.*, , DOI:10.1038/nchem.2471.
- 88 K. Luo, M. R. Roberts, N. Guerrini, N. Tapia-Ruiz, R. Hao, F. Massel, D. M. Pickup, S. Ramos, Y.-S. Liu, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *J. Am. Chem. Soc.*, 2016, **138**, 11211–11218.
- 89 M. Sathiya, G. Rousse, K. Ramesha, C. P. Laisa, H. Vezin, M. T. Sougrati, M. Doublet, D. Foix, D. Gonbeau, W. Walker, A. S. Prakash, M. Ben Hassine and L. Dupont, *Nat. Mater.*, 2013, **12**, 827–835.
- 90 H. Koga, L. Croguennec, M. Menetrier, K. Douhil, S. Belin, L. Bourgeois, E. Suard, F. Weill and C. Delmas, *J. Electrochem. Soc.*, 2013, **160**, A786–A792.
- 91 J. Rana, M. Stan, R. Kloepsch, J. Li, G. Schumacher, E. Welter, I. Zizak, J. Banhart and M. Winter, *Adv. Energy Mater.*, 2014, **4**, 1300998.
- 92 P. Yan, L. Xiao, J. Zheng, Y. Zhou, Y. He, X. Zu, S. X. Mao, J. Xiao, F. Gao, J. G. Zhang and C. M. Wang, *Chem. Mater.*, 2015, **27**, 975–982.
- 93 S.-H. Park, S.-H. Kang, I. Belharouak, Y. K. Sun and K. Amine, *J. Power Sources*, 2008, **177**, 177–183.
- 94 S.-H. Kang, S.-H. Park, C. S. Johnson and K. Amine, *J. Electrochem. Soc.*, 2007, **154**, A268.
- 95 K. Luo, M. R. Roberts, R. Hao, N. Guerrini, E. Liberti, C. S. Allen, A. I. Kirkland and P. G. Bruce, *Nano Lett.*, 2016, **16**, 7503–7508.
- 96 C. C. Wang, K. A. Jarvis, P. J. Ferreira and A. Manthiram, *Chem. Mater.*, 2013, **25**, 3267–3275.
- 97 W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang and J.-G. Zhang, *Energy Environ. Sci.*, 2014, **7**, 513–537.
- 98 H. Kim, G. Jeong, Y.-U. Kim, J.-H. Kim, C.-M. Park and H.-J. Sohn, *Chem. Soc. Rev.*, 2013, **42**, 9011.
- 99 D. Lv, Y. Shao, T. Lozano, W. D. Bennett, G. L. Graff, B. Polzin, J. Zhang, M. H. Engelhard, N. T. Saenz, W. A. Henderson, P. Bhattacharya, J. Liu and J. Xiao, *Adv. Energy Mater.*, 2015, **5**, 1400993.
- 100 J. B. Goodenough, *J. Solid State Electrochem.*, 2012, **16**, 2019–2029.
- 101 I. M. Aldous and L. J. Hardwick, *J. Phys. Chem. Lett.*, 2014, **5**, 3924–3930.
- 102 M. Herstedt, A. M. Andersson, H. Rensmo, H. Siegbahn and K. Edström, *Electrochim. Acta*, 2004, **49**, 4939–4947.
- 103 M. Nie, D. P. Abraham, Y. Chen, A. Bose and B. L. Lucht, *J. Phys. Chem. C*, 2013, **117**, 13403–13412.

- 104 Y. M. Lee, J. Y. Lee, H.-T. Shim, J. K. Lee and J.-K. Park, *J. Electrochem. Soc.*, 2007, **154**, A515.
- 105 A. Augustsson, M. Herstedt, J.-H. Guo, K. Edström, G. V. Zhuang, J. P. N. Ross, J.-E. Rubensson and J. Nordgren, *Phys. Chem. Chem. Phys.*, 2004, **6**, 4185–4189.
- 106 S. P. V. Nadimpalli, V. A. Sethuraman, S. Dalavi, B. Lucht, M. J. Chon, V. B. Shenoy and P. R. Guduru, *J. Power Sources*, 2012, **215**, 145–151.
- 107 C. Wang, A. J. Appleby and F. E. Little, *J. Electroanal. Chem.*, 2001, **497**, 33–46.
- 108 H. Zheng, K. Jiang, T. Abe and Z. Ogumi, *Carbon N. Y.*, 2006, **44**, 203–210.
- 109 M. Winter, J. O. Besenhard, M. E. Spahr and P. Novák, *Adv. Mater.*, 1998, **10**, 725–763.
- 110 K. Hong, L. Qie, R. Zeng, Z. Yi, W. Zhang, D. Wang, W. Yin, C. Wu, Q. Fan, W. Zhang and Y. Huang, *J. Mater. Chem. A*, 2014, **2**, 12733.
- 111 Y. Bai, Z. Wang, C. Wu, R. Xu, F. Wu, Y. Liu, H. Li, Y. Li, J. Lu and K. Amine, *ACS Appl. Mater. Interfaces*, 2015, **7**, 5598–5604.
- 112 E. Buiel and J. . Dahn, *Electrochim. Acta*, 1999, **45**, 121–130.
- 113 A. Ponrouch, A. R. Goñi and M. R. Palacín, *Electrochem. commun.*, 2013, **27**, 85–88.
- 114 E. Irisarri, A. Ponrouch and M. R. Palacin, *J. Electrochem. Soc.*, 2015, **162**, A2476–A2482.
- 115 T. Zheng, *J. Electrochem. Soc.*, 1995, **142**, 2581.
- 116 J. Zhao, L. Zhao, K. Chihara, S. Okada, J. Yamaki, S. Matsumoto, S. Kuze and K. Nakane, *J. Power Sources*, 2013, **244**, 752–757.
- 117 L. Shen, X. Zhang, E. Uchaker, C. Yuan and G. Cao, *Adv. Energy Mater.*, 2012, **2**, 691–698.
- 118 W. M. Zhang, X. L. Wu, J. S. Hu, Y. G. Guo and L. J. Wan, *Adv. Funct. Mater.*, 2008, **18**, 3941–3946.
- 119 L. Zhou, H. Bin Wu, Z. Wang and X. W. Lou, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4853–4857.
- 120 F. Chen, J. Wang, L. Huang, H. Bao and Y. Shi, *Chem. Mater.*, 2016, **28**, 608–617.
- 121 I. A. Leonidov, O. N. Leonidova, L. A. Perelyaeva, R. F. Samigullina, S. A. Kovyazina and M. V. Patrakeev, *Phys. Solid State*, 2003, **45**, 2183–2188.
- 122 K. M. Colbow, J. R. Dahn and R. R. Haering, *J. Power Sources*, 1989, **26**, 397–402.
- 123 W.-J. Zhang, *J. Power Sources*, 2011, **196**, 13–24.
- 124 A. Mauger and C. Julien, *Nanomaterials*, 2015, **5**, 2279–2301.
- 125 M. N. Obrovac and L. Christensen, *Electrochem. Solid-State Lett.*, 2004, **7**, A93.
- 126 C. J. Wen and R. A. Huggins, *J. Solid State Chem.*, 1981, **37**, 271–278.
- 127 M. T. McDowell, S. W. Lee, W. D. Nix and Y. Cui, *Adv. Mater.*, 2013, **25**, 4966–4985.
- 128 J. Saint, M. Morcrette, D. Larcher, L. Laffont, S. Beattie, J.-P. Pèrès, D. Talaga, M. Couzi and J.-M. Tarascon, *Adv. Funct. Mater.*, 2007, **17**, 1765–1774.
- 129 J. W. Kim, J. H. Ryu, K. T. Lee and S. M. Oh, *J. Power Sources*, 2005, **147**, 227–

233.

- 130 H. Wu and Y. Cui, *Nano Today*, 2012, **7**, 414–429.
- 131 D. Mazouzi, N. Delpuech, Y. Oumellal, M. Gauthier, M. Cerbelaud, J. Gaubicher, N. Dupré, P. Moreau, D. Guyomard, L. Roué and B. Lestriez, *J. Power Sources*, 2012, **220**, 180–184.
- 132 S. P. V. Nadimpalli, V. a. Sethuraman, S. Dalavi, B. Lucht, M. J. Chon, V. B. Shenoy and P. R. Guduru, *J. Power Sources*, 2012, **215**, 145–151.
- 133 H. Li, *Solid State Ionics*, 2000, **135**, 181–191.
- 134 H. Li, *Solid State Ionics*, 2002, **148**, 247–258.
- 135 Y. Zhang, X. G. Zhang, H. L. Zhang, Z. G. Zhao, F. Li, C. Liu and H. M. Cheng, *Electrochim. Acta*, 2006, **51**, 4994–5000.
- 136 Z. S. Wen, J. Yang, B. F. Wang, K. Wang and Y. Liu, *Electrochem. commun.*, 2003, **5**, 165–168.
- 137 Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano and Y. Takeda, *Electrochem. Solid-State Lett.*, 2004, **7**, A369.
- 138 X. H. Liu, L. Zhong, S. Huang, S. X. Mao, T. Zhu and J. Y. Huang, *ACS Nano*, 2012, **6**, 1522–1531.
- 139 I. Hong, B. Scrosati and F. Croce, *Solid State Ionics*, 2013, **232**, 24–28.
- 140 H. Kim, B. Han, J. Choo and J. Cho, *Angew. Chem. Int. Ed. Engl.*, 2008, **47**, 10151–4.
- 141 D. M. Piper, T. A. Yersak and S.-H. Lee, *J. Electrochem. Soc.*, 2012, **160**, A77–A81.
- 142 Y. An, B. C. Wood, J. Ye, Y.-M. Chiang, Y. M. Wang, M. Tang and H. Jiang, *Phys. Chem. Chem. Phys.*, 2015, **17**, 17718–17728.
- 143 D. Aurbach, Y. Talyosef, B. Markovsky, E. Markevich, E. Zinigrad, L. Asraf, J. S. Gnanaraj and H. J. Kim, in *Electrochimica Acta*, 2004, vol. 50, pp. 247–254.
- 144 H. B. Han, S. S. Zhou, D. J. Zhang, S. W. Feng, L. F. Li, K. Liu, W. F. Feng, J. Nie, H. Li, X. J. Huang, M. Armand and Z. Bin Zhou, *J. Power Sources*, 2011, **196**, 3623–3632.
- 145 S. Dalavi, P. Guduru and B. L. Lucht, *J. Electrochem. Soc.*, 2012, **159**, A642.

2 Characterisation Techniques

2.1 Powder X-ray Diffraction

Since the discovery of X-rays in 1895 by the German physicist Wilhelm Rontgen, this portion of the electromagnetic spectrum (wavelength $\lambda = 10^{-12} - 10^{-9}$ m) has been employed in a large number of scientific fields ranging from medicine to physics. One of the most common techniques used for the, qualitative and quantitative, structural and morphological characterisation of crystalline materials is X-ray diffraction¹. The technique is based on the ability of crystalline atomic and molecular structures to act as three-dimensional diffraction gratings for X-rays. In fact, the incident X-ray beam is scattered by the electrons of the atoms it interacts with once hitting the sample. Depending on the ratio between the inter-planar spacing of the analysed crystalline material and the wavelength of the incident X-ray, the scattered intensity diffracted by each plane can interfere either constructively or destructively (Figure 2.1). The conditions required for constructive interference were described first by Max von Laue and subsequently reformulated in a simpler way by Laurence Bragg in what is commonly known as Bragg's Law²:

$$n\lambda = 2d\sin\theta \quad (2.1)$$

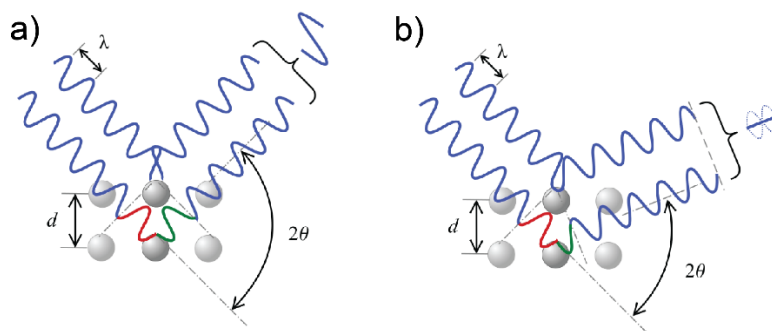


Figure 2.1 Diffracted X-rays interference; a) constructive, b) destructive. Image reproduced from Wikipedia².

Where n is a positive integer, λ is the wavelength of the incident beam, d is the interplanar spacing and θ is the incident angle. It is important to underline that λ and d must be of the same order of magnitude (10^{-10} m) to attain the phenomenon of diffraction. Usually X-ray diffraction experiments are carried out employing diffractometers in which the X-rays are generated striking a water-cooled metal target (usually Cu, Fe, Mo or Ag) with a beam of electrons, originating from a tungsten filament heated at high temperature via Joule effect, that have been accelerated by a high potential difference (30-40 kV). After being hit, the target emits a continuous spectrum of X-rays called 'white X-radiation' or Bremsstrahlung as well as two higher intensity emission lines called K_α and K_β (Figure 2.2). These two lines are the result of electrons removal from the innermost shell K ($n = 1$) of the metallic target by the high energy electrons impinging on it and subsequent relaxation of electrons from the higher shells to fill the electron hole. K_α emission occurs when electrons relax from shell L ($n = 2$) and K_β emission from electrons which relax from shell M ($n = 3$). Both K_α and K_β have a characteristic wavelength depending on the element that is employed as the target (Cu $K_\alpha = 154.18$ nm and $K_\beta = 13.923$ nm). X-ray diffraction experiments can be carried out both on single crystals and powders. In the case of single crystals, the result obtained will be a diffraction pattern composed by a number of discrete spots, each one relative to the position of the crystal planes with respect to the incident beam.

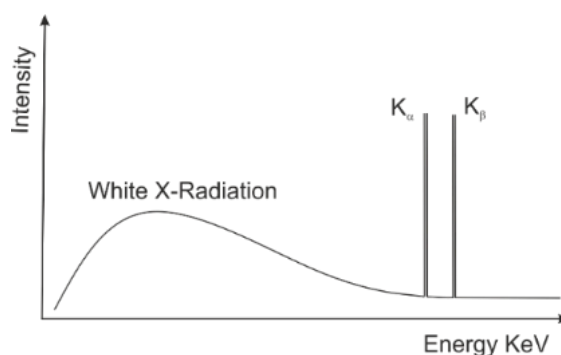


Figure 2.2 X-ray emission spectrum.

From the spots' relative positions and intensities, it is possible to determine the unit cell dimensions, the symmetry of the space group and the exact atomic positions in the crystal. The diffraction patterns obtained from crystalline powders, instead, appear completely different from that of single crystals. The powders are composed by a very large number of small crystals (known as 'crystallites') with randomly distributed orientations. Diffraction occurs from the planes in the crystallites which are correctly oriented to satisfy Bragg's conditions. Because there are many randomly oriented crystallites in a powder sample, the many discrete scattered X-ray beams are smeared on the surface of a cone protruding from the sample at the angle θ from the incident beam, which satisfies Bragg's Law (Figure 2.3). When projected onto the inside of a concentric sphere to the sample position (also known as the Ewald's sphere), the cross section of these cones are rings, rather than spots as seen for single crystals. X-ray detectors sample the Ewald's sphere, correlating the intensity (as peaks) of the diffracted beam to the angle with respect to the incident beam (2θ). Analysis of X-ray powder diffraction patterns has been extensively employed in this work to determine the structure and phase purity of synthesised materials. All measurements were performed in reflection mode using a Rigaku Smart-Lab X-ray Diffractometer equipped with a 3 kW rotating anode Cu, and a Ge 220 monochromator to select K_{α} radiation.

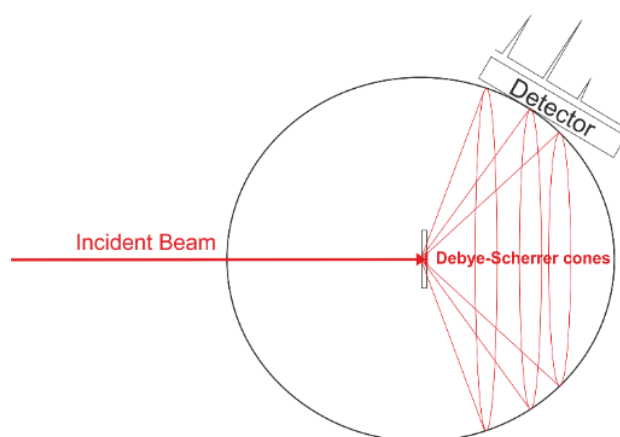


Figure 2.3 Cone shaped diffracted X-Rays in powder analysis

2.2 Rietveld Refinement

The diffraction data collected in our laboratory were analysed with the Rietveld refinement³ method to determine the crystal structure of the samples of interest. The refinement procedure is based on a least squares method to find the best fit between the experimentally collected data and a powder diffraction model that is built using the instrumental parameters and the sample structural parameters. This method has the advantage of overcoming the problem of reflections overlap in a powder diffraction pattern by considering the intensity of each experimental point as a singularly observed intensity⁴.

In a refinement process is either the definition of a model structure to fit the experimental data or the extraction of the diffraction peaks intensities to find out the symmetry through the Le Bail method⁵. Subsequently the first parameters to be refined are background and scale of the reflections intensities to get a reasonable structural starting point that is then followed by the refinement of parameters such as the peaks shapes, the unit cell dimensions and the coordinates of the atoms contained in it. A great deal of information about the studied crystal structure as well as the quality of the refinement are mostly determined by three parameters:

- The peaks positions (angle): gives information about the symmetry of the crystal and the dimensions of the unit cell (e.g. a shift towards a higher diffraction angle for a peak indicates a contraction in the distances between the planes originating the peak).
- The peaks intensities: reflect the relative strength of the diffraction and are proportional to several factors (form factor, displacement factor, multiplicity, Lorentz factor)¹ that give information about the atomic number of the species diffracting the X-rays, the sites occupied in the unit cell and the average atomic displacement due to the lattice vibrations. The peaks broadening: mostly related

to the crystallinity of the studied material (e.g. smaller crystal size = broader peaks) and to the resolution of the diffractometer employed in the analysis.

Another important parameter is also the Debye-Waller factor (B_{iso}) that describes the average displacement from the lattice point that an atom is supposed to occupy, accounting for the thermal vibrations of the lattice.

The quality of a refinement can be evaluated through mainly two factors:

- The residual weighted factor R_{wp} , defined as

$$R_{wp} = \left\{ \frac{\sum_i w_i (y_{i(obs)} - y_{i(calc)})^2}{\sum_i w_i y_{i(obs)}^2} \right\}, \text{ with } w_i = \frac{1}{y_{i(obs)}} \quad (2.2)$$

Where $y_{i(calc)}$ and $y_{i(obs)}$ are the calculated intensity and observed intensity respectively.

- The expected R factor, defined as:

$$R_{exp} = \left\{ \frac{(N-P+C)}{\sum_i w_i y_{i(obs)}^2} \right\}^{\frac{1}{2}} \quad (2.3)$$

Where N is the number of collected points, P the number of refined parameters and C the number of constraints employed.

R_{wp} provides information about the quality of the peaks refinement whilst R_{exp} on the quality of the collected data. The ratio between these two factors leads to the quality of the overall fitting defined as χ^2 that should approach the value of 1

$$\chi^2 = \left(\frac{R_{wp}}{R_{exp}} \right)^2. \quad (2.4)$$

2.3 Scanning Electron Microscopy and Energy Dispersive Spectroscopy

Scanning Electron Microscopy (SEM) is an imaging technique commonly used to investigate the morphology, particle dimension and topography of the analysed samples. In this technique, an electron beam is generated via a thermo-ionic process in which a

high current is passed through a filament (cathode) typically made of tungsten (W) or lanthanum hexaboride (LaB_6). The emitted electrons are focused by magnetic condenser lenses into a beam with a circular section of 1-5 nm diameter. The generated beam is subsequently moved in a raster-like fashion with the help of a pair of deflector plates in order to scan the analysed sample. Once the primary beam interacts with the sample the electrons lose their energy through repeated scattering and absorption processes within a teardrop-shaped volume denominated 'interaction volume' (Figure 2.4). The dimensions of the interaction volume can range from a few hundred nanometres to micrometres depending on the nature of the sample and the beam energy. The beam-sample interaction results in the generation of several detectable signals such as: high energy electrons by elastic scattering, secondary electrons by inelastic scattering,

Auger electrons and electromagnetic radiation. In the most common detection mode (secondary electron mode) the secondary electrons, generated by inelastic scattering, are collected to produce a detailed two-dimensional image of the sample surface.

Also, the more energetic back scattered electrons, generated by elastic scattering and emerging from a deeper region of the interaction volume, can be collected in order to get information about the bulk of the sample.

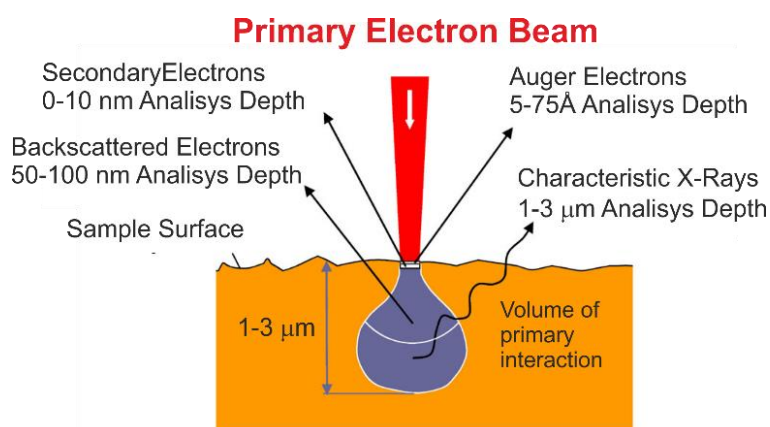


Figure 2.4 Interaction volume schematic. The respective depth of origin of the different detectable signals are indicated with respectively straight arrows for the electrons and undulated arrows for the electromagnetic radiation.

The electromagnetic radiation (X-rays) produced during the beam scan of the sample can provide useful information about the chemical composition of the analysed material. The X-rays result from the ejection of core level electrons in the sample by the primary electron beam which then allows higher energy electrons to drop down in the emptied levels via a radiative process. The energies of the emitted photons are specific to the constituent elements and the collection and discrimination of these energies is known as Energy Dispersive Spectroscopy (EDS). Non-conductive materials need to be coated with an ultrathin layer of gold or graphite before the SEM analysis in order to avoid build-up of charge during the sample scan. Conductive samples do not require any special preparation.

2.4 Magic Angle Spinning-Nuclear Magnetic Resonance (MAS-NMR)

MAS-NMR is a powerful solid-state NMR technique that is employed in order to study the chemical environments and structure that surround the chemical species of interest.

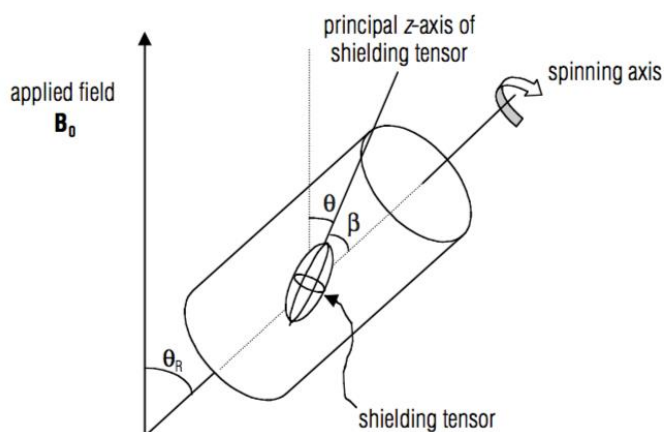


Figure 2.5 The magic-angle spinning experiment. The sample is spun rapidly in a cylindrical rotor about an axis inclined at $\theta_R = 54.74^\circ$ with respect to the external magnetic field (B_0). The anisotropy tensor is represented by an ellipsoid⁶.

In the more established liquid NMR technique, anisotropic interactions between the magnetic moments (spin) of the nuclei are averaged by the Brownian motions of the molecules in solution giving rise to very sharp peaks in the NMR spectra. In solid-state NMR, the nuclei are fixed inside a rigid lattice and the anisotropic interactions are not averaged, producing much broad peaks in the spectra which can be difficult to interpret.

There are many anisotropic interactions happening between the nuclei of interest and other nuclei in vicinity (dipolar interaction, paramagnetic interaction) or between the nuclei and the fields exerting on them (chemical shielding, quadrupolar interactions). To achieve a better resolved spectrum, it is fundamental to suppress anisotropy. Magic angle spinning (MAS) is by far the most common technique to obtain high resolution spectra by (partially) removing anisotropy. MAS is implemented by employing a fast spinning of the sample at an angle (so called magic angle $\theta_R = 54.74^\circ$) with respect to the external magnetic field (Figure 2.5). The magic angle is determined based on the fact that the anisotropic part of any interaction is modulated by the term of $3\cos^2\theta - 1$, where θ is the angle between external field (B_0) and the principle z-axis of the anisotropic tensor of every crystal in the sample. This time-averaged term can be further expanded into

$$3\cos^2\theta - 1 = \frac{1}{2}(3\cos^2\theta_R - 1)(3\cos^2\beta - 1) \quad (2.5)$$

where all the angles are defined in Figure 2.5. It is clear that if the controllable term of $(3\cos^2\theta_R - 1)$ is set to zero, i.e. $\theta_R = 54.74^\circ$, the anisotropy reduces to zero. In theory, with infinite MAS rate or a rate about 4 times greater than the anisotropy (measured in Hz), the spectrum should show no line broadening as in the case of liquid-state NMR. However, for technical difficulties, slower spinning is common, which produces a set of spinning sidebands⁶.

2.5 Gas Pycnometry

Pycnometry⁷ is a simple but reliable technique that allows for an accurate evaluation of the density (or more precisely the occupied volume) of a material. It is particularly useful in order to evaluate the densities of polycrystalline powders for which attaining large single crystals is challenging. The working principle of pycnometry is based on the utilisation of a fluid (in gas pycnometry usually helium), which is able to fill even the smallest pores present in the powder sample contained in a vessel of known volume.

During the measurement, helium is first pressurized at a known pressure (P_1) in a pre-chamber of known volume (V_1), and then allowed to expand into the sample chamber (the 'empty' volume of which is also known) until the equilibrium pressure between the chambers is reached.

Knowing the initial volumes of the chambers and the initial and equilibrium pressures, it is then possible to calculate the actual volume occupied by the powder, using Boyle's law, Equation (2.6).

$$P_1 V_1 = P_2 V_2 \quad (2.6)$$

Dividing the weight of the sample by the extracted volume yields the sample true density.

2.6 BET Surface Area

The accurate evaluation of the accessible surface area within a solid sample is of fundamental importance to understand the chemical and physical properties of a given material. In the field of batteries, large differences in surface area can yield dramatically different electrochemical performance (e.g. the larger the surface area of a graphitic carbon used as anode, the bigger the contact with the electrolyte that results in a larger first irreversible capacity due to the formation of the SEI upon discharge). The best way to measure the specific surface of finely divided and porous solids is through the Brunauer Emmett Teller or BET method. The BET model is based on the Langmuir model⁷ of a

monolayer gas physisorption on a homogeneous surface and it expands the model to multiple adsorbed layers. The gas of choice is usually nitrogen thanks to its small size and the relatively low price, but other gaseous species such as O₂, CO₂ and Kr can also be employed. The BET theory is based on the following equation that defines a curve known as 'isotherm':

$$\frac{1}{V\left[\frac{P_0}{P}-1\right]} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \left(\frac{P}{P_0}\right) \quad (2.7)$$

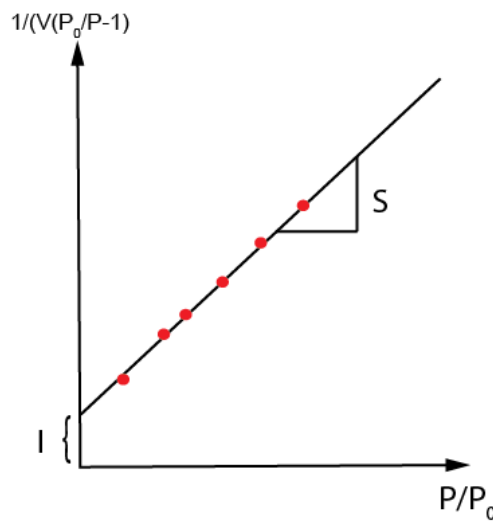


Figure 2.6 Example of a typical BET plot

where P is the equilibrium pressure of nitrogen, P_0 is the saturation pressure of nitrogen at the adsorption temperature, V is the volume of adsorbed nitrogen on the solid, C is the BET constant and V_m is the quantity of adsorbed nitrogen via a monolayer mechanism.

The measurement is operated through repeated cycles in which nitrogen is dosed inside a tube that is plunged into liquid nitrogen, where a known quantity of sample has been placed. Thanks to extremely sensitive pressure sensors V can be measured and the adsorption isotherm can be plotted as a straight line (BET plot, Figure 2.6) in which $\frac{1}{V\left[\frac{P_0}{P}-1\right]}$

is on the y-axis and P/P_0 on the x-axis. The intercept (I) and slope (S) of the BET plot can

be used to evaluate the BET constant C and the adsorbed monolayer volume V_m with the following expressions:

$$V_m = \frac{1}{S+1} \quad (2.8)$$

$$C = 1 + \frac{S}{I} \quad (2.9)$$

Once V_m is known, it is possible to evaluate the surface covered by the monolayer thanks to the following expression,

$$S_{\text{BET}} = \frac{V_m N_A \phi}{V m_s} \quad (2.10)$$

Where N_A is the Avogadro number, ϕ is the adsorption cross section of the adsorbate (the gas), V is the molar volume of the gas and m_s is mass in grams of the sample.

The instrument employed in this work to get BET surface area measurements was a Micromeritics 3Flex, and the adsorbed gas was nitrogen.

2.7 Resorcinol-Formaldehyde Gel Synthesis

The polycondensation of resorcinol and formaldehyde⁸, used in this work to synthesise all of the studied cathode materials, is an easy synthetic route to obtain various metal oxides at relatively low temperatures compared to the more traditional solid-state syntheses with the additional advantage of obtaining a more intimate mixture of the precursor species. In this procedure, the gel formed by resorcinol and formaldehyde acts as a “scaffold” to host the metal ions composing the final transition metal oxide. Under alkaline conditions formaldehyde reacts with resorcinol to give polycondensation compounds that can further react to form a crosslinked network (Figure 2.7). If an aqueous solution containing stoichiometric ratios of the TM-ions composing the final product is added to the resorcinol-formaldehyde mixture, the metal ions end up homogenously dispersed in the three-dimensional network once the RF gel is formed.

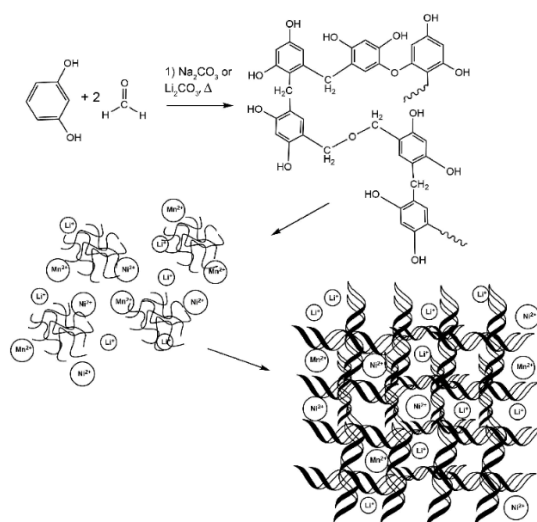


Figure 2.7 Polycondensation process leading to the formation of the resorcinol-formaldehyde gel.

The organic RF “scaffold” is subsequently removed through several heating steps in air or controlled atmosphere of oxygen allowing the formation of the desired transition metal oxide.

2.8 Electrochemical Characterisation

2.8.1 Basic Concepts

An electrochemical cell is a device able to convert the chemical energy involved in a chemical reaction into electricity (Galvanic cell) or vice versa to facilitate a chemical reaction through the use of external electrical energy (electrolytic cell)⁹. In an electrochemical cell, the energy-providing process is a redox reaction occurring at the electrode/electrolyte interfaces. During this process, the chemical energy of the reaction (Gibb’s free energy), is converted into electrical energy (a voltage difference) and vice versa.

Faraday’s first law (2.11) quantifies the amount of electrical charge that is transferred during the generic redox reaction $\text{Ox}^{z+} + ze^- \rightleftharpoons \text{Red}$:

$$Q = zF \frac{m}{M} \quad (2.11)$$

Where Q is the transferred charge, z is the number of electrons' equivalents, m is the equivalent mass, M is the molar weight of the reacting material and F is the Faraday's constant 96485 Cmol^{-1} , i.e. the electrical charge per mole of electrons.

The equation above can be rearranged as:

$$m = \frac{QM}{zF} \quad (2.12)$$

To minimize the equivalent weight m required to transfer the amount of charge Q during the reaction, a low molar weight and a high equivalent number z are desirable features for a good electrode material.

Each electrode material performance can be characterised through the quantification of important properties such as its specific capacity, energy density and specific energy.

The specific capacity (Q_{sp}) is defined as the amount of current (I) passed per unit mass (m) during the total time (t) of charge or discharge of the electrode,

$$Q_{sp} = I \frac{t}{m} \quad (2.13)$$

Q_{sp} is conventionally expressed in mAhg^{-1} (gravimetric specific capacity) or in mAhcm^{-3} (volumetric specific capacity). It is of paramount importance to maximise both the gravimetric and volumetric specific capacities of the electrode materials in order to achieve higher specific energy and energy density.

The energy density (W_{dens}) and the specific energy (W_e) have very similar formulations and are defined respectively as:

$$W_{dens} = \frac{\Delta G}{\sum_i n_i V_i} \quad (2.14)$$

and

$$W_e = \frac{\Delta G}{\sum_i n_i M_i} \quad (2.15)$$

Where ΔG is the Gibbs free energy associated to the electrochemical reaction, n_i is the number of moles of reactant i , M_i and V_i are its molar weight and molar volume. The

dimensions of the specific energy and energy density are respectively Whkg^{-1} and Whdm^{-3} .

³. Moreover, W_e and W_{dens} are related to each other through the molar density ρ_i ,

$$W_{\text{dens}} = W_e \sum_i \rho_i \quad (2.16)$$

The Specific Energy can also be expressed as,

$$W_e = Q_{\text{sp}} \Delta E \quad (2.17)$$

where ΔE is the average difference of potential occurring between the anode and cathode during the cell discharge (i.e. spontaneous electrochemical reaction). From (2.17), it is clear that an electrode material should possess a high specific capacity and the electrochemical reaction of charge/discharge should take place at high potential to attain a high specific energy.

2.8.2 Rate of Charge/Discharge and Kinetics

The rate at which a battery can be charged or discharged is a very important parameter in order to decide whether a certain type of battery is suitable for certain applications. For example, the battery employed in a portable electronic device such as a laptop should ideally be charged in the shortest time possible to allow the owner of the device not to wait for long before being able to use it.

In a lithium ion system, the rate at which a battery can be charged/discharged is governed by the law of electroneutrality. Hence the rate at which the lithium ions diffuse in the material and are intercalated/de-intercalated from it must be the same to the rate at which the electrons move through the external circuit connecting the cell electrodes. The rate limiting step in the majority of the intercalation/de-intercalation processes is the diffusion of lithium ions in the electrodes, which means that a high ionic conductivity is an essential feature to seek in high rate batteries. Several factors such as the operating temperature of the battery, the concentration of the ionic conducting salt in the electrolyte and the impedance due to the different components of the cell, can greatly impact the

kinetics of the electrons and ions transport hence influencing the electrochemical performance under different current regimes⁹.

Often the observed voltage profiles and capacities of an electrode deviate from what would be expected under thermodynamic equilibrium conditions due to kinetic limitations. For example, there might not be sufficient time to reach the expected compositional changes during the cell cycling because of the too high current rates employed to cycle the material under study.

The charge/discharge rate can be measured either as the charge quantity transferred per unit mass (mA g^{-1}) or can be expressed in terms of the rate to which the battery is charged/discharged relative to its maximum capacity (C-rate). The C-rate is inversely proportional to the number of hours necessary to fully charge/discharge the considered battery (rate of 2C = the cell is cycled with a current density able to charge or discharge the cell in $\frac{1}{2}$ hours).

2.8.3 Cyclability

For an electrode material to find practical application it is of paramount importance to be able to cycle with a capacity retention higher than 80% of the first cycle specific capacity for many hundreds of cycles¹⁰. In practice, the capacity tends to fade during the battery cycling due to several factors such as the electrolyte decomposition on the electrode surface and loss of contact between the electrodes particles. These phenomena limit the ionic mobility as well as the material participating in the chemical reaction, respectively, leading to progressive capacity fade. Cyclability is the measure of capacity retention against cycle numbers, which involves many major factors including the electrochemical reversibility of the redox reactions and the mechanical sustainability under strain cycle within the electrode materials, where intercalation/de-intercalation of lithium ions happens during repeated charging and discharging. It can be easily visualised in graphs where the specific capacity is plotted as function of the cycle number. In these plots both the total

charge and discharge specific capacity per each cycle are usually reported and they give a simple and effective tool to compare the performance of different electrode materials cycled in similar conditions. It is important to remember that the cycling rate can greatly affect the material performance, hence the rate at which the electrode is cycled must be always indicated.

2.8.4 Coin-cell Assembly

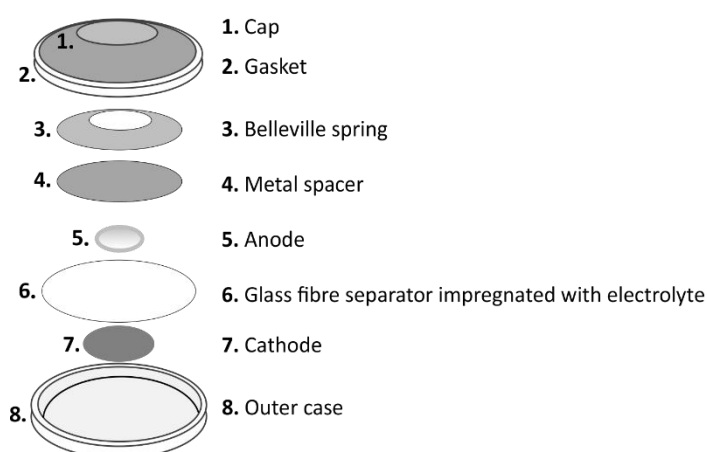


Figure 2.8 Exploded view of a coin-cell

Both the anode and cathode materials presented in this work have been thoroughly investigated through galvanostatic cycling. In order to do so, the electrodes were assembled into coin-cells with a manufacturer size of CR2325 (Figure 2.8), purchased from the National Research Council of Canada, under an inert argon atmosphere inside a glove box (MBraun LABmaster sp, O_2 and $H_2O < 0.1$ ppm). A lithium metal disc ($\varnothing = 18$ mm, 0.1 mm thick) was used as counter electrode with two glass fibre discs ($\varnothing = 22$ mm, Whatman GF-D) as separator, soaked with 0.2 mL of electrolyte.

2.8.5 Galvanostatic Cycling

The galvanostatic cycling (also known as chronopotentiometry) is a fundamental electrochemical technique employed to investigate the properties and electrochemical performance of a studied electrode material. The technique requires the use of an

electrochemical cell in which the working electrode (cathode) is composed of the material under study. During the measurement, a constant current is passed through the cell and the behaviour of the potential is registered. While the working electrode is de-lithiated (i.e. oxidised) the current sign is defined positive by convention whereas it is defined negative while the working electrode is lithiated (i.e. reduced). The sign of the current is inverted when a prefixed potential value is hit at high and low potential values (higher and lower cut-off values, respectively). The potential window in which the studied material is cycled needs to be large enough to include the potential at which the redox process of lithium insertion and removal takes place but not the potential at which detrimental side reactions of the electrolyte oxidation or reaction take place.

Ideally the measured curves of charge and discharge should be perfectly identical but this is never the case in practice. This happens due to different factors including: 1) the irreversibility of the redox reaction in both electrodes to a certain degree, 2) electrochemical polarisation due to the intrinsic impedance within different cell components and at their interfaces/interphases.

The galvanostatic measurement can be a very powerful tool to better understand the nature of the electrochemical reaction of insertion and extraction of lithium ions in/from the electrode material. In this regard, the Gibb's phase rule is helpful to explain why different type of electrode reactions give different curves.

$$f = C - P + 2 \quad (2.18)$$

Where f is the number of degrees of freedom, C is number the independent components and P the number of different phases in the considered system. In many cases the studied electrodes will be cycled at constant temperature and pressure (hence (2.18) is simplified to $f = C - P$). Considering a binary system with a lithiated and de-lithiated phase ($C = 2$ and $P = 2$), follows that $f = 0$. In other words, for a binary system where the two phases are well defined and separated by an interphase, there are no degrees of freedom, hence all the intensive variables, potential included, will be fixed (the

galvanostatic curve will show a plateau). Otherwise, when there is no clear interphase between the electrode lithiated and de-lithiated phase, it results that $P = 1$, $C = 2$ and $f = 1$ (the galvanostatic curve will appear sloping). From the above considerations, it is reasonable to conclude that a plateau region in a galvanostatic curve may originate from a two-phase lithium insertion/extraction process, whereas a sloping trend stems from a single-phase reaction.

2.8.6 Differential Capacity Plots

These kinds of plots can provide a useful tool to monitor and identify the redox reactions taking place in an active material during cycling. The change in capacity extracted/inserted from/into the studied material (known as differential capacity) is plotted versus the voltage at which this change occurs (dQ/dV vs. V , Figure 2.9). Several peaks usually appear in a plot. The position of each peak is characteristic of a specific process (e.g. change in oxidation state of a transition metal in the material), hence, by knowing the material composition, it is possible to speculate which redox reaction is at the origin of each peak in the plot. The peaks with positive value of differential capacity correspond to processes taking place during the de-lithiation, whereas the ones with negative value correspond to the processes during the lithiation.

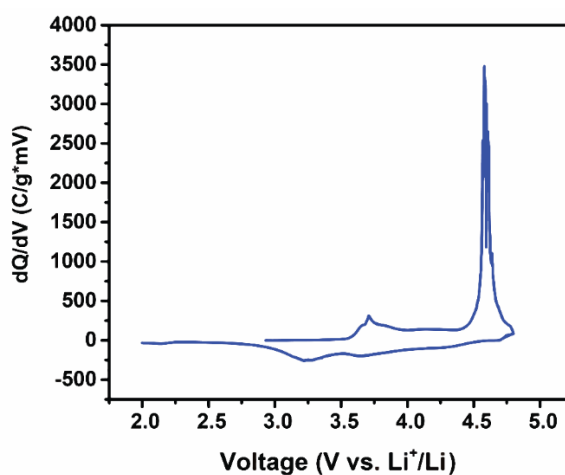


Figure 2.9 Differential capacity plot over the first cycle for $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$.

Ideally the positive and negative peaks should be identical and appear at the same voltage. Differences in the peaks shape and positions between lithiation and de-lithiation might be related to differences between the electrochemical processes of oxidation and reduction or be due to irreversibility problems affecting the material during the galvanostatic cycling.

2.8.7 Operando Electrochemical Mass Spectrometry (OEMS)

OEMS is a very useful technique that allows the detection of gaseous species evolved by the cell components during the electrochemical cycling. The technique is based on the use of a mass spectrometer coupled with an electrochemical cell. During galvanostatic cycling of the cell, a continuous flow of carrier gas, usually argon, is passed inside the cell and over the electrodes surface stripping the gaseous species evolved during the charge/discharge of the studied materials. Through an air-tight stainless-steel pipeline, the gas flow is injected into the ionisation chamber of the mass spectrometer, where it gets ionised by high energy electrons (70 eV). At this point the ionised gas mixture is separated in its different chemical components according to the mass/charge ratio (m/z) of each chemical species.

In this work, OEMS was carried out on the studied cathode materials employing a dedicated cell in *operando* setup, specifically built to carry out this kind of experiment (Figure 1.10). A PTFE based pellet (15-20 mg) of the materials of interest containing (weight percentages) 80% active material, 10% carbon Super P and 10% PTFE, was prepared and mounted on a stainless-steel mesh as working electrode. A circular lithium metal chip was employed as counter electrode and two glass fibre separators, soaked in 200 μL of electrolyte (1M LiPF_6 in propylene carbonate) were positioned in between the electrodes. A flow rate of 0.7 $\text{mL}\cdot\text{min}^{-1}$ of Ar was flowed through the cell during the galvanostatic cycling at a current rate of 15 $\text{mA}\cdot\text{g}^{-1}$.

It is important to underline that while OEMS has the great advantage of allowing an accurate and continuous monitoring of the gaseous species released by the cell during cycling, a compromise between sensitivity and response time had to be found in order to get good data. A high flow rate of carrier gas resulted in quick response while diluting the concentration of the gas developed by the cell hence pushing the sensitivity and detection limit of the mass spectrometer. A low flow rate of carrier gas delayed the instrument response excessively and exposed the cell to leakage risks. Moreover, a relatively volatile electrolyte such as LP30 (1M LiPF_6 in 1:1 mixture of ethylene carbonate, dimethyl carbonate) could not be used since the continuous gas flow of carrier gas would dry off the separator leading to quick cell death.

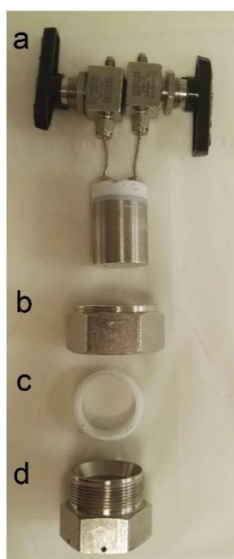


Figure 2.10 Components of the OEMS cell employed in the OEMS experiments: a) piston with taps connections, b) nut, c) PTFE o-ring, d) cell bottom part.

2.9 Spectroscopic Techniques

2.9.1 Raman Spectroscopy

Raman spectroscopy is a widely used technique which allows the identification of unknown compounds and helps in the structural characterisation of the known ones. The technique is based on the Raman effect in which a monochromatic LASER is usually the

source of choice, impinges on a sample inducing a transition from the ground vibrational state v to a virtual state that possesses an extremely short life-time. The excited state quickly relaxes radiatively to either the original vibronic state v (Rayleigh line), to a higher energy vibrational state than the ground state (Stokes line) or to a lower energy vibrational state in the ground electronic state (anti-Stokes lines). The signal obtained (Raman spectrum) from the sample is reported as intensity versus energy or frequency and is composed by a majority of elastically scattered light and many side bands respectively at higher and lower energy with respect to the Rayleigh line for the anti-Stokes and Stokes lines that compose the Raman inelastic scattering (Figure 2.11). Hence the Raman scattering peaks correspond to the excitation of vibrational modes (phonons in a non-molecular system) within the investigated sample. The information obtained from the Raman spectroscopy is similar and in many cases complementary to the one obtained from the Infrared Spectroscopy (IR). The Raman scattering allows for the excitation of vibrational modes that are not allowed by symmetry in IR spectroscopy (e.g. centrosymmetric molecules). Raman scattering substantially changes between single molecules and non-molecular solids with the sharp peaks for molecules that become broad features in the spectrum of a solid.

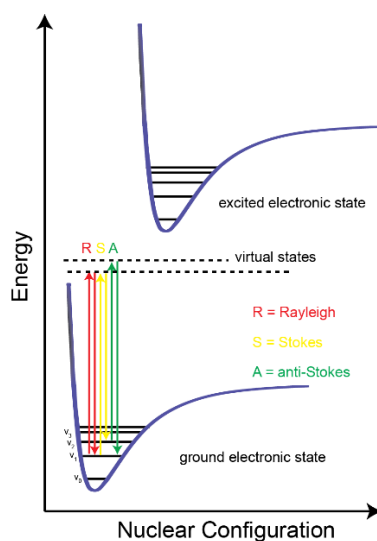


Figure 2.11 Franck-Condon diagrams for a ground and excited molecular electronic state which represent the Raman transitions corresponding to the excitations to virtual states located between the two electronic states.

Raman is mostly employed in materials science to identify unknown phases which in principle can be done rather easily with the help of a library of reference materials whose vibrational modes are employed as unique fingerprints for a certain compound. The most common setup in Raman analysis is the use of a LASER source coupled with an optical microscope. The microscope's lenses are used to focalize the laser beam and collect the Raman spectrum of a micrometric-sized spot in the material under study. In this work Raman spectroscopy was performed with a Renishaw InVia Raman spectrometer equipped with a diode laser ($\lambda = 785 \text{ nm}$).

2.9.2 X-ray Photoelectron Spectroscopy

XPS is a fundamental spectroscopic technique employed to obtain qualitative and quantitative information about the surface of the sample of interest. In a typical XPS experiment, the sample is placed in an ultra-high vacuum chamber and gets irradiated with a monochromatic X-ray beam. The beam energy is high enough so that when it encounters an atom it causes the ejection of a core-level electron, denominated photoelectron. The ejected photoelectron possesses a kinetic energy that is directly related to the characteristic binding energy of the core electron through the following equation:

$$E_k = h\nu - E_b - \phi \quad (2.19)$$

Where E_k is the electron kinetic energy, $h\nu$ is the X-ray energy, E_b is the electron binding energy and ϕ is the work function, corresponding to the minimum energy necessary to remove an electron from a solid. For a given atom and excitation energy $h\nu$, a range of kinetic energies is detectable which is dependent on the shell of origin of the detected photoelectrons (different binding energies) and each E_b is characteristic for each element. The possibility to measure E_k , hence E_b , means that the elemental composition of a sample can be characterised. Further than that, due to characteristic change in E_k of photoelectrons for the different oxidation numbers of the same atom, from XPS analysis it

is possible to get oxidation states and coordination environments of a chemical species in a solid matrix.

XPS is also a powerful technique to study the valence band structures of metals and semiconductors although its largest use and potential is the characterisation of solids surfaces. XPS surface selectivity is mostly due to the short mean free path of a photoelectron in a solid which enables only the electrons ejected from atoms very close to the surface (<100 nm) to escape from the solid.

2.9.3 X-ray Absorption Spectroscopy: XANES, EXAFS and SXAS

X-ray Absorption Spectroscopy, generally indicated with the acronym XAFS (X-ray Absorption Fine Structure), is a very powerful tool to get information about the electronic structure and environment of a specific atomic species.

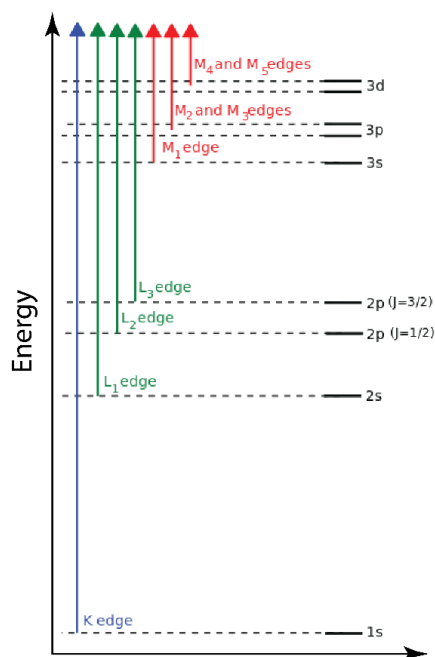


Figure 2.12 Nomenclature of the different absorption transitions. The letter is determined by the principal quantum number of origin n and the number by the energy position of that state (the number increases with the energy of the state).

Since the advent of synchrotron-based X-ray sources in the 1970' (10^{10} higher photon flux than lab-scale X-ray sources) and thanks to increasingly powerful computers to carry out data interpretation, XAFS techniques have been enormously developed opening new research avenues in all the fields of science. The X-ray absorption process results from the excitation of a core electron into a higher energy state by an incident photon. Depending on the energy of the incident beam, electrons belonging to different core levels can be excited. The energies required to excite core electrons of an atom can range on a wide energy scale (from <1 eV to >100 keV) due to the relative separations of atomic energy levels which are characteristic of each element and proportional to the atomic number Z . The electronic transitions in XAFS are labelled with different letters depending on the core level involved in the transition, so different labels will correspond to the different excited shells and $n = 1, 2, 3$ will give respectively transitions K, L, M (Figure 2.12). Each transition from the core levels to the Fermi energy and above results in a sharp discontinuity in the transition probability T_{if} and is denominated edge step (Figure 2.3).

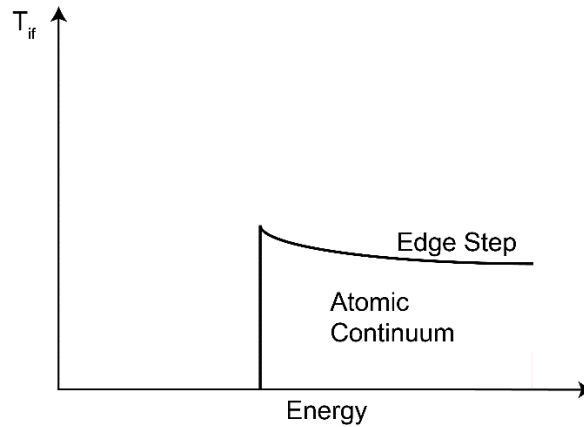


Figure 2.13 Schematic representation of an edge step corresponding to the excitation of the core electrons of an atom to above the Fermi energy.

The transition probability T_{if} can be evaluated through the Fermi golden rule

$$T_{if} = \frac{2\pi}{\hbar} (M_{if})^2 \delta(\epsilon_i - \epsilon_f - \hbar\nu) \rho(\epsilon_f) \quad (2.20)$$

Where M_{if} is a transition matrix element, ϵ_i and ϵ_f are the energy levels of the initial and final states, and $\rho(\epsilon_f)$ is the density of the final state. For the X-ray absorption process the transition matrix element is given by

$$M_{if} = \langle f | H_{int} | i \rangle \quad (2.21)$$

And the interaction Hamiltonian is taken to be

$$H_{int} = \frac{e}{m_e} \mathbf{p} \mathbf{A} \quad (2.22)$$

Where $\frac{e}{m_e}$ is the electron charge/mass ratio, $\mathbf{p}$ is the electric dipole moment and $\mathbf{A}$ is the vector potential. Since $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$ it appears clear how the probability of transition is related to the electric field of the electromagnetic wave that perturbs the system leading to the absorption of the X-ray. If we assume that when impinging on a homogeneous material of thickness dx , the intensity of the X-ray electromagnetic wave $I(x)$ is attenuated by a factor μ when it travels through the material, the attenuation $dI(x)$, is given as,

$$-dI(x) = I(x)\mu dx \quad (2.23)$$

The simple solution of which is,

$$I(x) = I_0 e^{-\mu x} \quad (2.24)$$

Where $I(x)$ is the intensity at the point x , I_0 is the intensity of the beam before the sample and μ is known as linear absorption coefficients. Equation (2.24) is better renowned as Lambert-Beer law. This law directly relates an experimental observable as the absorbance A , given as $I_0/I(x)$, of the sample with the probability of absorption $T_{if}(E)$ since the sample absorption cross section, $\sigma^{abs}(E)$, for an X-ray of energy E is directly proportional to T_{if} and the linear absorption coefficient μ is given as,

$$\mu = \rho_a \sigma^{abs} \quad (2.25)$$

Where ρ_a corresponds to the atomic number density for the arbitrary species a .

Transition selection rules

For the absorption of the X-ray electromagnetic radiation to occur, certain selection rules must be respected, that are generally referred to as dipole selection rules. Changes in the azimuthal and magnetic quantum numbers l and m_l are allowed, whilst changes of spin and spin projection quantum numbers s and m_s are not permitted when the electromagnetic wave in excitation is linearly polarized,

$$\Delta l = 0, \pm 1 \quad (2.26)$$

$$\Delta m_l = 0, \pm 1 \quad (2.27)$$

$$\Delta s = 0 \quad (2.28)$$

$$\Delta m_s = 0 \quad (2.29)$$

XAFS spectral regions

Much of the physics regarding the absorption of X-ray is already contained in the example of a simple isolated atom. In this system, transitions can occur from the ground level to upper levels with well-defined energy. When the energy of the radiation used to excite the sample matches the energy difference between the ground and excited state X-ray absorption will take place and a sharp peak, denominated Rydberg resonance, will appear in the corresponding T_{if} vs. incident energy plot (Figure 2.14-a).

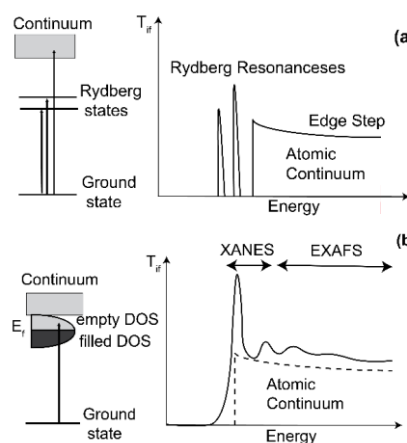


Figure 2.14 Schematic representation of the transition mechanism and corresponding absorption spectrum for: a) a free atom, b) a solid.

When the energy of the incident radiation becomes high enough to match and exceed that of the ionising energy of the atom, E_v , all electronic transitions become possible as empty states merge into a continuum. The resulting spectrum will present a series of sharp resonances and an edge step (Figure 2.4-a). For the XAS spectrum of a solid the picture is clearly more complex with many atoms and electrons involved although the concepts used to rationalize the spectrum feature are not that different from the single atom case. No Rydberg states are present in a solid but a band structure with its relative density of states (DOS). For a semiconductor (Figure 2.14-a) the states below the Fermi energy E_f are fully occupied and no transitions can occur. Between E_f and E_v , there are a number of empty states associated with the material specific density of states that are possible channels for the X-ray absorption. Transitions from the core levels into these states above the Fermi energy give a different, although conceptually close, picture with respect to the single atom case, in which no Rydberg lines are present and near edge resonances appear that are commonly denominated X-ray Absorption Near Edge Spectroscopy (XANES). Above E_v the states will merge into a continuum of states that will give an edge step similar to what observed for the single atom denominated Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS). Each of the two regions give complementary information about fundamental parameters such as the oxidation state, geometry and coordination environment of the atomic species to which the studied edge belongs to.

X-ray absorption near edge spectroscopy (XANES)

As stated in the technique name XANES analysis investigates the rising-edge region of an atom absorption spectrum. The final electronic states in the absorption process usually lie above the Fermi energy (Figure 2.14-b). These levels are also sensitive to the nature of the chemical bonds and valence state of the atom. Hence through a careful measurement of the main absorption edge position, the valence state of the species of interest can be determined.

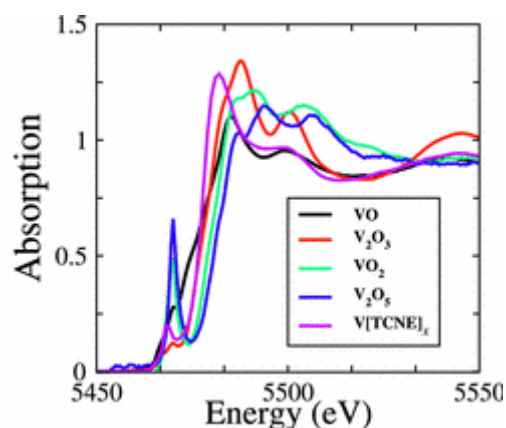


Figure 2.15 Comparison of the K-edge absorption spectra for vanadium with different oxidation numbers, reproduced from Haskel et al.¹¹.

A change in oxidation state results in a shift of the main edge in the XANES spectrum (Figure 1.15). The edge shifts are different for different edges and are increasingly larger going from K-edge to M-edge.

Moreover, while the main-edge position gives information about the effective charge on the absorbing atom, the relative positions and intensities of the edge's resolvable features can provide further details about the width and occupancy of the final states.

XANES spectroscopy, as well as EXAFS, can be performed in transmission or in fluorescence mode (Figure 2.16). The transmission mode provides the best signal to noise ratio as well as being more bulk sensitive.

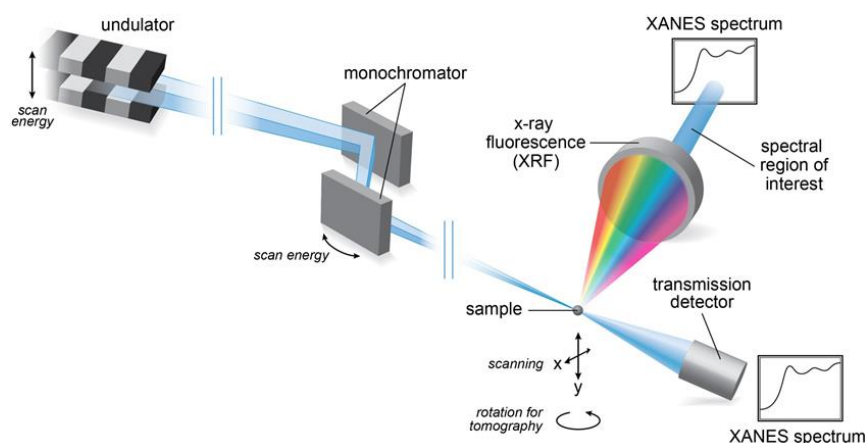


Figure 2.16 Schematic of a beamline end-station possessing both fluorescence and transmission set-up, reproduced from Brookhaven website¹².

Extended X-ray absorption fine structure spectroscopy (EXAFS)

EXAFS spectroscopy investigates the change of the absorption cross section as a function of energy over a wide range extending from the absorption edge up 1 keV after the edge towards higher energies (Figure 2.14-b). The technique is based on an interference effect originating from the interaction between a photoelectron ejected from an atom's core level by the resonant radiation and the electrons on neighbouring atoms. The interference creates a phase shift of the photoelectron's wave which can influence the absorption probability of the resonant X-ray radiation on the absorbing atom. The change in the absorption probability due to the interference creates a ripple in the EXAFS spectrum known as Krönig fine structure. Through the analysis of this ripple with suitable data processing procedures is possible to obtain information about the local structure surrounding the absorbing atom, in particular bonds length and structural geometry.

EXAFS can also be thought as an in situ electron scattering analysis in which the electron source is the absorbing atom itself. The great advantage of EXAFS over more traditional scattering techniques is the possibility to analyse local structures surrounding an atomic species of interest not only in crystalline materials but in amorphous phases as well as in disordered phases such as fluids.

Soft X-ray absorption spectroscopy (SXAS)

SXAS represent a very powerful technique to investigate light elements such as oxygen or lithium in which the electronic transitions due to the absorption of an X-ray photon, are too low in energy to be accessed with the high energy hard X-rays usually employed in more traditional XAFS techniques such as XANES and EXAFS analysis.

The working principle of SXAS is the same of XAS, with the exception that the wavelengths of the electromagnetic radiation employed fall in the soft X-ray region, i.e. < 2 keV.

The use of such low energy radiation, i.e. with low penetration depth, implies that special precautions need to be taken

- Samples are measured under vacuum
- Transmission set-up requires very thin samples p

As well, information about the bulk of the analysed samples is difficult to attain, unless the sample average particles dimensions fall in the nanometric range (<100 nm).

The spectroscopic information is usually collected through two main detection modes:

- Total Fluorescence Yield (TFY)

Fluoresce involves the radiative decay of electrons of lower binding energy filling the core holes created in absorption. The amount of fluorescence arising from a sample can be considered proportional to the absorption cross-section $m(E)$ to a limited extent for thin and diluted samples. Hence the detection of the total fluorescence is an indirect way to evaluate $m(E)$, avoiding energy dependent optimization of thickness and/or concentration for each sample in SXAS measurements.

A similar detection mode is PFY (Partial Fluorescence Yield) in which the photons resulting from a fluorescence process are discriminated with respect to their energy and selectively collected by a detector. PFY allows to remove the unwanted background radiation in the cases where this distorts the absorption spectra under interest. The PFY signal can be collected at a wavelength close to the excitation energy (resonant PFY) or far from it (non-resonant PFY). The biggest advantage of employing the latter type, non-resonant PFY, is the complete elimination of saturation effects since the fluorescence probability is independent from the incident energy. The non-resonant PFY is also known as inverse PFY or i-PFY^{13,14}.

Thanks to PFY thick and concentrated samples can be measured without major spectral distortions and loss of information.

TFY and PFY modes are usually able to give information about the bulk of the samples thanks to the larger escape length of photons respect to electrons.

- Total Electron Yield (TEY)

In TEY mode the total number of electrons (photoelectrons, Auger electrons, secondary electrons) emitted from the samples after irradiation is collected. The number of electrons emitted is proportional to the total number of core holes created during absorption. Hence the electrons emitted are proportional the absorption coefficient $m(E)$. Because of the short mean free path of the electrons, TEY mode is very surface sensitive and can be badly affected by surface charging phenomena in low conductive samples.

Resonant inelastic X-ray scattering spectroscopy (RIXS)

RIXS¹⁵ is a *photon in-photon out* synchrotron-based technique in which photons with wavelengths in the X-ray energy range are non-elastically scattered off the analysed sample. When interacting with the sample, part of the photons energy, momentum or polarisation can be transferred to the studied material and any change in the properties of the scattered light used for the analysis can be detected.

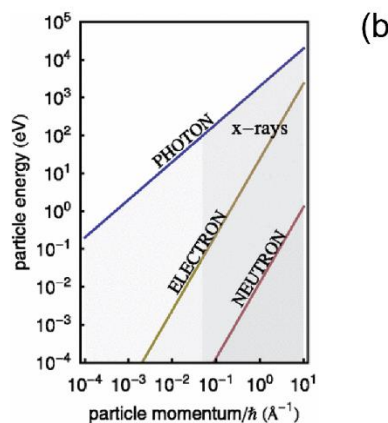
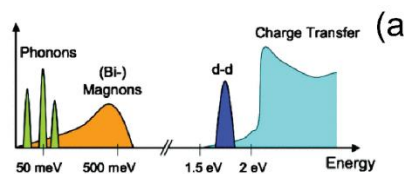


Figure 2.17 a) Elementary excitations and their relative energy ranges for strongly correlated electron materials such as transition metal oxides b) Scattering phase-space representation showing the range of energies and momenta that can be transferred in a scattering process of an elementary particle (photon, electron, neutron). X-rays (shaded area) are able to cover all the neutron and most of the electron phase-spaces, reproduced from Ament et al.¹⁵

The difference between the properties of the light impinging on the target and the light coming out of it compose the RIXS spectrum. A very wide range of elementary excitations, ranging from phonons to charge-transfer, can be probed thanks to the vast scattering phase space of photons with respect to neutrons or electrons (Figure 2.17 a and b).

The use of a resonant wavelength in excitation, meaning a wavelength that corresponds to an x-ray transition of the system (e.g. a metal edge), can greatly enhance the RIXS signal increasing the scattering cross-section.

RIXS is also a bulk-sensitive technique and, although dependent on the frequency of the radiation used to probe the material and the experimental geometry, the probing depth can range from 5 μm in the hard X-rays to 0.1 μm in the soft X-rays. Since the materials analysed in this work were all nanosized particles RIXS has to be considered a bulk-sensitive technique for our samples.

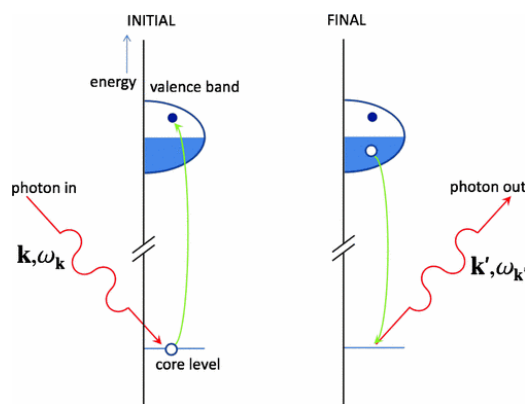


Figure 2.18 Schematic representation of a direct RIXS process in which the incoming X-ray excites a core electron into the empty valence band leaving a core hole in the system. The core is then filled by the decay of an electron from a state close to the Fermi energy with concomitant emission of an X-ray, reproduced from Ament et al.¹⁵

An important constraint on the ability of RIXS to probe elementary excitations is that these must be charge neutral. This is a consequence of the fact that RIXS does not add or remove charge to the system under study allowing to probe for example the electron-hole continuum. The most common type of RIXS is the direct one which can be qualitatively explained as follows: as the incoming photons is adsorbed by the material, a core electron is excited into an empty state of the valence band (Figure 2.18) creating a core electron hole. The resulting system is highly unstable and decays after 1-2 fs with an electron from a different state in the valence band to fill the core electron hole. The result is an electron-hole exciton located in the conduction band that possess energy and momentum equal to the difference between the energy and momentum of the incident photons and the scattered photons respectively. The core hole can also be filled non-radiatively via an Auger process in which an electron from the valence band fills the core hole, expelling at the same time another electron, although non-radiative decay channels are not relevant to RIXS.

2.10 References

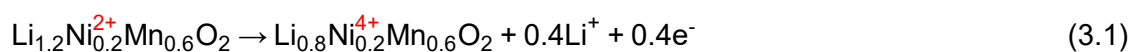
- 1 A. R. West, *Solid State Chemistry and Its Applications*, 1984.
- 2 Bragg's Law, https://en.wikipedia.org/wiki/Bragg%27s_law, (accessed 20 November 2017).
- 3 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65–71.
- 4 L. B. Mccusker, R. B. Von Dreele, D. E. Cox, D. Louër and P. Scardi, *J. Appl. Crystallogr.*, 1999, **32**, 36–50.
- 5 A. Le Bail, H. Duroy and J. L. Fourquet, *Mater. Res. Bull.*, 1988, **23**, 447–452.
- 6 M. J. Duer, *Solid-State NMR Spectroscopy Principles and Applications*, Blackwell Science Ltd, Oxford, UK, 2001.
- 7 Technical Articles | Micromeritics, <http://www.micromeritics.com/Library/Technical-Articles-Research-Applications.aspx>, (accessed 31 December 2017).
- 8 K. Luo, M. R. Roberts, R. Hao, N. Guerrini, E. Liberti, C. S. Allen, A. I. Kirkland and P. G. Bruce, *Nano Lett.*, 2016, **16**, 7503–7508.
- 9 R. A. Huggins, *Advanced batteries: Materials science aspects*, Springer US, Boston, MA, 2009.
- 10 Battery Life and How To Improve It, <http://www.mpoweruk.com/life.htm>, (accessed 31 December 2017).
- 11 D. Haskel, Z. Islam, J. Lang, C. Kmety, G. Srajer, K. I. Pokhodnya, A. J. Epstein and J. S. Miller, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2004, **70**, 54422.
- 12 BNL|NSLS-II-Beamlines|SRX|Techniques, <https://www.bnl.gov/ps/beamlines/srx/techniques/>, (accessed 23 December 2017).
- 13 A. J. Achkar, T. Z. Regier, H. Wadati, Y. J. Kim, H. Zhang and D. G. Hawthorn, *Phys. Rev. B - Condens. Matter Mater. Phys.*, , DOI:10.1103/PhysRevB.83.081106.
- 14 H. Wadati, A. J. Achkar, D. G. Hawthorn, T. Z. Regier, M. P. Singh, K. D. Truong, P. Fournier, G. Chen, T. Mizokawa and G. A. Sawatzky, *Appl. Phys. Lett.*, , DOI:10.1063/1.4711801.
- 15 L. J. P. Ament, M. van Veenendaal, T. P. Devereaux, J. P. Hill and J. van den Brink, *Rev. Mod. Phys.*, 2011, **83**, 705–767.

3 Anion Redox activity in the layered 3d TM oxide $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$

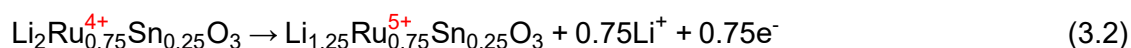
3.1 Background

Transition metal oxides are the conventional materials employed for cathodes in lithium ion batteries. In these materials, the charge (electrons) is stored through changes in the oxidation number of the transition metal^{1–4} (transition metal redox activity e.g. $\text{Mn}^{4+}/\text{Mn}^{5+}$ for LiMn_2O_4). This limits the amount of lithium ions per formula unit that can be extracted and inserted during cycling (energy density of the material), together with other factors, more closely related to the structural nature of the studied material, such as the availability of crystallographic sites for lithium to be stored and open pathways for the conduction of the alkali metal ions. If the oxide ions could contribute to the overall redox activity of the material in addition to the transition metal, then, in principle, cathode materials with much higher capacity could be realized allowing for the extraction of lithium ions beyond the TM redox activity in materials such as the Li-rich layered oxides (i.e. in $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ only 0.4 Li^+ are extracted due to the $\text{Ni}^{4+}/\text{Ni}^{2+}$ couple). Anionic contributions to the redox activity in cathodes during cycling were first reported for chalcogenides ($\text{S}^{2-} \rightleftharpoons \text{S}^{(2-n)-} + n\text{e}^-$)^{5–7}. In the last decade oxygen redox chemistry has also been recognized to occur in LiCoO_2 ^{8,9} and more recently in other 3d and 4d transition metal^{10–13} oxides such as $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ and $\text{Li}_2\text{Ru}_{1-x}\text{Sn}_x\text{O}_3$, respectively .

In fact, the presence of oxygen redox activity was hypothesized due to the observation of excess, anomalous capacity in these materials, which could not be explained by transition metal redox activities shown in the following equations:



Expected Capacity from Tm redox (126 mAhg^{-1}), experimentally observed capacity ($>300 \text{ mAhg}^{-1}$).



Expected Capacity from Tm redox (120 mAhg^{-1}), experimentally observed capacity ($>250 \text{ mAhg}^{-1}$).

In the equations reported above, Ru and Ni are expected to be the only redox active centres with Ni going from an oxidation number of 2+ to 4+ and Ru from 4+ to 5+. No further oxidation of the metals is expected since the t_{2g} electrons are too low in energy to be accessed within the relevant voltage window (2-4.8V vs Li^+/Li). Also, Mn and Sn both possess a formal oxidation number of 4+ and are expected to be inactive meaning that their d electrons are too low in energy to be accessed. Nonetheless, as already mentioned, excess capacity has been observed for both these materials and attributed to oxygen redox activity. In this chapter the oxygen redox activity in $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ is examined in detail.

Aim of the chapter:

To investigate, quantify and understand the nature of the charge compensation processes occurring in $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$.

Objectives of the chapter:

- Synthesis of the material through a sol-gel route and characterise its structure and electrochemical performance.
- Study the gas loss processes of the material on cycling.

Monitor the electronic structure changes in the material during cycling, via spectroscopic techniques such as Soft X-ray Absorption (XAS) and Resonant Inelastic X-ray Spectroscopy (RIXS).

3.2 Experimental Methods

The experimental conditions for sample characterisation and analysis are summarised in the following section. For more details on the techniques employed see Chapter 2.

3.2.1 Synthesis of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$

A formaldehyde-resorcinol sol gel synthetic route¹⁴ was employed to synthesise the layered lithium nickel manganese oxide, $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$, all the reagent ratios were calculated in order to obtain 0.01 mol of the final product. Stoichiometric amounts of $\text{Li}_2\text{CH}_3\text{CO}_2 \cdot 2\text{H}_2\text{O}$ (99.0 %, Sigma Aldrich), $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (>99.0 %, Sigma Aldrich) and $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (99.0 % Sigma Aldrich) were dissolved in 50 mL of water with 0.25 mmol of Li_2CO_3 (99.0 %, Sigma Aldrich) corresponding to 5% moles of lithium with respect to the 0.01 moles of synthesized material. At the same time 0.1 mol of resorcinol (99.0 %, Sigma Aldrich) was dissolved in 0.15 mol of formaldehyde (36.5 % w/w solution in water, Fluka). Once all the reagents were completely dissolved in their respective solvents, the two solutions were mixed, and the mixture was vigorously stirred for one hour until the colour changed from light green to light brown. The resulting solution, containing 5 % molar excess of lithium, was subsequently heated in an oil bath at 80 °C until the formation of a homogeneous white gel.

The gel was finally dried at 90 °C overnight and then heat treated at 500 °C for 15 hours and 800 °C for 20 hours. The gel was finally dried following a three-step process: 90 °C overnight, 500 °C for 15 hours and 800 °C for 20 hours. The obtained powder a dark-brown in colour.

3.2.2 Electrodes Preparation

The cathode electrodes were prepared in the form of pellets composed of a mixture of active material, carbon super-P (Timcal) and polyethylene tetrafluoride (PTFE) in an 8:1:1 mass ratio respectively.

Once weighed in the correct ratio the powder mixture was homogenised with a mortar and pestle. Subsequently, 0.5 mL of isopropyl alcohol (Sigma Aldrich) was added drop by drop to allow for a better homogeneity of the components distribution within the pellet. The wet powders were continuously kneaded in the mortar until all the alcohol was evaporated and a uniform and compact pellet was attained. The pellet was then roll pressed down to a thickness of 125 μm and cut into small pieces that were dried overnight under dynamic vacuum at 80 °C before being assembled into coin cells.

3.2.3 Coin Cell Preparation

After being completely dried the electrodes were assembled into coin-cells from CR2325 coin-cells parts, provided by the National Research Council of Canada, under an inert Argon atmosphere inside a glove box (MBraun LABmaster sp, O_2 and H_2O < 0.1 ppm). A lithium metal disc ($\varnothing$ = 18 mm, 0.1 mm thick) was used as counter electrode with two glass fibre discs ($\varnothing$ = 22 mm, Whatman GF-D) as separator, soaked with 0.2 mL of LP30 Selectilyte electrolyte (1M LiPF_6 in 1:1 w/w ethylene carbonate: dimethyl carbonate, provided by BASF)

3.2.4 Analysis and Characterisation

Structural and morphological characterisation

The morphology of the prepared layered oxide was studied via Scanning Electron Microscopy with a Zeiss Merlin microscope and its structure was investigated with several techniques: Powder X-ray Diffraction (PXRD) was carried out utilising a Rigaku SmartLab equipped with a 3 kW Cu rotating anode and BET surface area was evaluated employing a Micromeritics 3Flex. Raman spectra of the synthesised material were collected at different points of charge with a Renishaw InVia Raman spectrometer equipped with a laser diode (λ = 785 nm). Synchrotron based techniques such as X-ray Absorption Near Edge Spectroscopy (XANES), Soft X-ray Absorption Spectroscopy (SXAS) and Resonant Inelastic X-ray Spectroscopy (RIXS) were also employed to characterise the structural

evolution of the sample and to monitor changes in the oxidation states of its components at different states of charge. XANES measurements on Mn and Ni k-edge were performed at beamline B-18 at the Diamond Light Source (Harwell, UK). SXAS and RIXS measurements were collected on beamline 8.0.1 at the Advanced Light Source (ALS, Berkeley USA).

Electrochemical characterisation

$\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ was characterised electrochemically through galvanostatic cycling performed with a BioLogic VMP3 potentiostat. A pellet of the material was assembled into a Swagelok test cell specifically machined to carry out an Operando Electrochemical Mass Spectrometry (OEMS) measurement. The mass spectrometry measurement involved in the OEMS experiment was performed with a Thermo-Fisher quadrupolar mass spectrometer.

3.3 Structural and Morphological Characterisation

Powder X-ray diffraction

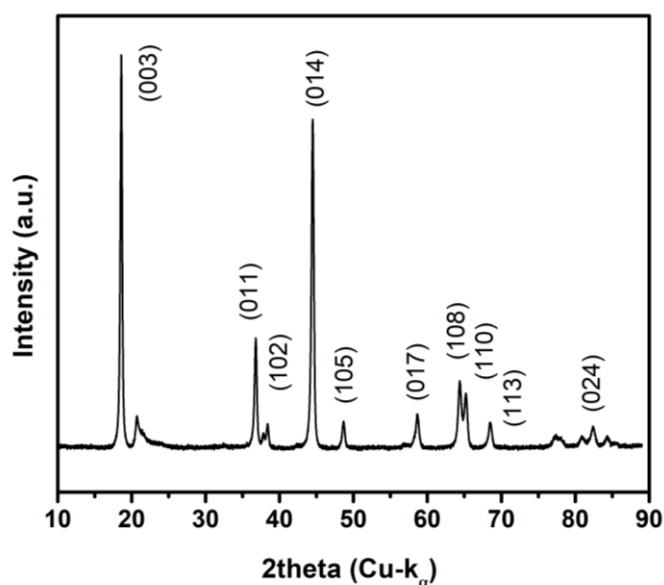


Figure 3.1 Diffraction pattern of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ synthesised via resorcinol-formaldehyde sol-gel route.

The layered lithium nickel manganese oxide was synthesised with the RF gel method and a powder X-ray diffraction pattern was collected on the obtained material (Figure 3.1). The diffraction pattern is in good agreement with the data reported in the literature¹⁵ and the material appears crystalline without presence of extra-peaks due to impurities. It is possible to observe the presence of a very strong peak at low diffraction angle (19° 2θ), corresponding to the 003 plane, which is a typical feature of layered structures.

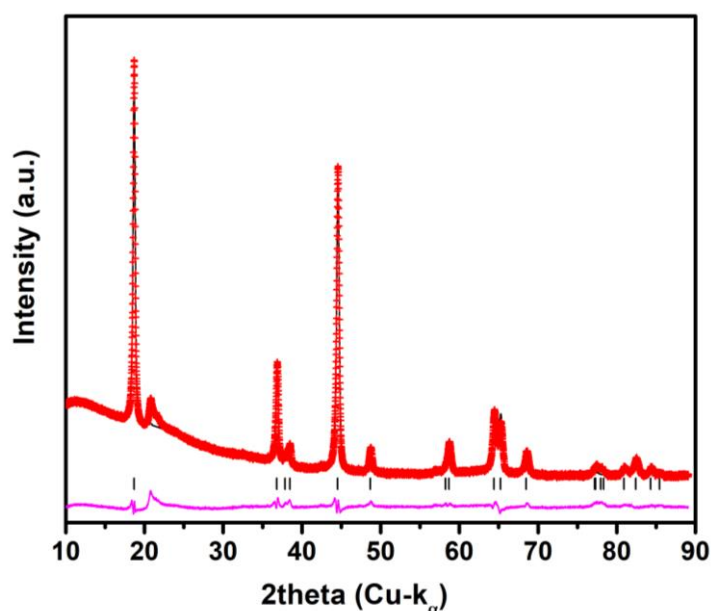


Figure 3.2 Fitting from Rietveld refinement of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ diffraction pattern. In the figure are shown the experimental pattern (red crosses), the calculated pattern (black line), the difference between the calculated and experimental patterns (fuchsia line) and the position of the expected reflections according to the model unit cell $R\bar{3}m$ (black ticks). Peaks in the range 22° - 24° 2θ were excluded from the refinement.

The diffraction pattern was used to refine the structure of the synthesised oxide. The Rietveld refinement¹⁶ was performed with FullProf suite software and the experimental data were fitted with an $R\bar{3}m$ model. The pattern fitting is shown in Figure 3.2. In the experimental data it is possible to observe the presence of all the reflections expected from the $R\bar{3}m$ symmetry model except for the peaks positioned in the range 22° - 24° 2θ degrees that are not refined in the $R\bar{3}m$ model. This is due to the symmetry of the $R\bar{3}m$ unit cell which does not take into account the in-plane local ordering of the cations at the origin of the 22° - 24° peaks in accord with previous observations¹⁷.

Table 3.1 Cell parameters obtained via the Rietveld refinement method for the synthesised $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$. The software employed to perform the refinement was FullProf Suite.

Atom	Site	x	y	Z	Occupancy
Li(1)	3b	0	0	0	1
Li(2)/Ni(2)/Mn(1)	3a	0	0	0.5	0.2/0.2/0.6
O(1)	6c	0	0	0.24166(25)	1
Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂, space group R$\bar{3}$m					
a = 2.8592(1) Å, c = 14.253(1) Å $\chi^2 = 1.91$, R_{wp} = 11.2					

The refinement data, (Table 3.1) confirm that the material has the layered-type structure adopted by the archetypal compound $\alpha\text{-NaFeO}_2$ (LiCoO_2) where three types of layers ($\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}$ layer, lithium layer and oxygen layer) are alternating with an ABC fashion (Figure 3.3), with the transition metals and the lithium ions sitting in octahedral sites.

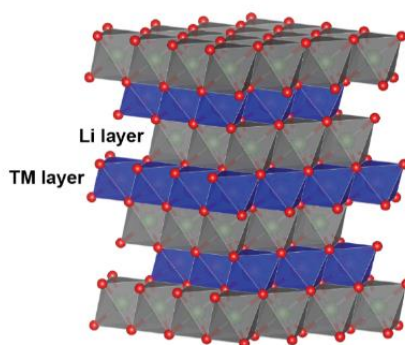


Figure 3.3 Structure of the Li-rich layered synthesised oxide obtained from refinement of the PXRD diffraction pattern. The structure was drawn with the software VESTA. It is possible to observe the superimposed layers of lithium and transition metals layers, separated by the oxygen layers. The lithium and TM ions seat in octahedral sites

Scanning Electron Microscopy and BET Surface Area

The SEM images collected at different magnification values (Figure 3.4) show a homogeneous and narrow distribution in the particles dimensions, ranging between 50 and 150 nm diameter with the presence of agglomerates up to 2-3 μm in size.

The particles appear to have a polyhedral shape with the presence of local agglomerates. The nanometric dimensions of the prepared material particles contributes as well to the samples relatively large surface area which was evaluated through BET analysis of the synthesised oxide and estimated to be $13.06 \text{ m}^2\text{g}^{-1}$ (Figure 3.19, Appendix).

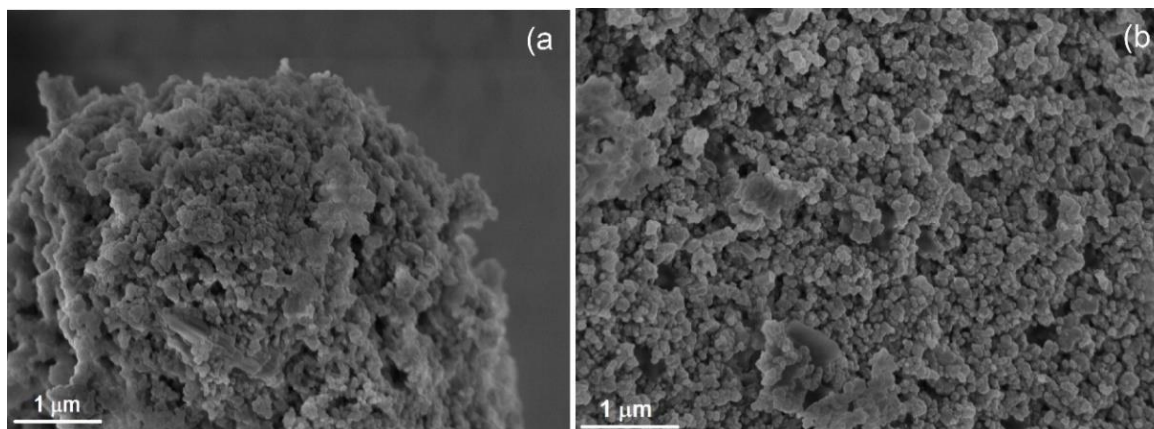


Figure 3.4 SEM images of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ particles collected with an enlargement of 18000x and a voltage of 4 kV. The particles present an homogeneous distribution in size with local agglomerates.

3.4 Electrochemical Characterisation

Once assembled into coin cells the material was galvanostatically cycled between 2.0 and 4.8 V vs. Li^+/Li for 100 cycles with a current of 50 mA g^{-1} .

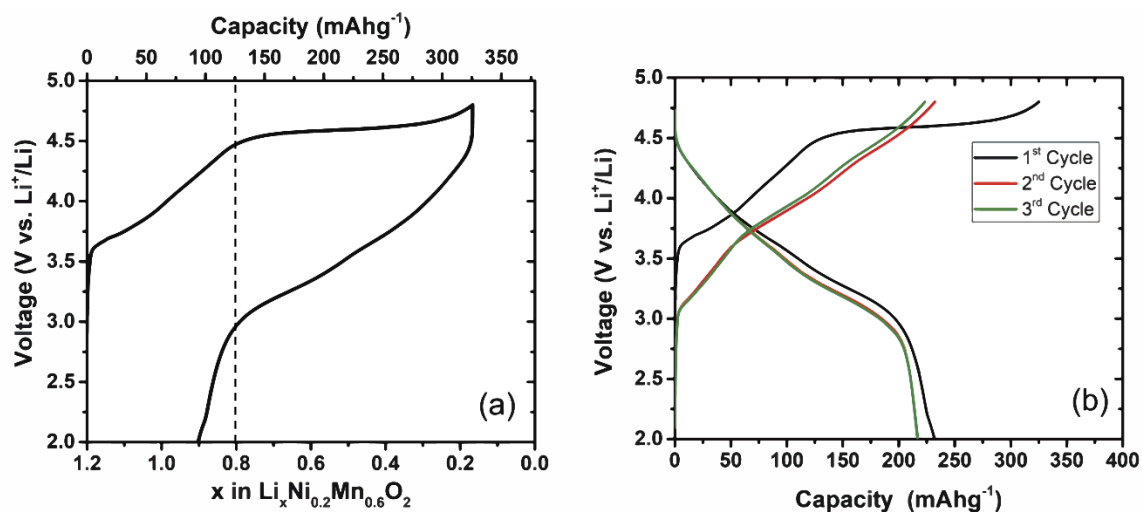


Figure 3.5 Behaviour of the potential curve during the process of extraction/insertion of lithium ions; a) during the first cycle, b) in the first three cycles. The difference between

the first and the subsequent charges appears evident with the presence of a long 4.6 V plateau in the first one.

In Figure 3.5 the electrode voltage profile is shown for the first cycle as a function of the equivalents of lithium ions extracted from the material during the charge, up to 4.8 V vs. Li⁺/Li and subsequently re-inserted during the discharge to 2 V vs. Li⁺/Li. During the charge process the potential rises gradually from the OCV of the pristine material (~3 V vs. Li⁺/Li) with a constant slope up to 4.5 V vs. Li⁺/Li where a long plateau region begins. The upper voltage cut-off is reached at the end of the plateau where the potential rises once again and finally hits the 4.8 V cut-off.

The final capacity displayed during the first charge (325 mAhg⁻¹), is in large excess to the expected redox activity of the solely Ni²⁺ to Ni⁴⁺ oxidation (Figure 3.5-a, dashed line) which would correspond to only 126 mAhg⁻¹ as shown in Equation (3.3).

$$Q_{\text{Ni}} = \frac{nF}{3.6\text{MW}} = \frac{0.4 \text{ eqmol}^{-1} \times 96485 \text{ C/eq}}{3.6 \text{ sh}^{-1} \times 85.03\text{gmol}^{-1}} = 126.08 \text{ mAhg}^{-1} \quad (3.3)$$

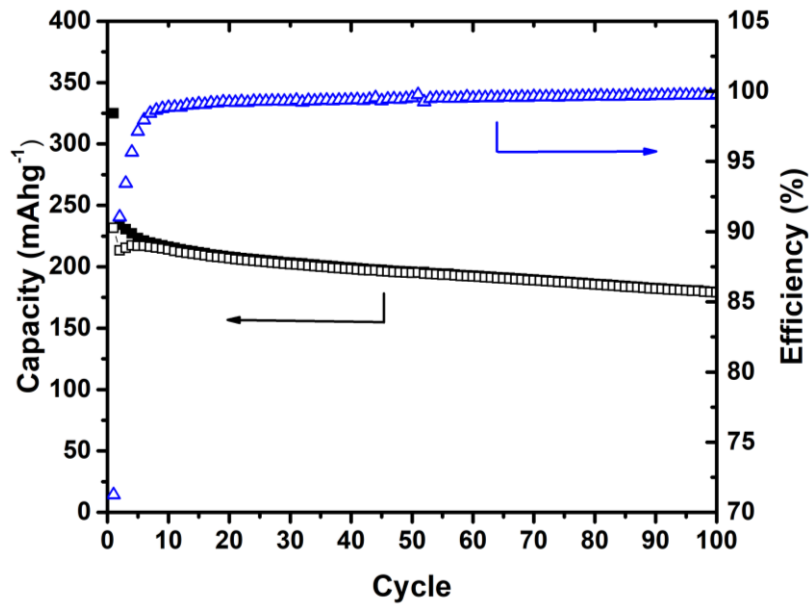


Figure 3.6 Electrochemical performance capacity (left y-axis) of the synthesised material, cycled in galvanostatic conditions and coulombic efficiency (right y-axis) per each cycle. The first charge shows poor coulombic efficiency (blue triangles) between the charge (black squares) and discharge (white squares) process, due to the non-reversibility of the plateau region during the first charge.

The following discharge curve does not show the presence of any plateau with the electrode potential constantly dropping as the lithium ions are intercalated back in the structure until the lower 2 V cut-off is reached.

The hysteresis between the charge and the discharge potential curves in the first cycle and their different shapes suggest the presence of two different mechanisms occurring during the charge/discharge process in the electrode layered structure. In the first charge the electrode delivers a capacity corresponding to the extraction of almost all the lithium contained in the lattice although in the following discharge only part of the extracted capacity can be re-inserted accounting for a coulombic efficiency of ~70% (Figure 3.6, blue triangles). It is important to notice that the plateau region, centred around 4.6 V, is characteristic of the first charge only and does not appear in the following cycles as can be seen in Figure 3.5-b.

In Figure 3.6 the galvanostatic cycling is presented for the synthesised material over 100 cycles, at a rate of 50 mA g⁻¹, together with the coulombic efficiency per cycle.

The material shows good and stable performance comparable with the cycling stability shown by other layered oxides such as LiCoO₂. The capacity is well retained over cycling although a progressive loss in the charge extracted and inserted in the material is observed corresponding to a capacity loss of 33% from the 2nd to the 100th cycle. The first cycle shows the biggest discrepancy between the charge and discharge values of capacity. The coulombic efficiency, given as the ratio between the discharge and charge capacity values for each cycle, appears to increase rapidly in the first ten cycles, improving from 70% to >98.9% in the 10th cycle, reaching stable values higher than 99.5% during subsequent cycles. The steady improvement in efficiency can be associated with a stabilization process of the electrode surface occurring during the first cycles that might be due to irreversible oxidation at high voltage of surface adsorbed species and the partial decomposition of the electrolyte to form a thin passivating layer

similar to the solid electrolyte interphase observed at the low voltage regime in the anodes.

3.5 Gas Evolution During the First Cycle

To investigate the origins of the extra capacity shown during the first charge OEMS (Operando Electrochemical Mass Spectrometry) analysis was performed on the studied material. The electrochemical cell employed was specifically designed for the experiment (see Chapter 2). The gaseous species evolved during the galvanostatic cycling which were detected together with the Argon, employed as gas carrier, were CO_2 and O_2 . Plotting the traces for the rates of the evolved gases in synchrony with the galvanostatic curve (Figure 3.7) it is possible to notice that the carbon dioxide appears before oxygen at a potential of 4 V vs. Li^+/Li and continues to be evolved until the upper cut-off, spiking up at the beginning and at the end of the 4.6 V plateau. Also, the oxygen trace appears with a spike-like shape at 4.63 V and reaches its maximum evolution rate at 4.8 V.

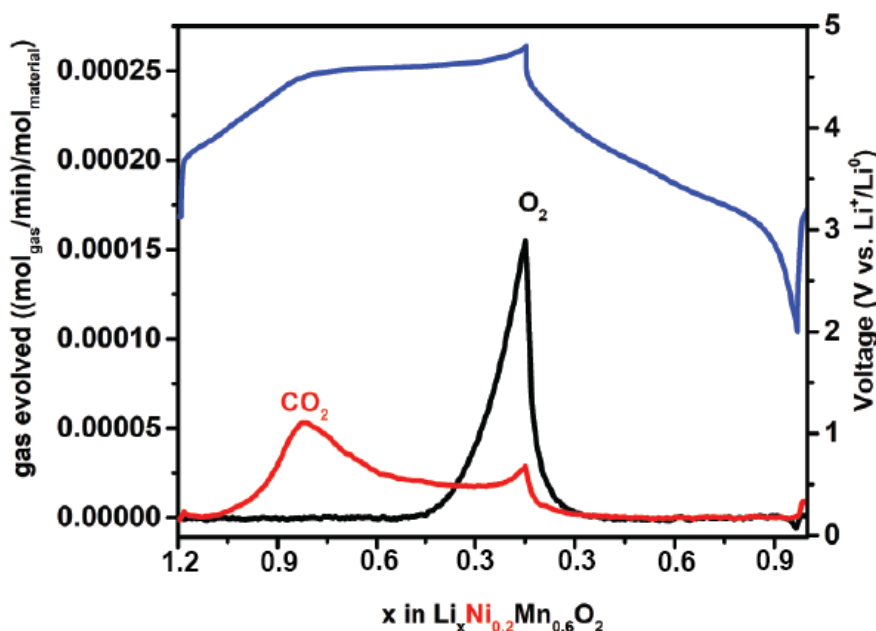


Figure 3.7 OEMS analysis of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$. In the figure the galvanostatic cycling of the studied material over the first cycle (blue line), the oxygen trace (black line), the carbon dioxide trace (red line) are reported. The right Y-axis represents the electrode potential while the left Y-axis the gas release rate expressed as moles of gas per minute per mole of active material, both axis reported as function of lithium equivalents

extracted/inserted, X-axis. Argon was used as a carrier gas with a flux rate of 0.7 mL min⁻¹ and the electrode was cycled against metallic lithium at a rate of 15 mAg⁻¹ between 2 and 4.8 V vs. Li⁺/Li for all the materials. The electrolyte employed was a 1M solution of LiPF₆ in PC.

The traces for the two gases were carefully integrated to find out the amount of gas released per mole of electrode active material. The amounts of gases obtained from data analysis were compared with the amounts previously measured in our laboratory for the spinel¹⁸ LiNi_{0.5}Mn_{1.5}O₄ which exhibits a plateau at a similar voltage. Whilst no O₂ is evolved in the spinel compound, the amount of CO₂ was found to be more than 2 orders of magnitude higher for Li(Li_{0.2}Ni_{0.2}Mn_{0.6}O₂) (see Appendix). The evolution of CO₂ for the spinel material is observed at the very end of the lithium extraction process around 5 V vs. Li⁺/Li (Figure 3.17) and it is probably related to the partial oxidation of the PC electrolyte at high potential, whilst in the case of the Li-rich layered oxide (Figure 3.7) CO₂ appears to be released during the whole de-lithiation process, indicating a different nature for the gas origin in the two materials. This result appears to indicate that the majority of the released gases are associated with oxygen loss from the lattice of Li(Li_{0.2}Ni_{0.2}Mn_{0.6}O₂) and are not due to electrolyte decomposition or oxidation of surface species. From the gas quantification it was then possible to calculate the amount of charge (electrons) deriving from the formation of CO₂ and O₂.

To do so, the reactions between oxidized oxygens in the lattice and propylene carbonate (PC), used as a solvent for the electrolyte, were considered. In these reactions, widely investigated in the field of Li-O₂ batteries¹⁹, the oxygen is assumed to be released from the lattice as superoxide O₂⁻ at high voltage values and, according to Freunberger et al,²⁰ attacks the PC electrolyte leading to the formation of carbon dioxide and water (3.4), as follows:



Thanks to Equation (3.4) it is possible to calculate the charge released by the formation of carbon dioxide. The charge due to the release of molecular oxygen was calculated as

coming from direct oxygen loss from the lattice at high voltage (>4.6V) via the following reaction,



The results for the integration of the CO₂ and O₂ traces in Figure 3.7 are reported in the table below

Table 3.2 Quantification of the charge due to the release of the gaseous species during cycling

Gas Species	moles of gas evolved / formula unit	mAhg ⁻¹
CO ₂	0.0294	37.06
O ₂	0.0241	30.4

In the table it is possible to observe that the charge due to the released gases adds up to 67.4 mAhg⁻¹. The summation of this amount of charge to the expected charging capacity due to the oxidation of nickel contained in the material (126 mAhg⁻¹, see Equation

(3.3)) corresponds to 190 mAhg⁻¹ and is more than 140 mAhg⁻¹ lower if compared to the 330 mAhg⁻¹ total exhibited during the first charge to 4.8 V (see Figure 3.5a)

It becomes evident at this point that some other process must be involved in the first charge of the material. Hence, to better understand the electrochemical behaviour and investigate the changes in the lattice during the first cycle, a thorough ex-situ spectroscopic characterization of the material at different points of charge was carried out.

3.6 Spectroscopic Investigation

X-ray absorption near edge spectroscopy

XANES analysis was carried out on nickel and manganese K-edge for samples of the synthesized Li-rich oxide at different states of charge over the first cycle (Figure 3.8). The XANES spectra were collected and analysed with the help of Dr. David Pickup.

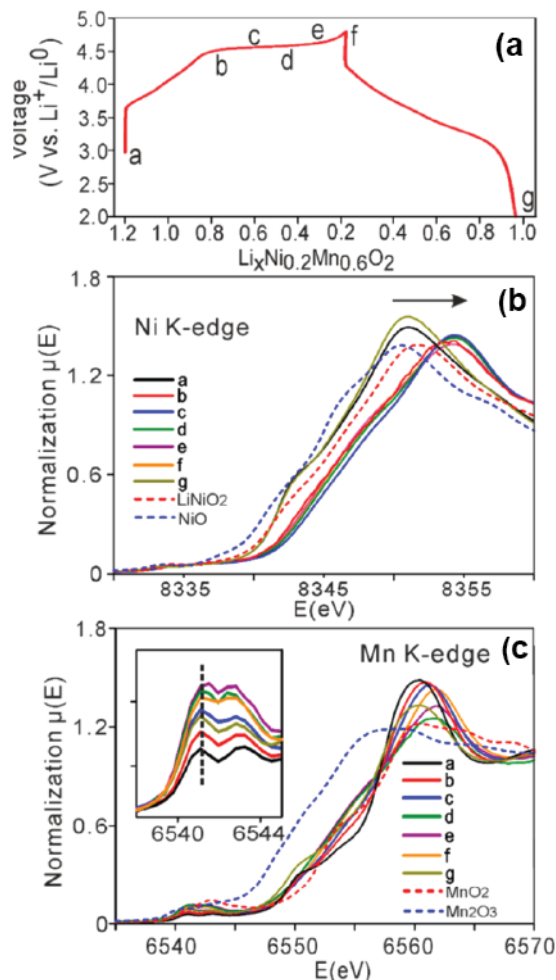


Figure 3.8 XANES spectra for nickel (panel B) and manganese (panel C) K-edges. The spectra were collected ex-situ on samples at different points of charge along the first cycle (panel A). The spectra for the different points (a-g) are reported with the same colour scheme for both Ni and Mn (solid lines). Standards for both elements with different oxidation numbers are also reported: LiNiO_2 for Ni^{3+} , NiO for Ni^{2+} and MnO_2 for Mn^{4+} , Mn_2O_3 for Mn^{3+} , (dashed lines). The inset graph in panel C shows an enlargement of the pre-edge peaks for Mn K-Edge. Data reported from ref. ¹³.

The Ni K-edge (Figure 3.8-a), shows a continuous shift towards higher energies during charge from the pristine up to the 4.6 V plateau, indicating a progressive increment in the average oxidation number from Ni^{2+} towards Ni^{4+} , in good agreement with the expected TM redox activity. The edge position remains unchanged over the plateau up to the end

of charge. On discharge the edge position shifts back, corresponding to a Ni^{2+} demonstrating the reversibility of the redox process occurring at the nickel centres.

For the manganese it is the pre-edge that gives the most useful information about the oxidation number of the metal. The pre-edge behaviour is shown in the inset graph of Figure 3.8-c and it does not change its position over the different states of charge along the first cycle. This implies that the manganese maintains a +4 formal oxidation number over the whole cycle and it does not partake in the electrochemistry. The interpretation of the XANES data appears consistent with previous works^{10,21}, showing that no further oxidation of the transition metals can be associated with the extra capacity observed during the first charge of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$.

Another possible mechanism able to account for the extra charge extracted would be the oxidation of the oxide ions in the cathode lattice, which has already been observed in the case of LiCoO_2 ⁹.

To verify this hypothesis Soft X-ray Absorption Spectroscopy (SXAS) and Resonant Inelastic X-ray Spectroscopy (RIXS) experiments were performed.

Soft X-ray absorption spectroscopy

Soft X-ray Absorption measurements of the oxygen K-edge were collected on our Li-rich material ex-situ at different states of charge along the first cycle (Figure 3.9). This technique was used to probe the density of electron-holes in the valence band above the Fermi energy. In the absorption spectrum of the pristine material (Figure 3.9-i) it is possible to observe the presence of two main regions. The first one between 525 and 535 eV (shaded region) corresponds to the transitions between the O 1s core shell and the O 2p valence shell hybridized with the transition metals 3d orbitals. Its area is sensitive to the presence of hole states density just above the Fermi energy^{21,22}.

The second region, above 535 eV corresponds to transitions between the O 1s core shell and the transition metals' 4s-p orbitals, well above the Fermi energy. A change in the spectral weight, i.e. the peaks area, in the 525-535 eV region reflects a change in the hole states density on the oxygen.

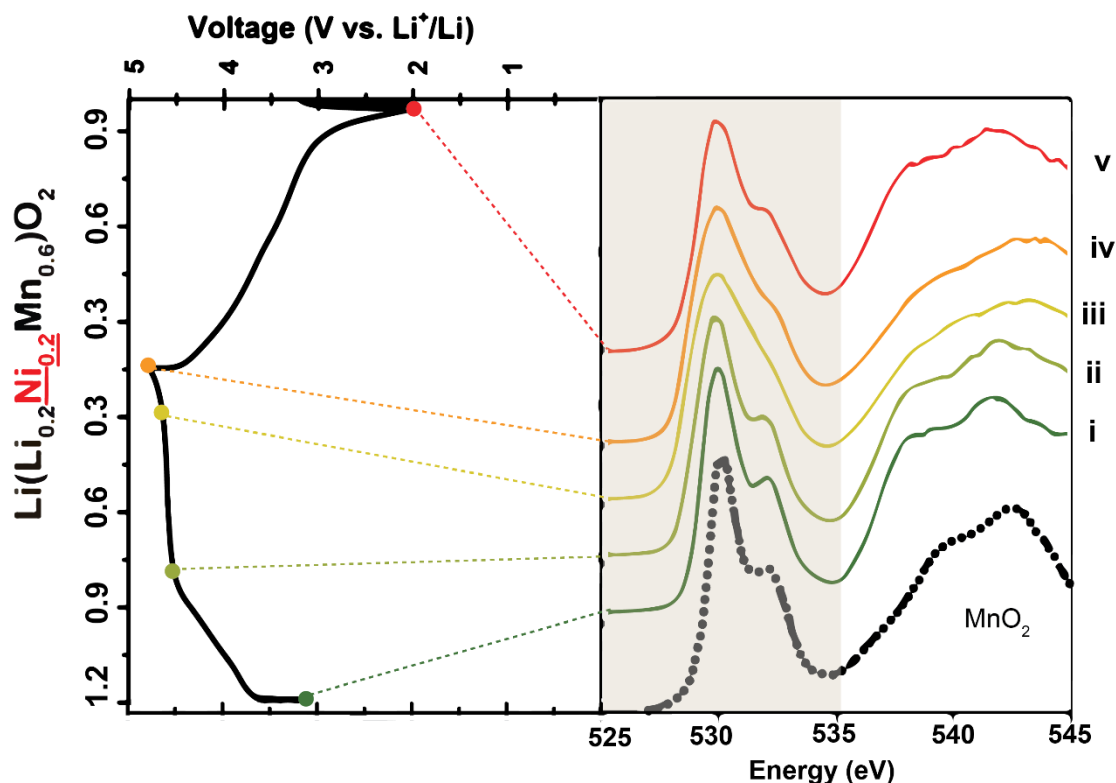


Figure 3.9 Soft X-ray Absorption spectra for the oxygen K-edge of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (i-v) and for the reference material MnO_2 ²³ (dotted line). The spectra were collected ex-situ at different points over the first cycle (coloured spots, left panel). The pre-edge area (shaded region) corresponds to the transitions from the oxygen 1s core level into the energy states immediately above the Fermi energy.

From Figure 3.9 it is possible to observe a progressive increase in the pre-edge peak area passing from the pristine (Figure 3.9-i) to the material charged to the end of the plateau region, whilst no appreciable change can be noticed between the end of the plateau (Figure 3.9-iv) and the end of charge (Figure 3.9-v). Figure 3.10 shows the trend for the oxygen pre-edge area at the different points over the first cycle. The peak areas show an 8.75 % increase between the pristine and the point at the beginning of the plateau. This value matches well with the expected increment due to the oxidation of Ni^{2+}

to Ni^{4+} which would theoretically be a 8.69% increment (see appendix). As well the hole states density keeps increasing over the plateau of a further 8.5% (Figure 3.10-iii), corresponding to the extraction of about 0.43 electrons per formula unit.

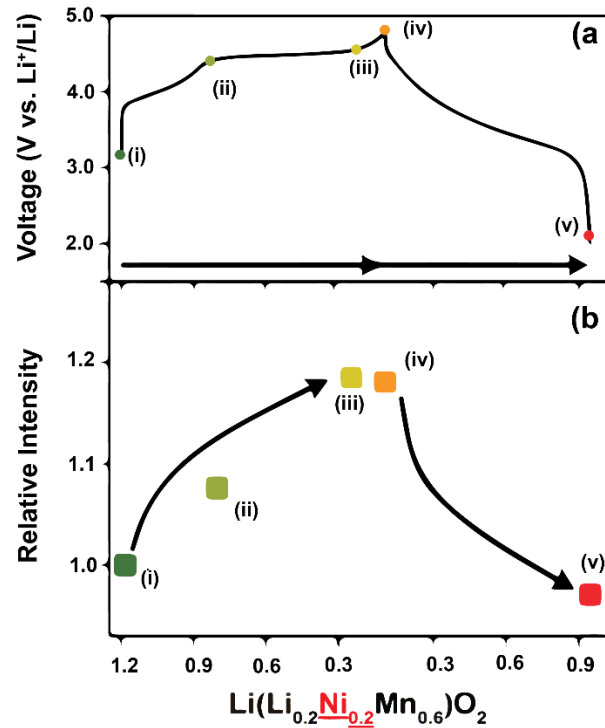


Figure 3.10 Integration values of the oxygen K-edge pre-edge area (coloured squares) at the different points over the first galvanostatic cycle of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$. The values have been normalized to the area of the pre-edge of the pristine material.

The charge extracted as hole states on the oxygen across the plateau in addition to the charge due to gas release (see paragraph 3.5) in the same region appears to match with the overall charge released between the points ii and iii in Figure 3.10. Furthermore, no change is noticed in the spectral profile between points iii and iv at high potential values, confirming the results from OEMS and the oxygen release from the lattice to be the dominant process in charging the material between those potential values.

Finally, it can be noticed how the spectrum for point v goes back to an area value close to the one of the pristine material, indicating that the hole states generated over the charge are reversible.

Raman spectroscopy

Since the oxygen redox activity along the 4.6 V plateau had been proven through the SXAS measurements, the next step was the investigation of the nature of the electron holes and the possible species involved. It is known, that for sulphides the redox activity on sulphur involves the formation⁶ of S_2^{2-} . Hence the plausible formation of O_2^{2-} during the charge of our Li-rich oxide was investigated using Raman Spectroscopy. Raman spectra were collected between 200 and 1200 cm^{-1} on $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ at different states of charge (Figure 3.11) and were compared with the spectra of chemical compounds containing the peroxide species such as Li_2O_2 , Na_2O_2 and ZnO_2 .

In none of the Li-rich oxide samples were vibrations detected between 750 and 900 cm^{-1} (Figure 3.11 red-dashed rectangle), corresponding to the O-O stretching frequency in peroxide species. Whereas peroxide stretching bands are present in all the three spectra of Li_2O_2 , Na_2O_2 and ZnO_2 .

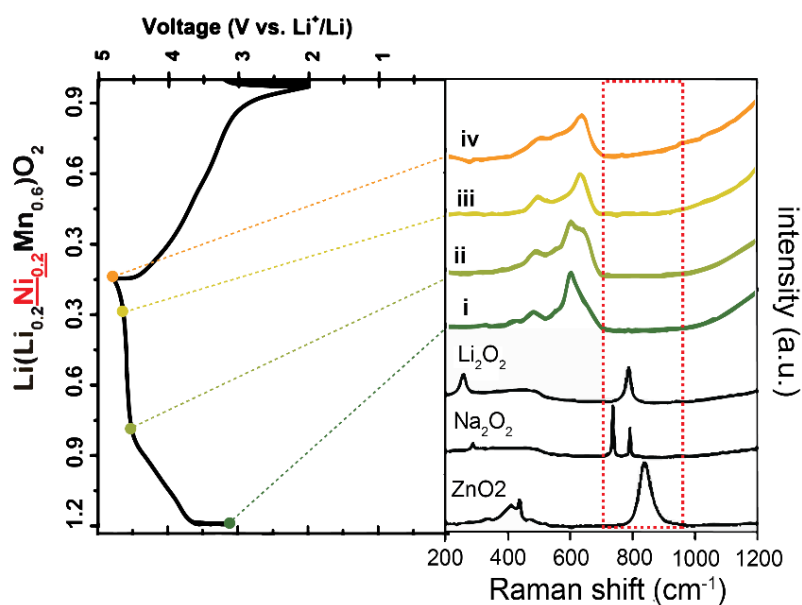


Figure 3.11 Raman spectra for $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ collected between 200 and 1200 cm^{-1} at different points over the the first charge (spectra i-iv). The measured spectra are reported together with the spectra for ZnO_2 , Na_2O_2 and Li_2O_2 respectively collected in the same frequency range. It is possible to observe, in the case of the peroxides, the presence of the O-O stretching peak in the range 700-950 cm^{-1} (red-dashed rectangle).

This result leads to the conclusion that no true peroxide species (O-O length of 1.45 Å) is formed as a consequence of the electron holes formation on oxygen during the charge. As well, no conclusion can be drawn about the formation of peroxo-like species in which the oxygen-oxygen bond is longer than 1.45 Å as these would have a lower stretching frequency although no material references exist to verify this.

Resonant inelastic X-ray spectroscopy

Further investigation into the nature of the hole states created on oxygen was carried out with RIXS measurements. This technique, which could be regarded as complementary to SXAS, investigates the emission of photons as electrons as they transition from the valence band into the core level of a chemical species. In our case the emission between the oxygen 2p band, and the oxygen 1s core level was measured on $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ samples at different states of charge (Figure 3.12). The excitation energy employed was 531.5 eV, corresponding to the valley between the main peak and the shoulder in the absorption pre-edge region of the SXAS spectrum (Figure 3.9).

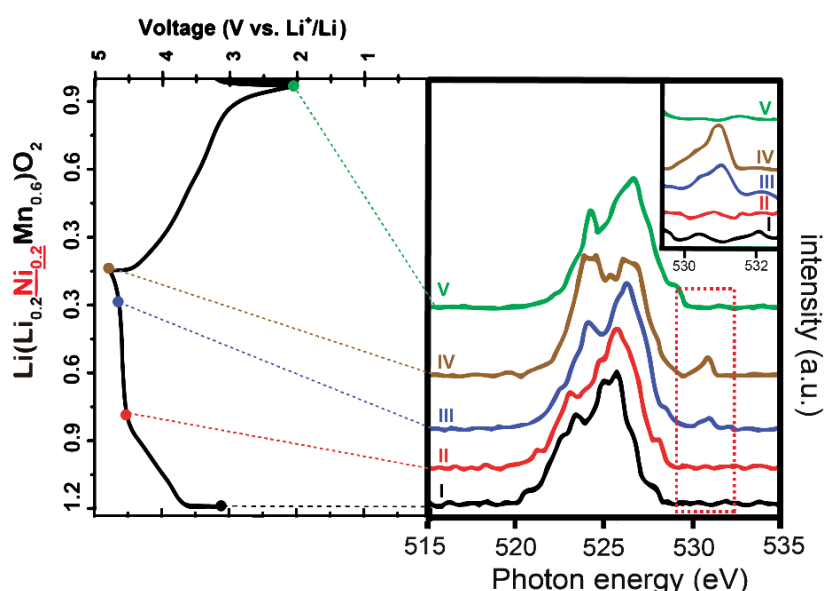


Figure 3.12 RIXS spectra for $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ collected with an excitation energy of 531.5 eV at different points over the the first charge (spectra i-iv). The elastic peak,, completely absent in the pristine material, slowly appears as the material is charged to 4.8 V (enlargement).

As already mentioned, the spectra in Figure 3.12 were collected on the synthesised material at different states of charge. Very little change is appreciable between spectra i and ii confirming the result obtained from the XAS. Instead, relevant change in the spectral weight is present in spectra iii and iv corresponding to the end of the plateau region and end of charge respectively. The spectral weight redistribution can be ascribed to a change in the density of states for the O 2p band. As well in spectra iii and iv the elastic peak at 531.5 eV appears, indicating that new states are consistent with the presence of localized holes on the oxygen. These new features, present in the oxygen RIXS spectrum for $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ charged to the end of the plateau region, seem to be reversible for spectrum v, corresponding to the end of the discharge, in which the spectral weight looks similar to that of the pristine material with no presence of the elastic peak.

This result points towards a model in which the oxygen plays an active role in the electrochemistry of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$, allowing the extraction of charge beyond the TM redox activity, thanks to the formation of reversible localized electron-hole states on the oxygen atoms.

3.7 Role of Chemical Environment on Oxygen Redox Activity

As already discussed at the beginning, the lithium rich material is characterized by a layered structure in which the oxygen atoms sit in octahedral sites coordinated by three lithium ions from the lithium layer and three cations from the transition metal layer (Figure 3.13-a)

Due to the simultaneous presence of lithium, nickel and manganese ions within the TM layer and their different charge/size ratios, the cations undergo an ordering process (Figure 3.13-c) during the material synthesis indicated by the superstructure peaks in the PXRD diffraction pattern around 22° - 24° degrees 2theta (Figure 3.1). As a consequence, different environments for the coordination of the oxygens from the transition metal layer side are present in the material (Figure 3.13-b, d) and the formation of localized electron-holes might be induced by a specific kind of environment.

Further information concerning the location of these hole states can be obtained from the analysis of Ni and Mn XANES K-edge behaviour along the plateau region.

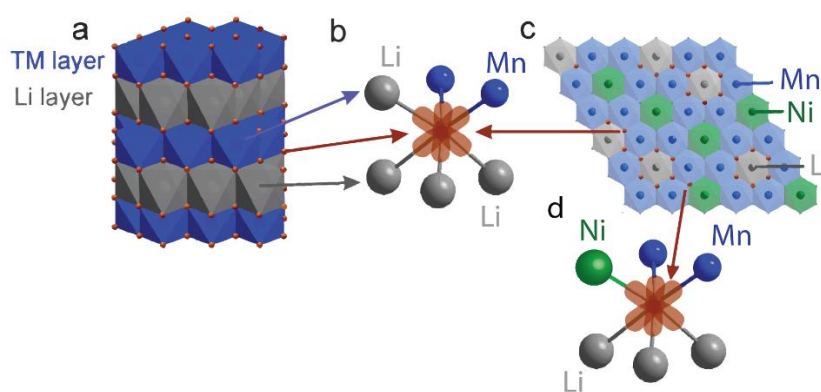


Figure 3.13 Schematic representation of: a) the $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ layered structure, b) and d) the possible environments for the coordination of the oxygen, c) the metal ions ordering within the transition metal layer.

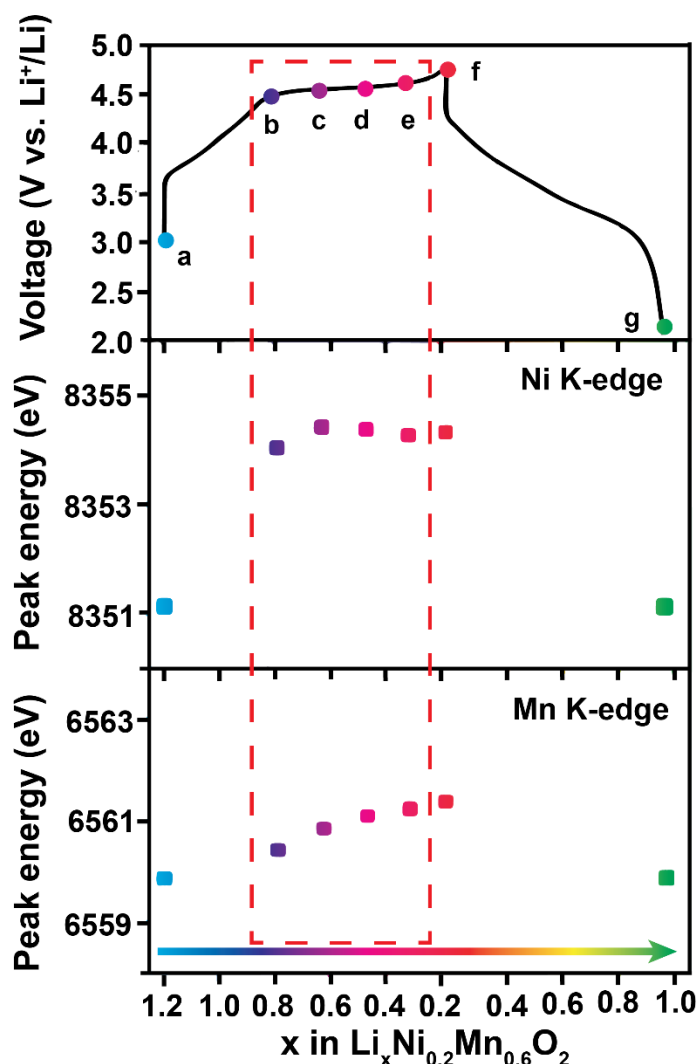


Figure 3.14 Peak position for the XANES nickel and manganese K-edge in $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ at different points over the first galvanostatic cycle (points a-g, top panel). The shaded region corresponds to the points collected on the plateau. Data collected and analyzed with the help of Dr. David Pickup.

In Figure 3.14 are shown the positions of the 1s-4p K-edge peaks for Ni and Mn at different points over the first cycle. It is possible to observe how over the plateau region no relevant shift is present for the Ni edge, whereas a continuous shift towards higher energies is happening at the Mn edge.

The shift on the Mn edge is compatible with a redistribution in the density of states around the manganese ions during the extraction of lithium. The metals K-edge behaviour seems to point towards the idea that an environment in which the oxygens are coordinated by manganese rather than nickel, on the TM layer side, could promote oxygen redox activity.

To further explain this idea, one has to consider the interactions occurring between the oxygens and the surrounding metals²⁴. On the alkali-metal layer side a relatively ionic interaction is expected between the O^{2-} 2p and Li^+ 2s orbitals due to large difference in energy of the orbitals involved with the oxygen orbitals lying at lower energies. On the TM layer side instead, oxygens can be coordinated by either lithium and manganese or nickel and manganese (Figure 3.13-b and -d). The interaction between lithium and oxygen will be the same as for the alkali metal layer case whilst the Ni/Mn-O interaction between the O^{2-} 2p and TM $3d(e_g)/4p/4s$ orbitals form σ -type molecular orbitals presenting different degrees of covalency depending on the transition metal involved and the TM $nd(t_{2g})$ orbitals remain non-bonding (Figure 3.15).

In $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ the Fermi energy is expected to lie at the non-bonding E_g^* molecular orbital originating from the mixing of the oxygen 2p and nickel e_g states.

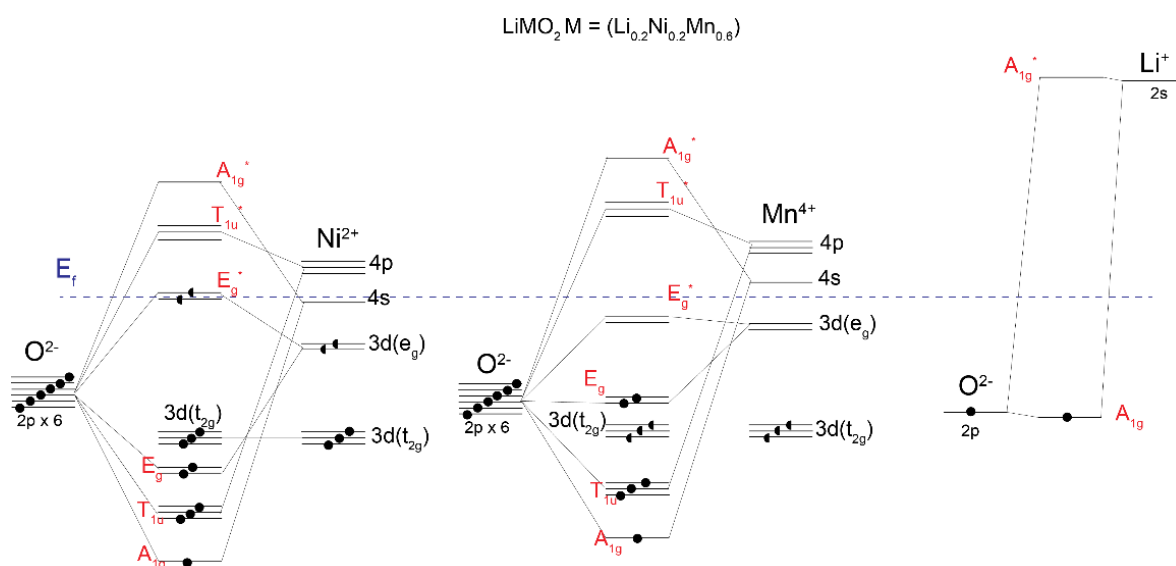


Figure 3.15 Diagram reporting the molecular orbitals generated from the orbital mixing of $2O^{2-}$ and $Ni^{2+}/Mn^{4+}/Li^+$ in the layered $LiMO_2$ where $M = (Li_{0.2}Ni_{0.2}Mn_{0.6})$.

Because the nickel orbitals are higher in energy than the oxygen ones, the e_g^* molecular orbital present a more $nd(e_g)$ character of nickel, hence extracting charge at the Fermi energy means that nickel gets oxidized.

Once Ni^{2+} ($t_{2g}^6 e_g^2$) is oxidized to Ni^{4+} ($t_{2g}^6 e_g^0$), the energy of the bonding E_g molecular orbitals drops (due to the removal of electrons from the antibonding E_g^*) and is expected to be close to the oxygen valence band, strengthening their σ bond nature (more covalent character). Additionally, the energy of the E_g molecular orbitals, deriving from $Mn(e_g)$ - $O(2p)$ mixing, does not change during the charge presenting a more ionic σ interaction with respect to the $Ni(e_g)$ - $O(2p)$ ones due to the higher difference in energy between the interested atomic orbitals. In the resulting band structure picture, the oxygens coordinated by Li^+ and Mn^{4+} , on the TM side, appear to have a more ionic character than the ones coordinated by Ni^{4+} and Mn^{4+} and are expected to present a localized character, meaning that the Mn/Li-coordinated oxygens states would lie in a narrow band at the top of the oxygen valence band (Figure 3.16).

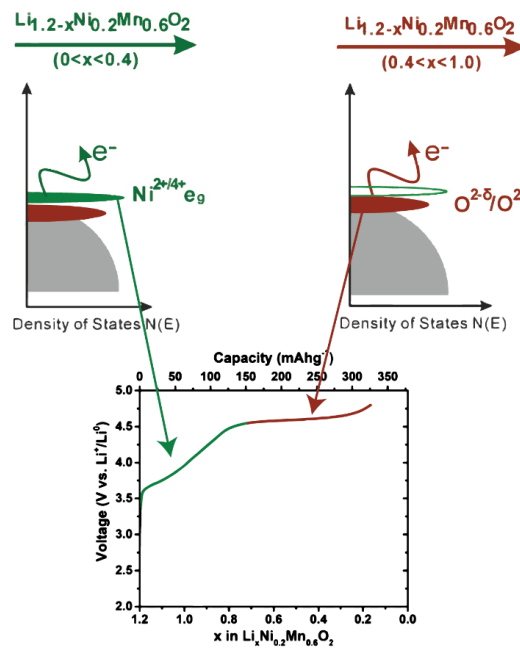


Figure 3.16 Representation of the Density of States (DOS) bands evolution during $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ first charge, following the model obtained from the spectroscopic analyses at different states of charge.

The oxygen redox activity would originate from this localized band leading to the formation of electron holes on the oxygens at high potential values (Figure 3.16).

3.8 Conclusions

The layered oxide $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ shows an unusually high capacity which goes far beyond the transition metal redox activity. During the first charge it is possible to extract more than one lithium per formula unit and the galvanostatic curve is characterized by the presence of a high voltage plateau centred around 4.6 V vs. Li^+/Li .

In the attempt to explain the mechanism underpinning the electrochemical performance of the material several techniques were employed. Thanks to the use of OEMS, SXAS, XANES and RIXS combined, it was possible to determine that the capacity observed, beyond TM redox (corresponding to the extraction of 0.4 e^- /formula unit), was due to anionic redox activity on the oxygen. Along the high voltage plateau about 0.43 e^- per formula unit were extracted through the formation of oxygen electron-holes, whilst the charge extracted across the charge as molecular CO_2 and O_2 accounted for 0.21 electrons per formula unit. The summation of the three contributions (i.e. TM redox, oxygen redox and gas loss) corresponds to the extraction of 1.04 electrons per formula unit over the whole charge, that well matches with the 325 mAhg^{-1} ($= 1.031$ electrons per mole of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$) extracted in the first charge.

Oxygen redox activity was found to be promoted by a more ionic environment in which oxygen is surrounded by Mn and Li and not by Ni. This kind of environment raises the energy of electrons corresponding to the oxygens involved, thus allowing the formation of electron-holes within the potential stability window of the electrolyte.

Thanks to the ability to store charge on both the transition metal centre and the oxygen, the cobalt-free Li-rich $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ showed that a significant gain in performance over other well established cathode systems such as the stoichiometric NMC oxides is possible both in specific and volumetric energy density. Nonetheless, the cycling stability

of the Li-rich system and the retention of its average cycling potential²⁵ still need to be greatly optimized. Further challenge will be that of stabilizing the oxygen redox process over the oxygen loss to minimize the material degradation over cycling.

3.9 Appendix

OEMS analysis on the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

OEMS was performed on the high voltage spinel structure $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ employing identical setup within a different voltage window (3-5.2 V vs. Li^+/Li) with respect to the ones used for the lithium-rich $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$. In Figure 3.17 is shown the result attained from the analysis.

It is possible to notice the complete absence of molecular oxygen-loss over the entire charge, although a small amount of carbon dioxide spikes at the end of charge around 4.8-5.2 V vs. Li^+/Li which can be ascribed to the oxidative decomposition of a small amount of electrolyte at this high potential.

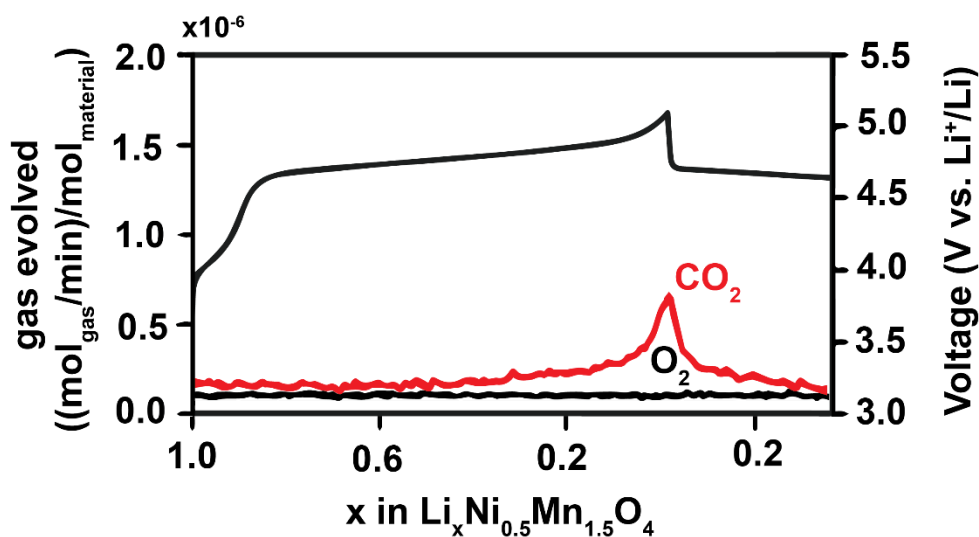


Figure 3.17 OEMS analysis of the spinel $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$. Here, the galvanostatic cycling of the studied material over the first cycle, the Oxygen trace (black line), the carbon dioxide trace (red line). The right Y-axis represents the electrode potential while the left Y-axis the gas release rate expressed as moles of gas per minute per mole of active material, both axis reported as function of lithium equivalents, X-axis. Argon was used as carrier gas with a flux rate of 0.7 mLmin^{-1} and the electrode was cycled against metallic lithium at a rate of 15 mAg^{-1} between 2 and 5.1 V vs. Li^+/Li for all the materials. The electrolyte employed was a 1M solution of LiPF_6 in PC.

Evaluation of SXAS transitions contributions

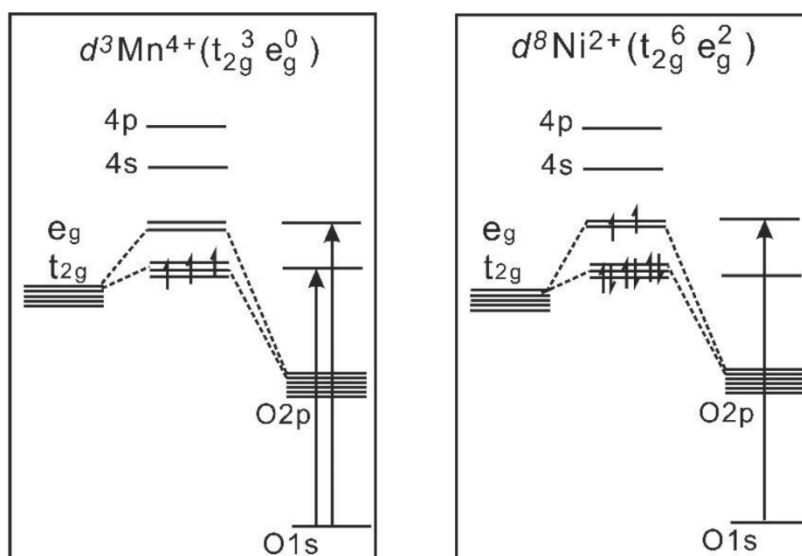


Figure 3.18 Schematics of the possible SXAS absorption transitions at the oxygen K-edge (O^{1s} to O^{2p}) for the layered system $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$. In the oxide lattice the oxygen 2p valence orbitals are hybridized with the partially filled transition metals 3d orbitals.

The contributions for the different transitions at the oxygen K-edge²⁶ for $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ can be obtained considering that the oxygen 2p orbital in the material is hybridized with the transition metals 3d valence orbitals (Figure 3.18): the dominant transition metal ion is the $d^3 \text{Mn}^{4+}$, 0.6 equivalents per formula unit. The possible SXAS transitions from the core O 1s level associated with the manganese-hybridized oxygen valence orbitals are 7, 3 spin down in the t_{2g} , 2 spin up and 2 spin down in the e_g , hence 4.2 transitions per formula unit are expected ($0.6 \times 7 = 4.2$). With Ni^{2+} are associated 2 spin down from the O 1s to the $\text{Ni}^{2+} e_g$, which accounts for 0.4 transitions ($0.2 \times 2 = 0.4$). This means that when the nickel is oxidized during the charge from Ni^{2+} to Ni^{4+} , 0.4 new electron holes are generated in the DOS to be added to the 4.6 holes present in the pristine. Supposing that the nickel oxidation is the only electrochemical process happening in the 'sloped' region the total holes states at the end of the sloped region will be 5 ($= 4.6 + 0.4$). Hence an 8.6% increment in the number of holes states in which core

electrons can be excited due to the absorption of suitable X-ray wavelength is expected in the DOS of the material at the beginning of the 4.5V plateau.

Since the possible transitions associated with manganese hybridized orbitals represent 91% of the total the shape for the oxygen K-edge absorption spectrum in $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ is almost identical to that for MnO_2 (Figure 3.9). The peaks positions and ratios are almost the same, with the first more intense peak associated to the t_{2g} and spin down e_g transitions and the second associated to the spin up e_g transitions.

BET analysis

In order to attain reliable data the Y-intercept and the parameters C and Q_m must be positive. A minimum of three 9 after the comma are desirable in the correlation coefficient.

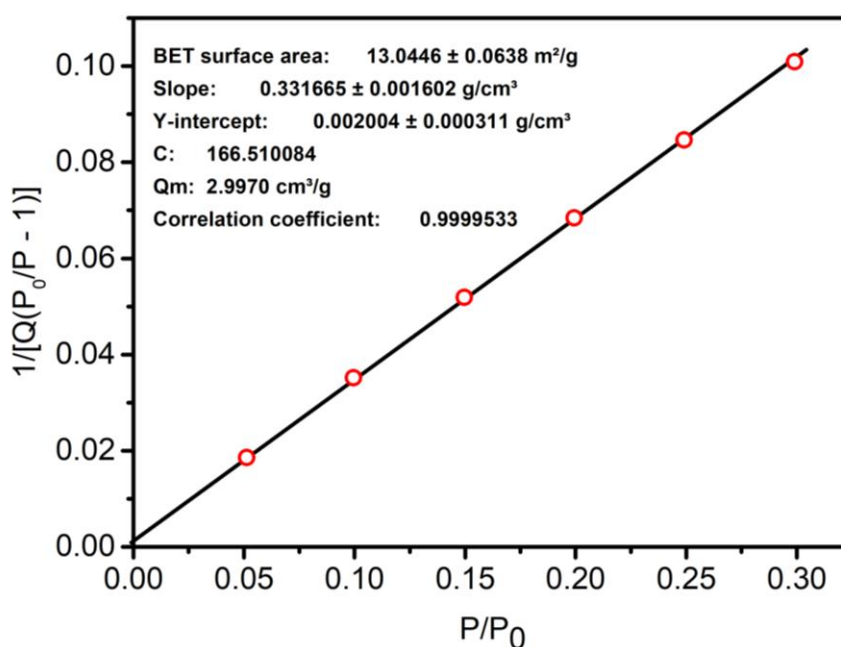


Figure 3.19 BET surface area plot for $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$

3.10 References

- 1 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, 1980, **15**, 783–789.
- 2 T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi and H. Komori, *Electrochim. Acta*, 1993, **38**, 1159–1167.
- 3 Z. Lu, D. D. MacNeil and J. R. Dahn, *Electrochem. Solid-State Lett.*, 2001, **4**, A200.
- 4 K. Kang, *Science (80-.)*, 2006, **311**, 977–980.
- 5 C. H. W. Fong, Rosamaría; Dahn, J.R.; Jones, *J. Electrochem. Soc.*, 1989, **136**, 3206.
- 6 J. B. Goodenough and Y. Kim, *J. Solid State Chem.*, 2009, **182**, 2904–2911.
- 7 J. Rouxel, *Chem. - A Eur. J.*, 1996, **2**, 1053–1059.
- 8 J. Graetz, A. Hightower, C. C. Ahn, R. Yazami, P. Rez and B. Fultz, *J. Phys. Chem. B*, 2002, **106**, 1286–1289.
- 9 W. S. Yoon, K. B. Kim, M. G. Kim, M. K. Lee, H. J. Shin, J. M. Lee, J. S. Lee and C. H. Yo, *J. Phys. Chem. B*, 2002, **106**, 2526–2532.
- 10 H. Koga, L. Croguennec, M. Menetrier, K. Douhil, S. Belin, L. Bourgeois, E. Suard, F. Weill and C. Delmas, *J. Electrochem. Soc.*, 2013, **160**, A786–A792.
- 11 N. Yabuuchi, M. Takeuchi, M. Nakayama, H. Shiiba, M. Ogawa, K. Nakayama, T. Ohta, D. Endo, T. Ozaki, T. Inamasu, K. Sato and S. Komaba, *Proc. Natl. Acad. Sci.*, 2015, **112**, 7650–7655.
- 12 M. Sathiya, G. Rousse, K. Ramesha, C. P. Laisa, H. Vezin, M. T. Sougrati, M. L. Doublet, D. Foix, D. Gonbeau, W. Walker, A. S. Prakash, M. Ben Hassine, L. Dupont and J. M. Tarascon, *Nat. Mater.*, 2013, **12**, 827–835.
- 13 K. Luo, M. R. Roberts, N. Guerrini, N. Tapia-Ruiz, R. Hao, F. Massel, D. M. Pickup, S. Ramos, Y.-S. Liu, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *J. Am. Chem. Soc.*, 2016, **138**, 11211–11218.
- 14 K. Luo, M. R. Roberts, R. Hao, N. Guerrini, E. Liberti, C. S. Allen, A. I. Kirkland and P. G. Bruce, *Nano Lett.*, 2016, **16**, 7503–7508.
- 15 Z. Lu, L. Y. Beaulieu, R. A. Donabarger, C. L. Thomas and J. R. Dahn, *J. Electrochem. Soc.*, 2002, **149**, A778–A791.
- 16 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65–71.
- 17 Y. S. Meng, G. Ceder, C. P. Grey, W.-S. Yoon, M. Jiang, J. Bréger and Y. Shao-Horn, *Chem. Mater.*, 2005, **17**, 2386–2394.
- 18 S. Patoux, L. Daniel, C. Bourbon, H. Lignier, C. Pagano, F. Le Cras, S. Jouanneau and S. Martinet, *J. Power Sources*, 2009, **189**, 344–352.
- 19 M. Balaish, A. Kraytsberg and Y. Ein-Eli, *Phys. Chem. Chem. Phys.*, 2014, **16**, 2801.
- 20 S. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P.

Novák and P. G. Bruce, *J. Am. Chem. Soc.*, 2011, **133**, 8040–8047.

- 21 K. Luo, M. R. Roberts, R. Hao, N. Guerrini, D. M. Pickup, Y.-S. Liu, K. Edström, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *Nat. Chem.*, , DOI:10.1038/nchem.2471.
- 22 S. Hy, W.-N. Su, J.-M. Chen and B.-J. Hwang, *J. Phys. Chem. C*, 2012, **116**, 25242–25247.
- 23 B. Gilbert, B. H. Frazer, A. Belz, P. G. Conrad, K. H. Nealson, D. Haskel, J. C. Lang, G. Srajer and G. De Stasio, *J. Phys. Chem. A*, 2003, **107**, 2839–2847.
- 24 M. Okubo and A. Yamada, *ACS Appl. Mater. Interfaces*, 2017, **9**, 36463–36472.
- 25 M. Bettge, Y. Li, K. Gallagher, Y. Zhu, Q. Wu, W. Lu, I. Bloom and D. P. Abraham, *J. Electrochem. Soc.*, 2013, **160**, A2046–A2055.
- 26 F. M. F. De Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky and H. Petersen, *Phys. Rev. B*, 1989, **40**, 5715–5723.

4 From oxygen loss to oxygen redox: nickel doping effect in lithium-rich materials

4.1 Background

The parent compound from which the layered lithium-rich materials¹ derive is $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$, also known as Li_2MnO_3 .^{2–5} Typically, low capacities are observed for this material except when it is prepared as small nanoparticles^{6,7}. When Ni is substituted for some of the Li and Mn ions in $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$ a significant increase in the observed capacities for large particle materials are observed⁸. As shown in the previous chapter the large capacities seen in $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ stem from oxidation of both the Ni^{2+} towards Ni^{4+} and oxidation of the oxide ions through a combination of oxygen redox^{9,10} and oxygen-loss¹¹. Hence, the substitution of Li and Mn with Ni has been shown to play an important role in determining the electrochemical mechanisms underpinning the material's performance. A thorough characterization of the materials $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$ with a series of x values is needed to help getting a better understanding of how these materials work. The nickel centres play a fundamental role in these materials as they are expected to be the only electrochemically active ones¹² in $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$, with the nickel being oxidized from +2 towards +4, and when Ni is absent the observed capacity of materials is extremely low especially when not prepared as nanoparticles. In the case of the parent compound $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ no capacity would be expected since the manganese in this material is already in a +4 oxidation state. It would then be expected that the capacity would increase with the amount of nickel substitution x. However, as introduced in the previous chapter the anionic redox process occurs above 4.4 V vs. Li^+/Li . Here, the contribution of anionic redox processes to charge compensation as a function of the Ni content will be further investigated.

Aim of the chapter:

The effects on the nature of the electrochemical activity due to increasingly higher Ni substitution in the parent compound Li_2MnO_3 is investigated in this chapter. A series of lithium rich materials, with generic formula $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$, which can also be considered as a solid solution between Li_2MnO_3 and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, were synthesized. Their structures and electrochemical performance are carefully characterized, and particular attention is devoted to understanding if and to what extent the presence of nickel effects the oxygen redox activity present in these materials.

4.2 Experimental Methods

The experimental conditions for the samples characterisation and analysis are summarised in the following section. For more details on the techniques employed in this chapter see Chapter 2.

4.2.1 Synthesis of the Materials

The formaldehyde-resorcinol sol gel synthetic route was employed to synthesise the layered materials with general formula unit $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$ with $x = 0, 0.06, 0.12, 0.2, 0.3$, all the reagents ratios were calculated in order to obtain 0.01 mol of the final product.

Stoichiometric amounts of $\text{Li}_2\text{CH}_3\text{CO}_2 \cdot 2\text{H}_2\text{O}$ (99.0 %, Sigma Aldrich), $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (>99.0 %, Sigma Aldrich) and $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (99.0 % Sigma Aldrich) were dissolved in 50 mL of water with 0.25 mmol of Li_2CO_3 (99.0 %, Sigma Aldrich) corresponding to 5% moles of lithium with respect to the 0.01 moles of synthesized material. At the same time 0.1 mol of resorcinol (99.0 %, Sigma Aldrich) was dissolved in 0.15 mol of formaldehyde (36.5 % w/w solution in water, Fluka). Once all the reagents were completely dissolved in their respective solvents, the two solutions were mixed and the mixture was vigorously stirred for one hour until the colour changed from light green to light brown. The resulting

solution, containing 5 % molar excess of lithium, was subsequently heated in an oil bath at 80 °C until the formation of a homogeneous white gel.

The gel was finally dried at 90 °C overnight and then heat treated at 500 °C for 15 hours and 800 °C for 20 hours. Once ready, the samples were mixed with carbon super P and PTFE to prepare the electrodes pellets following the procedure illustrated in Chapter 2 where is also described the coin-cells assembly.

4.2.2 Analyses and Characterisation

Structural and morphological characterisation

The morphology of the prepared layered oxides was analysed by Scanning Electron Microscopy with a Zeiss Merlin microscope. The surface area and true densities of the materials were evaluated employing a Micromeritics 3Flex BET-Surface area and a Micromeritics Accupyc II 1340 pycnometer, respectively

The structure of the samples was examined with several techniques: Powder X-Ray Diffraction (PXRD) which was carried out utilising a Rigaku SmartLab equipped with a 9 kW Cu rotating anode. Magic-Angle Spinning (MAS) NMR spectra were collected on the materials with a Bruker Avance III 400WD magnet. Synchrotron based techniques such as Soft X-ray Absorption Spectroscopy (SXAS) and Resonant Inelastic X-Ray Spectroscopy (RIXS) were also employed to characterise the samples electronic structure of materials at different states of charge. Spectra were collected for each sample at the oxygen K-edge, manganese and nickel L-edge. The energy ranges employed to collect the different edges were respectively: 525-545 eV for oxygen K-edge, 637-658 eV for manganese L-edge and 855-875 eV for nickel L-edge. The data were obtained through the analysis of the 2-D ccd detector image, acquired at the different edges, sampling the pixels corresponding to the oxygen fluorescence (inverse partial fluorescence yield^{13,14} mode, see Chapter 2). SXAS and RIXS measurements were collected on three beamlines, respectively beamline 8.0.1 at the Advanced Light Source

(ALS, Berkeley USA), ADDRESS beamline at the Swiss Light Synchrotron (SLS, Villigen Switzerland) and beamline BL12XU at Spring8 Synchrotron (Osaka, Japan).

Electrochemical characterisation

The series of layered oxides was characterised electrochemically through galvanostatic cycling performed with a *BioLogic VMP3* and a *Maccor 4600* series potentiostats. All the samples were assembled into stainless steel coin cells against metallic lithium and cycled between 2 and 4.8 V vs. Li^+/Li for 100 cycles at a current rate of 50 mA g^{-1} . The electrolyte employed was LP30 (a 1M solution of LiPF_6 in 1;1 w/w ratio of EC:DMC).

As well one pellet of each material was assembled into a Swagelok test cell specifically machined to carry out an Operando Electrochemical Mass Spectrometry (OEMS) measurement. The mass spectrometry measurement involved in the OEMS experiment was performed with a Thermo-Fisher quadrupolar mass spectrometer.

4.3 Results and Discussion

In this section, initially the structural and morphological characterisation is presented for the members of the prepared series of materials. This is followed by a study of the electrochemical performance through galvanostatic cycling and an investigation of the gaseous species evolved in each material over the first cycle by means of OEMS analysis. Finally, a detailed spectroscopic study at different states of charge in the first galvanostatic cycle is presented.

4.3.1 Structural and Morphological Characterisation of Pristine Materials

The obtained powders for the different compounds were very fine with different colours, ranging from vivid orange for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ to a dark brown for the $\text{Ni} = 0.3$ material. Such a strong variation in colour is indicative of very different electronic structures.

Powder X-Ray diffraction

The X-ray diffraction patterns of the as synthesized powders are reported as stacked plots in Figure 4.1.

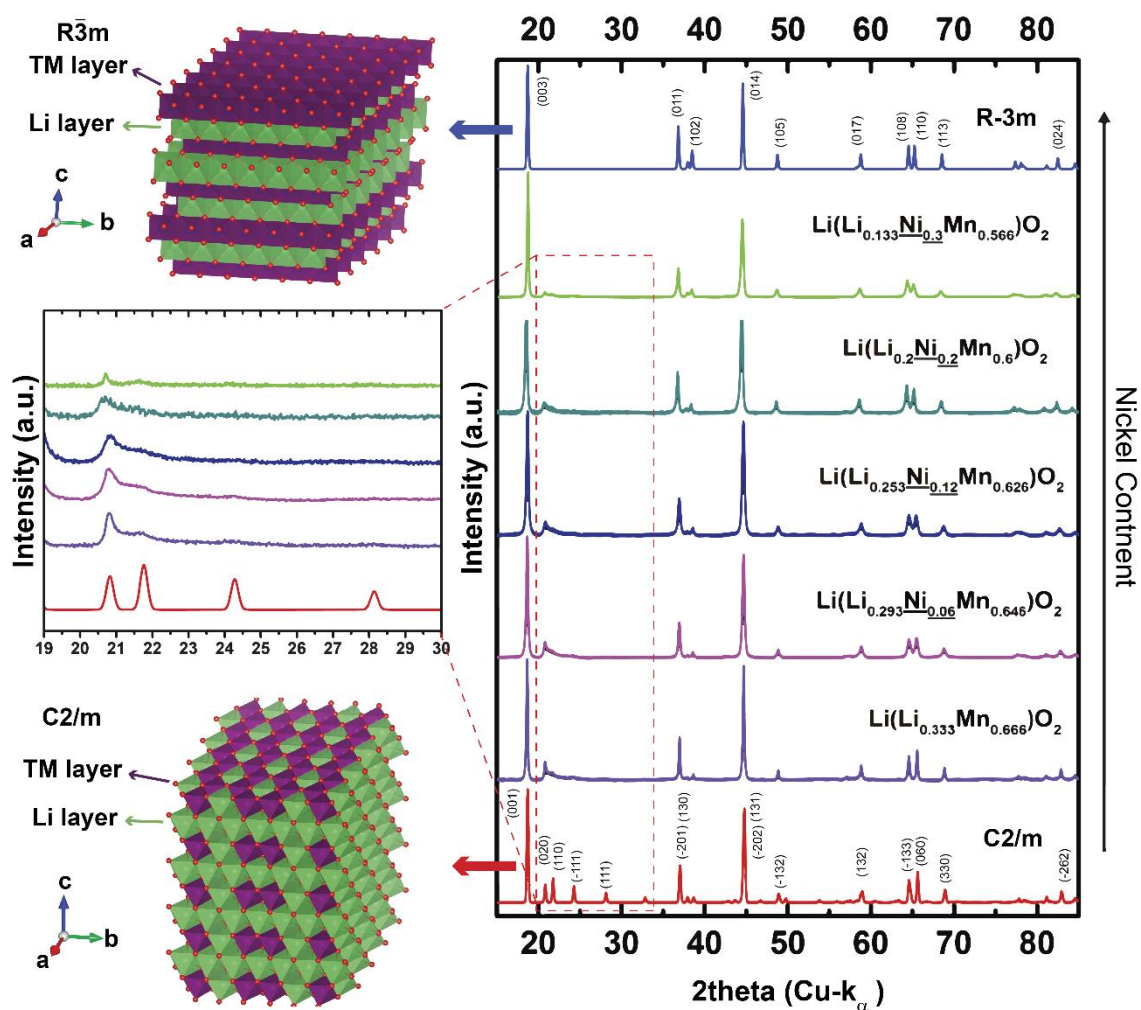


Figure 4.1 Right panel: Powder X-ray Diffraction patterns of the synthesised materials compared with the calculated patterns of the C2/m and R $\bar{3}$ m symmetry lattice shown at the bottom and top of the figure respectively. On the left-hand side the structures for the C2/m and R $\bar{3}$ m are reported. The enlargement shows the details of the reflections associated with the cation ordering in the TM layer that is lost as the Ni content increases. All of the patterns appear to show the major peaks consistent with a close-packed layered structure such as LiTmO₂ with a R $\bar{3}$ m space group (Figure 4.1).

Additional peaks are observed in the range 20-30 2θ degrees which cannot be assigned to the R $\bar{3}$ m space group highlighted in the expanded cut out of the figure. The order derives from the atomic radii and charge density differences between Li⁺ (0.59 Å),

Ni^{2+} (0.69 Å) and Mn^{4+} (0.83 Å) and appears the strongest in the structures of $\text{Li}(\text{Li}_{0.33}\text{Mn}_{0.66})\text{O}_2$ and the low nickel substituted oxides. In the Li_2MnO_3 end member the 2:1 ratio of Li : Mn allows for the formation of a perfect honeycomb (Figure 4.2).

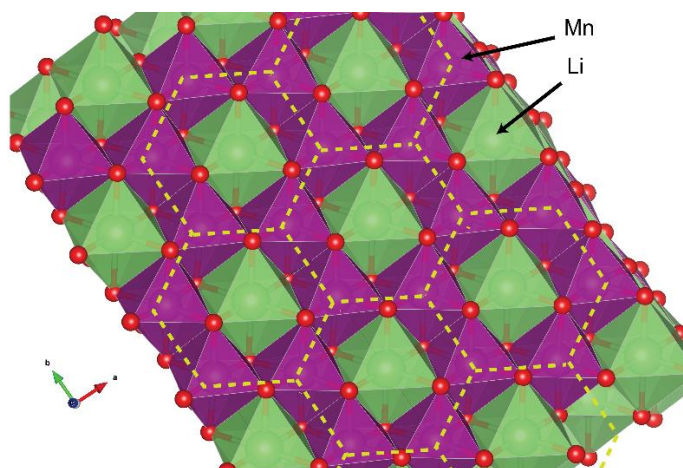


Figure 4.2 Honeycomb ordering of Mn^{4+} ions around Li^+ ions within the transition metal layer of Li_2MnO_3 .

This ordering fits to a $C2/m$ space group as shown in Figure 1.2. However, as nickel is substituted into the material the long range in-layer ordering is progressively lost. This is mainly due to the substitution of 1 Mn^{4+} and 2 Li^+ for 3 Ni^{2+} to maintain the charge balance. Since Ni^{2+} and Li^+ have a similar atomic radius in comparison to Mn^{4+} the Ni^{2+} will preferentially occupy Li sites. Since the differential scattering cross section for X-rays of Ni and Mn are very close the ordering of the ions becomes less easy to resolve with X-rays and the peaks in the 20-30 2theta degree range are lost. No presence of extra-peaks due to impurities were observed.

The diffraction patterns were used as a basis to perform structural refinements with the Rietveld method¹⁵ using the FullProf suite software. In Table 4.1 the cell parameters attained from the refinements of the diffraction patterns of the different materials are reported.

Table 4.1 Parameters obtained from the Rietveld refinement of the synthesized materials

Composition	a(Å)	c(Å)	Space group	c/a	R _{wp}	χ ²
Li_{1.33}Mn_{0.66}O₂	2.84291(7)	14.2176(7)	R$\bar{3}$m	5.001073	11.15%	3.71
Li_{1.293}Ni_{0.06}Mn_{0.645}O₂	2.84442(6)	14.2013(6)	R$\bar{3}$m	4.992687	8.83%	3.52
Li_{1.253}Ni_{0.12}Mn_{0.626}O₂	2.84929(5)	14.2119(6)	R$\bar{3}$m	4.987874	9.43%	2.06
Li_{1.2}Ni_{0.2}Mn_{0.6}O₂	2.8569(1)	14.244(1)	R$\bar{3}$m	4.985824	22%	2.20
Li_{1.13}Ni_{0.3}Mn_{0.56}O₂	2.8651(1)	14.2564(1)	R$\bar{3}$m	4.975882	12.6%	1.14

All of the structures were refined employing an R $\bar{3}$ m space group symmetry which means that the region containing the superstructure peaks between 20 and 30 2theta degrees was excluded during the refinement procedure. Table 4.1 shows a clear trend in the lattice constants *a* and *c*, as well as for the ratio *c/a* in which a smooth variation in the parameters values is observed as the nickel content is increased. This result confirms what already observed by Dahn et al.⁸ that Li_(4/3-2/3x)Ni_xMn_(2/3-1/3x)O₂ with x = 0, 0.06, 0.12, 0.2 and 0.3 can be considered a solid solution series.

Magic angle spinning nuclear magnetic resonance

MAS-NMR spectra were collected for the NMR-active isotope ⁶Li on the whole series of materials. The mass normalized spectra, reported in

Figure 4.3, show the presence of two paramagnetic shifts (i.e. peaks), centered at 1900 and 770 ppm, corresponding to the two sites for lithium ions in the structure. Following what has been already reported^{16,17,18} the isotropic shift centred at 1900 ppm is attributed to lithium belonging to [LiMn₆] configuration (including the distorted versions of it), within the transition metal layer.

Additionally, the isotropic shift at 770 ppm is assigned to lithium sites in the lithium layer. Note, due to the lower temperature (268K) at which the NMR measurements were carried

out, the shifts are different from those reported (especially for the transition metal lithium), as paramagnetic shifts can be very temperature-sensitive.

As well, beside the two isotropic shifts at 1900 and 770 ppm, it is possible to observe the presence of several so-called “spinning side-bands” in the spectra. The side-bands arise as nuclei in the sample rotor “feel” the modulation of the magnetic field due to the magic-angle spinning. Spinning side-bands appear on both sides of the isotropic shifts at a distance equal to the spinning frequency or its integer multiples.

The spectra show a clear trend with very sharp peaks in the case of $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ that tend to broaden and decrease in intensity as the nickel amount increases. MAS-NMR gives information on the local environment surrounding the lithium ions and the peaks sharpness in the spectra can be associated with the local ordering around lithium. A progressive loss of sharpness can be observed as the nickel content is increased although the chemical shift (i.e. the peaks positions) remains the same for all the materials.

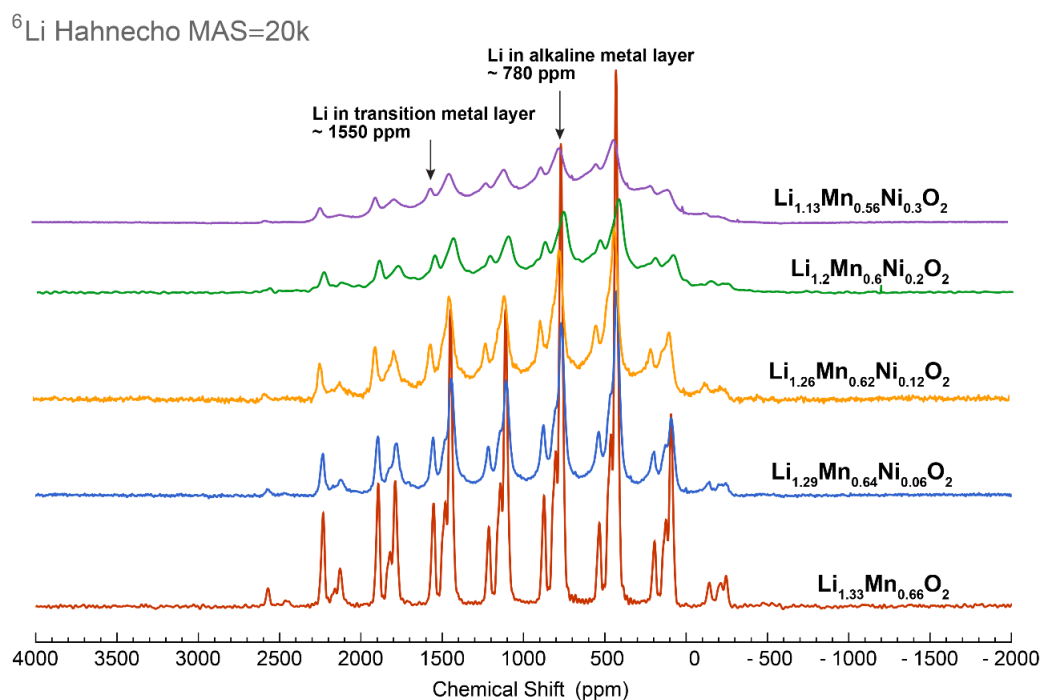


Figure 4.3 ^6Li MAS-NMR spectra collected with rotor-synchronised Hahnecho pulse sequence on the whole series of synthesised materials. The intensities were normalised based on the sample mass. The MAS rate was 20 kHz. The spectra are presented in a

stacked fashion with increasing nickel doping going from bottom up. The data were collected with the help of Dr. Liyu Jin.

This result could be explained through two main phenomena:

- The generation of distorted lithium sites in both TM and Li layers, as nickel is progressively substituted to lithium and manganese in the lattice.
- A higher concentration of stacking faults in the materials, with high nickel content, due to local compositional inhomogeneity originated from the different sizes of the TM.cations¹. Especially the progressive substitution of Ni²⁺ for Li⁺ and Mn⁴⁺ leads to local structural mismatching between the layers resulting in the presence of stacking faults.

In both cases the long-range order present across the lattice in the parent compound Li_{1.333}Mn_{0.666}O₂ is broken leading to a progressive broadening of the NMR resonances.

This is in good agreement with the loss of superstructure peaks in the PXRD patterns (Figure 4.1) due to the Ni substitution.

Scanning electron microscopy, BET surface area and pycnometry

Particle size and morphology can significantly influence the electrochemical performance of a material¹⁹. To mitigate variation resulting from morphology identical preparation methodologies were used. To validate the success of this SEM images recorded with the same magnification were recorded and reported in Figure 4.4. This shows that all compositions contain an approximately similar narrow particle size distribution, within the same dimensional ranges, with diameters between 50-150 nm and similar polyhedral shapes. Additionally, for all samples the presence of bigger agglomerates of particles was observed with dimensions in the range of 0.5 to 1 microns. As it can be noticed, the quality of the images appears to increase with the nickel content. This could be due to an increase in the electronic conductivity (i.e. better SEM images) of the oxides as nickel is substituted. In support of this idea there is the experimental evidence that the materials

change drastically in colour going from the vivid orange of the parent compound $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ to a dark brown of the $\text{Ni}_{0.3}$ oxide.

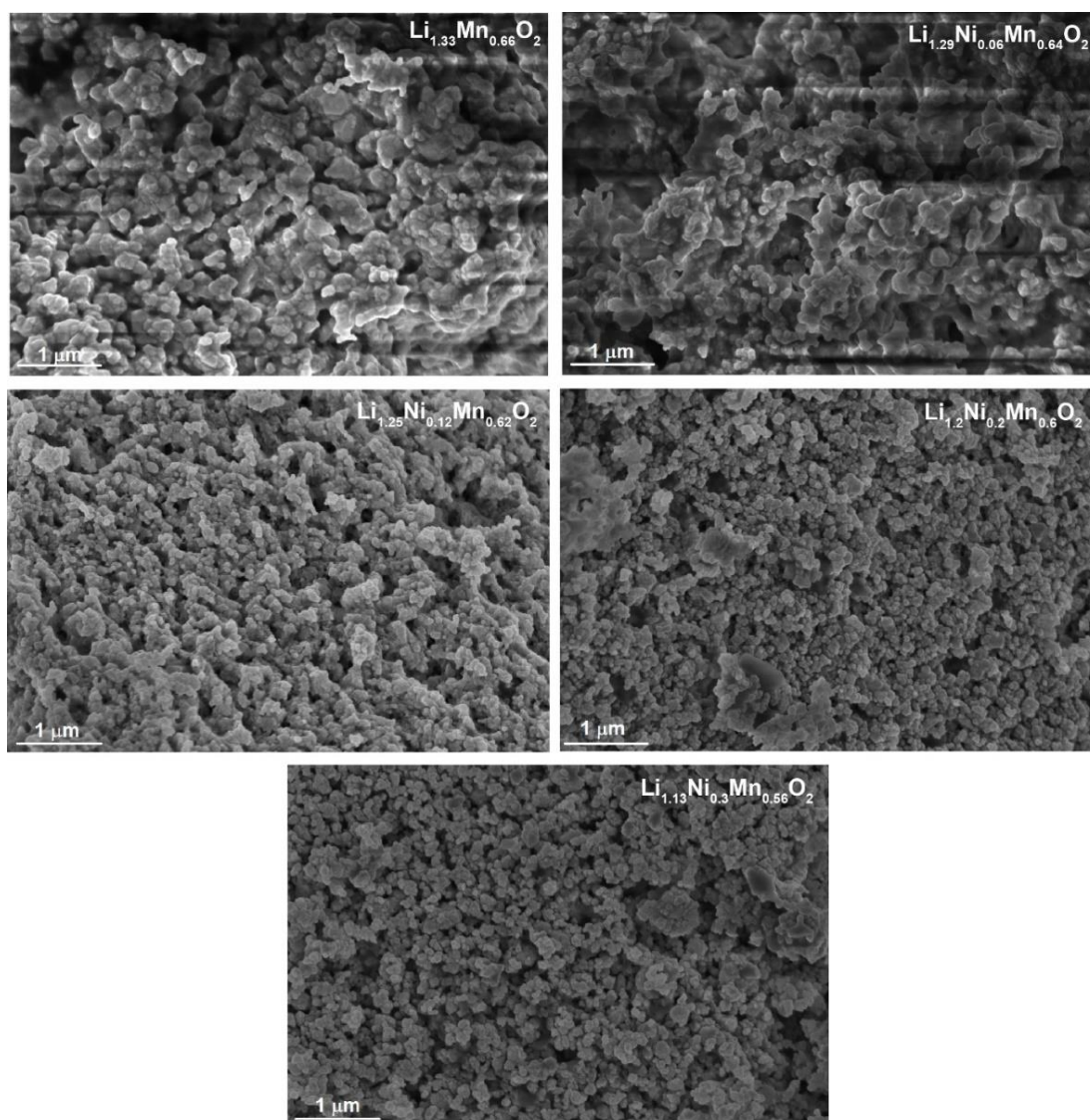


Figure 4.4 SEM images of the synthesised materials. Images were collected at 18000x enlargement and 4 kV with a current of 110 μA .

The series of layered oxides was further characterized with BET surface area. In Table 4.2 are reported the values of surface area for each sample. All compositions show comparable surface areas in the range 9.5 to 14 $\text{m}^2 \text{g}^{-1}$, and therefore it is not anticipated that any of these materials would show significant differences because of surface area variations. The measurements were repeated to check the reliability of the data and the standard deviation between the different measurements is reported as well in Table 4.2.

Table 4.2 BET Surface Area values for the synthesized materials. The full data set is reported in Appendix.

Sample (Ni substitution)	Surface (m ² g ⁻¹)	Standard deviation (m ² g ⁻¹)
0	9.6	0.28
0.06	13.8	0.56
0.12	12.7	0.35
0.2	13.0	0.60
0.3	13.7	0.58

The true density of the samples were also measured via pycnometry analysis and the obtained densities are reported in Table 4.3 and compared with the crystallographic density values obtained from the refinements of PXRD patterns. As expected the density values increase as more nickel is substituted in the structure of Li_{1.33}Mn_{0.66}O₂. An excellent agreement exists between the experimental and refined densities is observed with the highest discrepancy being lower than 2.5%.

Table 4.3 Comparison of density values obtained from Rietveld refinement and pycnometry for all the compounds

Sample (Ni substitution)	Refined Density (gcm ⁻³)	Measured Density (gcm ⁻³)	Discrepancy (%)
0	3.89	3.89	0
0.06	3.98	3.94	1.1
0.12	4.09	4.02	1.8
0.2	4.2	4.11	2.2
0.3	4.3	4.22	1.9

Thanks to the density values obtained from the pycnometry and the surface areas measured in the BET analysis it is possible to evaluate the average particle diameter of each sample. The calculation was carried out under the approximation that all the particles had a spherical shape. The use of spheres for the particles shape allows for a straightforward determination of the average diameter which is done resolving the following system of two equations and two unknowns:

$$\pi d^2 N = A_{\text{BET}}$$

$$\frac{\pi d^3 N}{6} = \frac{m}{\rho_{\text{pycnometry}}}$$

In which **d** is the average diameter, N is the number of particles in 1 gram of material, m is the mass of material arbitrarily taken to be 1 g, A_{BET} is the surface area and $\rho_{\text{pycnometry}}$ is the measured density. The unknowns are **d** and N. The diameters values obtained for each material are reported in Table 4.4.

Table 4.4 average particle diameter calculated for each of synthesized materials

Sample (Ni substitution)	Diameter (nm)
0	159.67
0.06	110.35
0.12	117.06
0.2	111.78
0.3	103.25

Despite the approximation on the particles morphology the values obtained from the calculation consistent with the approximate average diameter (150-200 nm) of the particles shown in the SEM images (Figure 4.4).

4.4 Electrochemical Characterisation

Figure 4.5 shows the potential curves during the charge and subsequent discharge of the first cycle for the different materials. All the samples present a high voltage plateau centered around 4.5 V vs. Li^+/Li similar to the load curves introduced in the previous chapter, whereas the presence of a sloped region at the beginning of the charge progressively increases in length with the amount of nickel doping.

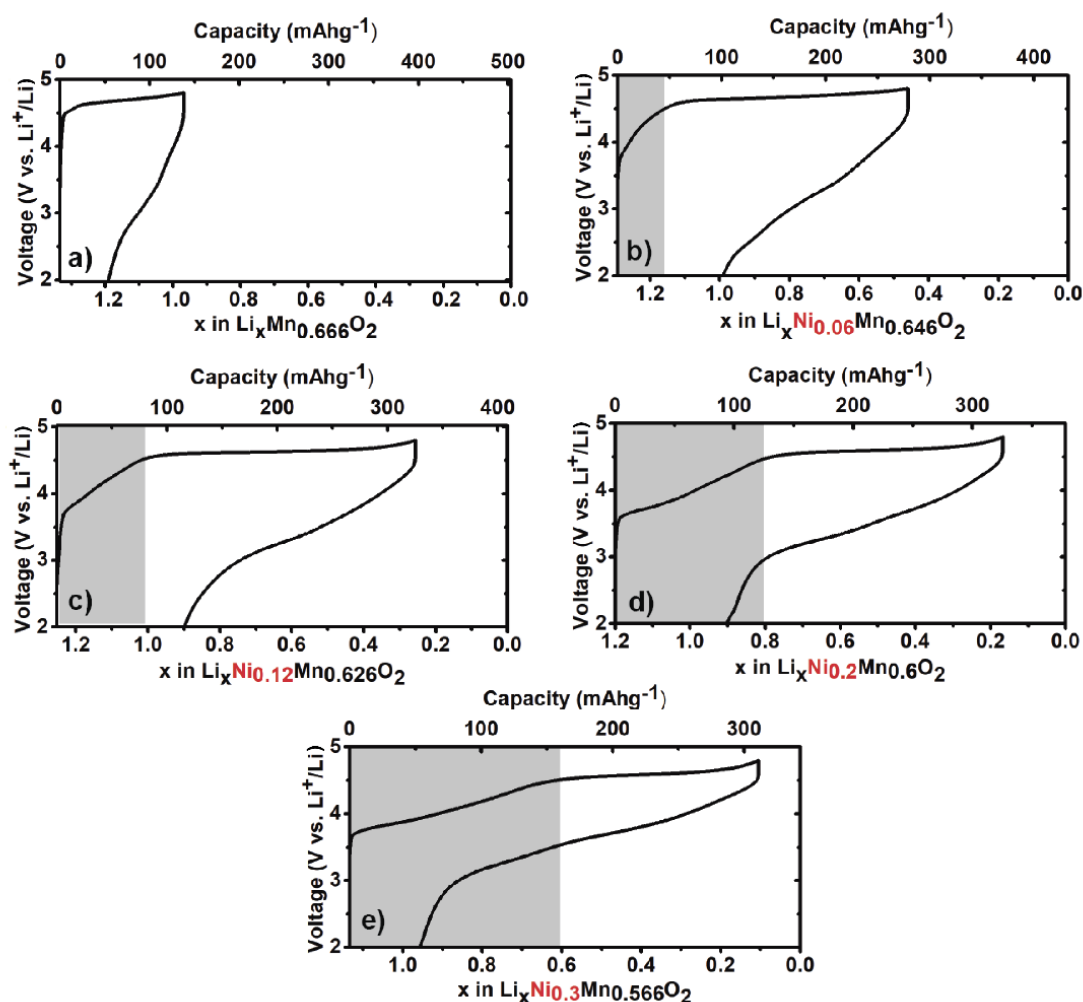


Figure 4.5 First cycle galvanostatic load curves for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (a), $\text{Li}_{1.29}\text{Ni}_{0.06}\text{Mn}_{0.64}\text{O}_2$ (b), $\text{Li}_{1.25}\text{Ni}_{0.12}\text{Mn}_{0.62}\text{O}_2$ (c), $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (d) and $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (e). The grey-shaded regions represent the theoretical capacities expected for each material, based on the electrochemical activity of the redox couple $\text{Ni}^{2+}/\text{Ni}^{4+}$.

The extension of this 'sloped' region, already attributed in the previous chapter to the oxidation of nickel from Ni^{2+} toward Ni^{4+} , appears to be in good agreement with the amount of lithium (i.e. charge) that would be extracted accounting for solely the nickel redox activity (shaded regions) discussed earlier. Hence, as expected, $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ does not show any pre-plateau region whilst the $\text{Ni} = 0.3$ substituted oxide presents more than 150 mAhg^{-1} . The high potential plateau varies in length for the different materials and for all the samples it does tend to curl up towards the end, before hitting the upper cut-off at $4.8 \text{ V vs. Li}^+/\text{Li}$.

During the first discharge, none of the materials show the presence of a reversible plateau, indicating a difference in the thermodynamic pathways followed during the extraction (charge) and insertion (discharge) of lithium ions from/in the lattice of each sample, as already observed for the $\text{Ni} = 0.2$ substituted oxide.

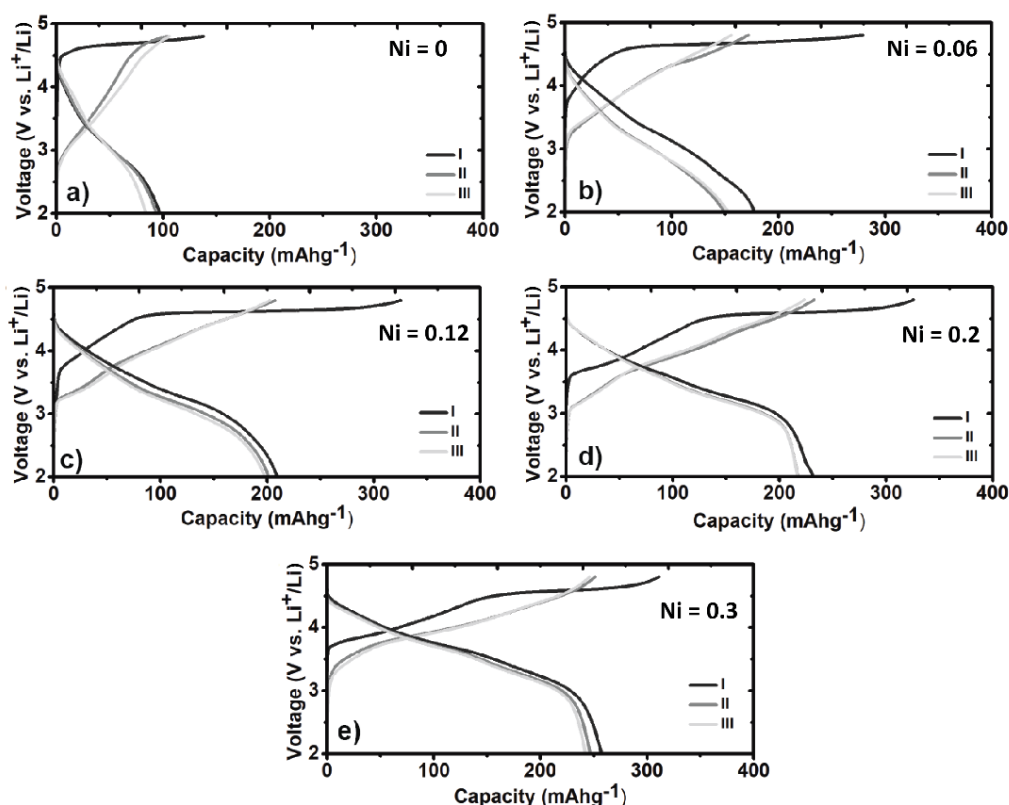


Figure 4.6 Single centred curves for the first three cycles of $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (a), $\text{Li}_{1.29}\text{Ni}_{0.06}\text{Mn}_{0.64}\text{O}_2$ (b), $\text{Li}_{1.25}\text{Ni}_{0.12}\text{Mn}_{0.62}\text{O}_2$ (c), $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (d) and $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (e), reported versus specific capacity.

Despite having been discussed in several previous works^{5,20} it is important to stress that no electrochemical activity is expected for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ since manganese has already an oxidation state of +4. As well no extraction of charge beyond the nickel redox activity would be foreseen for the other materials. The presence of the high plateau is then due to different electrochemical processes with respect to the conventional transition metal center redox activity.

The behavior of the potential during the charge appears to dramatically change for all the samples from the second cycle, as shown in Figure 4.6, in which the plateau region completely disappears, although the extracted charge still goes far beyond the nickel activity, while the discharge profiles do not seem to undergo the same reshaping process.

In the case of the low nickel substituted materials an important drop in capacity and average potential for both charge and discharge is already visible in the second and third cycles. The high nickel content materials instead (i.e. the $\text{Ni} = 0.2$ and $\text{Ni} = 0.3$ Figure 4.7 d and e) show a very stable cycling with minimal losses in capacity and average working potential. The good capacity retention over multiple cycles for the $\text{Ni} = 0.2$ and $\text{Ni} = 0.3$ substituted materials is proved as well in Figure 4.7 in which the cyclability for all materials over 100 cycles at a rate of 50 mAg^{-1} is reported, together with the coulombic efficiencies, given as the ratio between the capacity values displayed over discharge and charge per each cycle. For all the materials the first cycle presents the lowest coulombic efficiency value probably due to the presence of irreversible processes such as the gas loss during the first charge. The coulombic efficiencies appear to quickly improve from the first cycle values, around 60-70%, to values higher than 98% within the first five cycles. However, with this regard $\text{Li}_{1/33}\text{Mn}_{0.66}\text{O}_2$ and $\text{Li}_{1.29}\text{Ni}_{0.06}\text{Mn}_{0.64}\text{O}_2$ (Figure 4.7 a and b) are an exception, showing an initial loss in efficiency to then increase again from around the 10th cycle onwards.

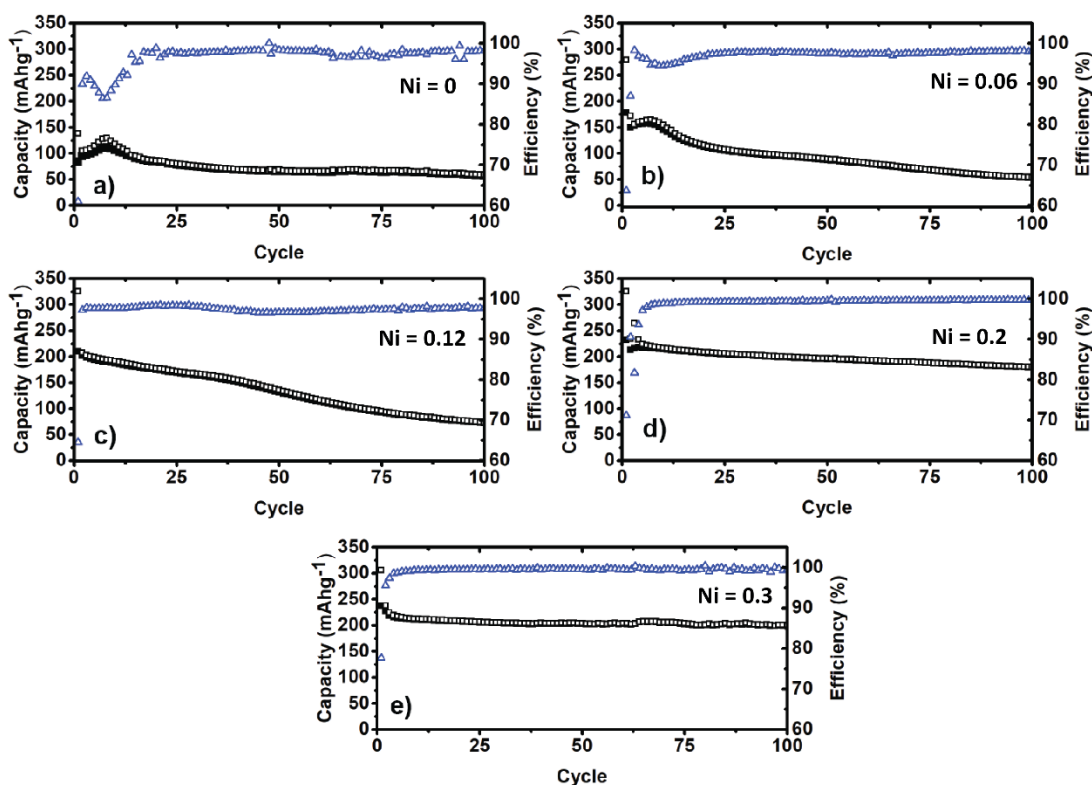


Figure 4.7 Galvanostatic cycling performance over the first 100 cycles in charge (white squares) and discharge (black squares) for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (a), $\text{Li}_{1.29}\text{Ni}_{0.06}\text{Mn}_{0.64}\text{O}_2$ (b), $\text{Li}_{1.25}\text{Ni}_{0.12}\text{Mn}_{0.62}\text{O}_2$ (c), $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (d) and $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (e). The coulombic efficiency as the ratio $Q_{\text{discharge}} / Q_{\text{charge}}$ is also reported (blue triangles).

It seems that when the nickel substitution increases to $x = 0.12$ a significant improvement in terms of the electrochemical performance is seen suggesting that there has been a change in the nature of the charge storage mechanism.

The capacity retention shows a general trend whereby the amount of nickel present in the material gives rise to higher capacities and more stable cycling with exceptionally stable performance seen for the materials where $x > 0.2$ material. Particularly interesting is the cycling stability of the $\text{Ni} = 0.3$ material (Figure 4.7 e) which is even more stable than the $\text{Ni} = 0.2$ (Figure 4.7 d) with cycling, whereas for all the other materials (Figure 4.7 a, b and c) it is possible to observe a dramatic and progressive loss in the values of specific capacity displayed as they get closer to 100 cycles.

4.5 Gas Evolution During the First Cycle

Gas evolution for the Ni = 0.2 composition was presented in the previous chapter. Here Operando Electrochemical Mass Spectrometry was performed on the whole set of samples to get an insight on the origin of the extra-capacity that is observed during the first cycle (shaded regions Figure 4.8).

The experimental set up employed was identical to the one used in the previous chapter.

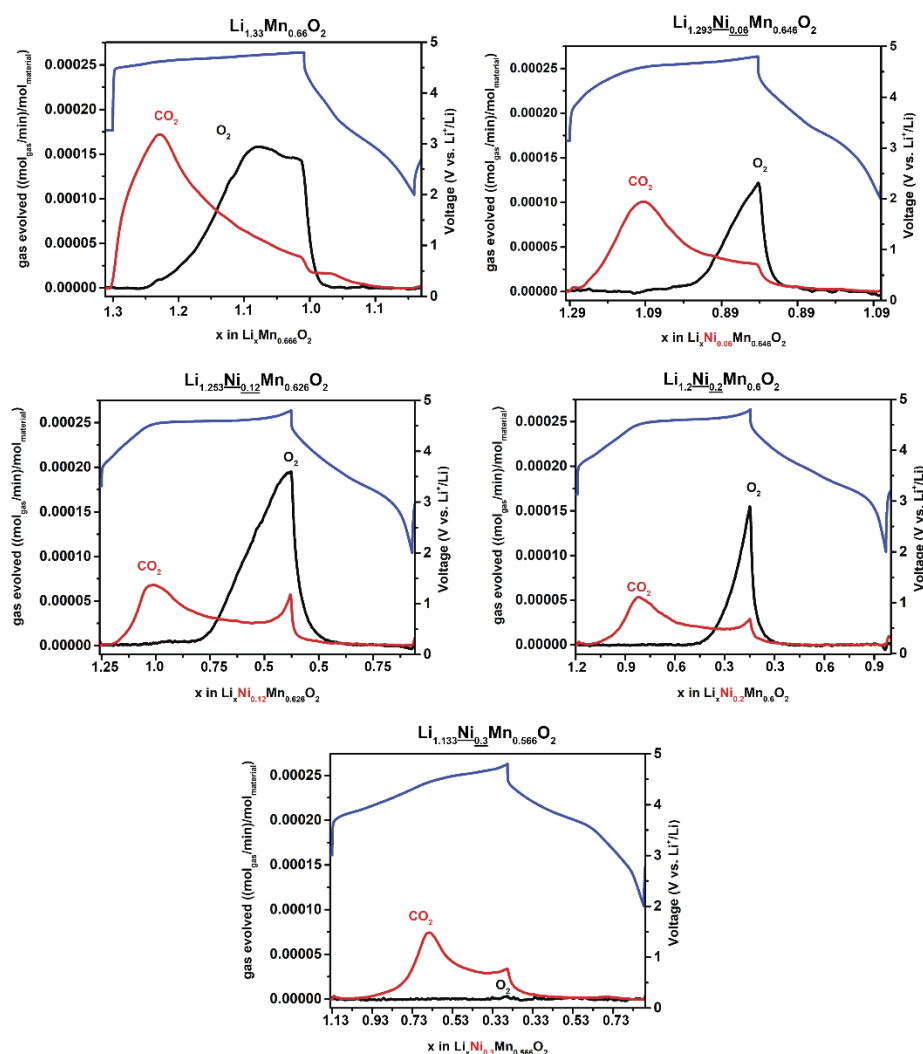


Figure 4.8 OEMS analysis of the nickel substituted materials $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$, for $x = 0, 0.06, 0.12, 0.2$ and 0.3 reported in panels (a to (e) respectively. In each panel are shown the galvanostatic curve during the first cycle (blue line), the oxygen trace (black line), the carbon dioxide trace (red line) of a different material. The left y-axis represents the electrode potential while the right y-axis the gas release rate expressed as moles of gas per minute per mole of active material, both axis reported as function of lithium

equivalents, x-axis. Argon was used as carrier gas with a flux rate of 0.7 mL/min and the electrode was cycled against metallic lithium at a rate of 15 mAg⁻¹ between 2 and 4.8 V vs. Li⁺/Li for all the materials. The electrolyte employed was a 1M solution of LiPF₆ in PC.

In Figure 4.8, the traces for the gases evolved during cycling synchronized with their respective galvanostatic curve are shown, for each material.

CO₂ and O₂ were the only gaseous species detected for all the samples and a clear trend appears from Figure 4.8, with a progressively lower amount of gas released as the amount of dopant nickel increases.

CO₂ is detected first in all cases, peaking at the beginning of the high potential plateau (around 4.5 V vs. Li⁺/Li) region, especially in the case of the Ni = 0 and 0.06 materials (Figure 4.8 panels (a and (b red line), and progressively decreasing until the end of the charge. A second sharp and more pronounced peak is observed in the CO₂ traces of the Ni = 0.12, 0.2 and 0.3 materials (Figure 4.8 panels (c to (e red line) towards the end of the 4.5 V plateau region. Overall, the amount of CO₂ released over the first charge decreases in line with the increase in nickel substitution but is never eliminated and differently from the behaviour observed for the spinel LiNi_{0.5}Mn_{1.5}O₄ (Appendix, chapter 3) it is present over the whole first charge in all the studied materials.

O₂ appears to be released in a spike-like fashion that reaches its maximum towards the end of charge in all the materials. The spike shape in the oxygen trace becomes progressively sharper with the nickel content from Ni = 0 to Ni = 0.2 (Figure 4.8 panels (a to (d black line). Additionally, the release start point shifts towards the end of the plateau as more nickel is substituted and the overall released quantity decreases from Ni = 0 to Ni = 0.3. It is important to remark the almost complete suppression of O₂ and a strong reduction in the amount of detected CO₂ in the case of the high Ni substitution Li_{1.133}Ni_{0.3}Mn_{0.566}O₂ (panel (e Figure 4.8) in comparison to the other materials. This result is suggestive of the important role played by nickel as in stabilizing the oxide structures at high potentials by reducing the oxygen loss process.

It is worth remembering that for the layered oxides studied in this chapter the amount of detected gases during cycling was well above the amount detected in the case of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ () cycled in identical conditions. This allows us to rule out a major contribution in gas loss due to the decomposition of the electrolyte.

To get a clearer idea of the differences between the materials in terms of the amounts of released gases the traces of CO_2 and O_2 evolved for each material were carefully integrated to quantify the moles of evolved gas per mole of material. The amount of charge (i.e. electrons) extracted in relation to the gas evolution was calculated considering for CO_2 the reactions between highly reactive reduced oxygen species in the materials and the PC electrolyte, Equation (4.1), and for O_2 considering a process of pure oxygen loss at high potential, as already shown for the $\text{Ni} = 0.2$ case in Chapter 3, Equation (4.2)



The results obtained from the integration of the gas traces for the different materials are reported in Table 4.5

Table 4.5 Evaluation of total amount of CO_2 and O_2 released over the first cycle for the Ni-substituted layered oxides. The specific capacity accounted for the moles of gas lost is reported between brackets.

Material	O_2 (moles of gas evolved per formula unit)	CO_2 (moles of gas evolved / formula unit)
$\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$	0.0323 (44.55 mAhg^{-1})	0.039 (55 mAhg^{-1})
$\text{Li}_{1.29}\text{Ni}_{0.06}\text{Mn}_{0.64}\text{O}_2$	0.0186 (24.91 mAhg^{-1})	0.0342 (45.80 mAhg^{-1})
$\text{Li}_{1.25}\text{Ni}_{0.12}\text{Mn}_{0.62}\text{O}_2$	0.0741 (96.65 mAhg^{-1})	0.0459 (60 mAhg^{-1})
$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$	0.0241 (30.38 mAhg^{-1})	0.0294 (35 mAhg^{-1})
$\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$	0.0018 (2.18 mAhg^{-1})	0.0307 (37.1 mAhg^{-1})

It appears evident from the results of the integration that the two species CO_2 and O_2 follow two different behaviours as the nickel content in the structure is increased.

The quantity of CO_2 evolved tends to remain quite stable from $\text{Ni} = 0$ to $\text{Ni} = 0.12$ with a slight decrease in the case of the higher substituted materials $\text{Ni} = 0.2$ and 0.3 although it never gets completely eliminated. Conversely, O_2 appears to peak going from the parent compound $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ to the $\text{Ni} = 0.12$ substituted one to then steeply drop until almost disappearing in the case of $\text{Ni} = 0.3$.

The different behaviour of the two gases might be rationalized looking at the reactions associated with the formation of CO_2 , Equation (4.1), and O_2 , Equation (4.2), in which carbon dioxide is originated from the reaction of highly reactive superoxide species, generated from the oxidation of oxygen in the lattice during charge, and the electrolyte (PC), whilst molecular oxygen is associated with a process of direct oxygen loss from the lattice of the materials. This implies that the nickel doping plays a fundamental role in the stabilisation of the lattice preventing oxygen release as a result of the oxygen redox process at high voltage values against Li^+/Li .

An even clearer picture of the important effect played by nickel in terms of limiting the gas release can be obtained from Figure 4.9 in which for each material a bar chart shows the charge associated with CO_2 (orange bar) and O_2 (grey bar) loss relative to the total charge due to gas release (yellow bar) and the total amount of charge extracted over the first charge (blue bar). Looking at the trends of the yellow and blue bars is clear that for the low and no nickel doping materials the charge extracted and associated with gas release represents 50% or more of the overall capacity displayed. At the same time as the nickel content increases the charge related to gas loss firmly drops.

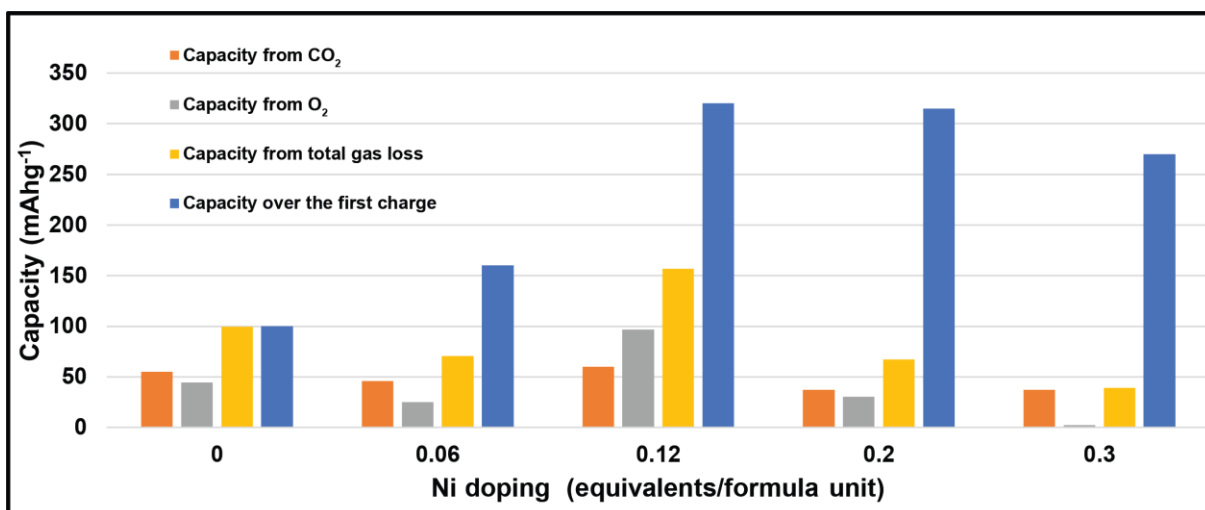


Figure 4.9 Different contributions to the gas loss compared with the overall charge extracted from the materials.

As already seen for the Ni = 0.2 substituted material in the previous chapter it can be noticed that the amount of charge associated with the total gas loss (yellow bars, Figure 4.9) added to the expected capacity from the Ni redox activity (shaded regions Figure 4.5) does not account for the overall charge extracted during the first charge, indicating the presence of oxygen redox activity as well for the other compounds in the series.

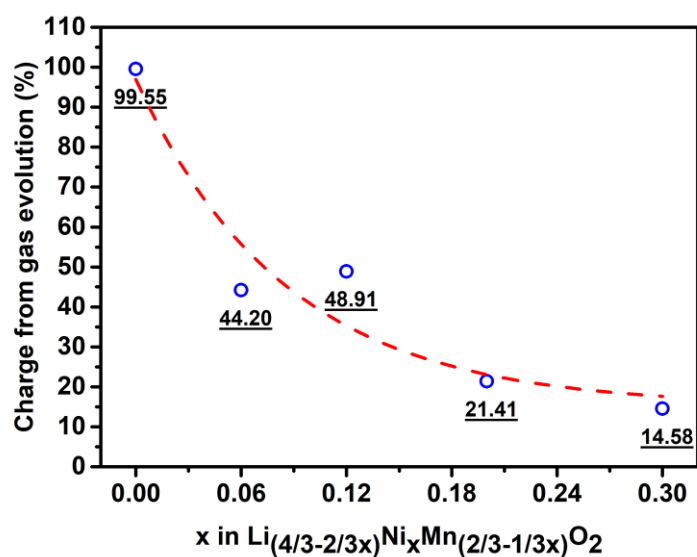


Figure 4.10 Percentage of the first charge specific capacity due to gas evolution.

Only in the case of the parent compound $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ it can be observed that actually all the capacity exhibited over the first charge is accounted for by gas loss, in good agreement with previous studies^{5,21} in which it was concluded that the electrochemical activity in this material was prevalently associated with gas loss during the first charge followed by the activation of Mn III/IV redox couple in the subsequent cycles.

By plotting the ratios between the charge related to gas loss and the overall charge extracted in the first charge against the content of dopant in the structure a striking trend is attained (figure 1.6). The trend shown in Figure 4.10 is even more explicative than what observed in Figure 4.9 confirming the idea of the role played by nickel in the suppression of oxygen loss for these materials.

4.6 Spectroscopic Characterisation

Soft X-ray absorption spectroscopy

X-ray absorption spectra were collected at the oxygen K-edge, manganese L-edge and nickel L-edge for three members of the series, $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$, $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$. The spectra were collected ex-situ at different points over the first cycle and are reported in Figure 4.11, Figure 4.12, Figure 4.13.

O-SXAS

In Figure 4.11 the oxygen SXAS spectra are reported which have been collected for the samples at different points over the first cycle. As discussed previously, the oxygen SXAS K-edge is characterised by the presence of a pre-edge region, between 528 and 534 eV (dashed red line, Figure 4.11), that corresponds to the transitions between the oxygen 1s orbital and the oxygen 2p-transition metal 3d hybridized orbitals sitting right above the Fermi energy²². The two peaks at 530 and 532.5 eV are due to the transition metals d-orbital splitting due to the crystal field and spin exchange effects^{22–24}. The main edge region, >534 eV, corresponds to transitions from the oxygen 1s and the oxygen 4s-4p orbitals, well above the Fermi energy. The pre-edge region is of high interest since it is

sensitive to the generation of new states in the conduction band near the Fermi energy that would result in higher number of transitions during the absorption measurement, hence a higher pre-edge area. From the OEMS results it would be expected a progressively higher oxygen redox activity as more nickel is substituted in the parent compound lattice of $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$.

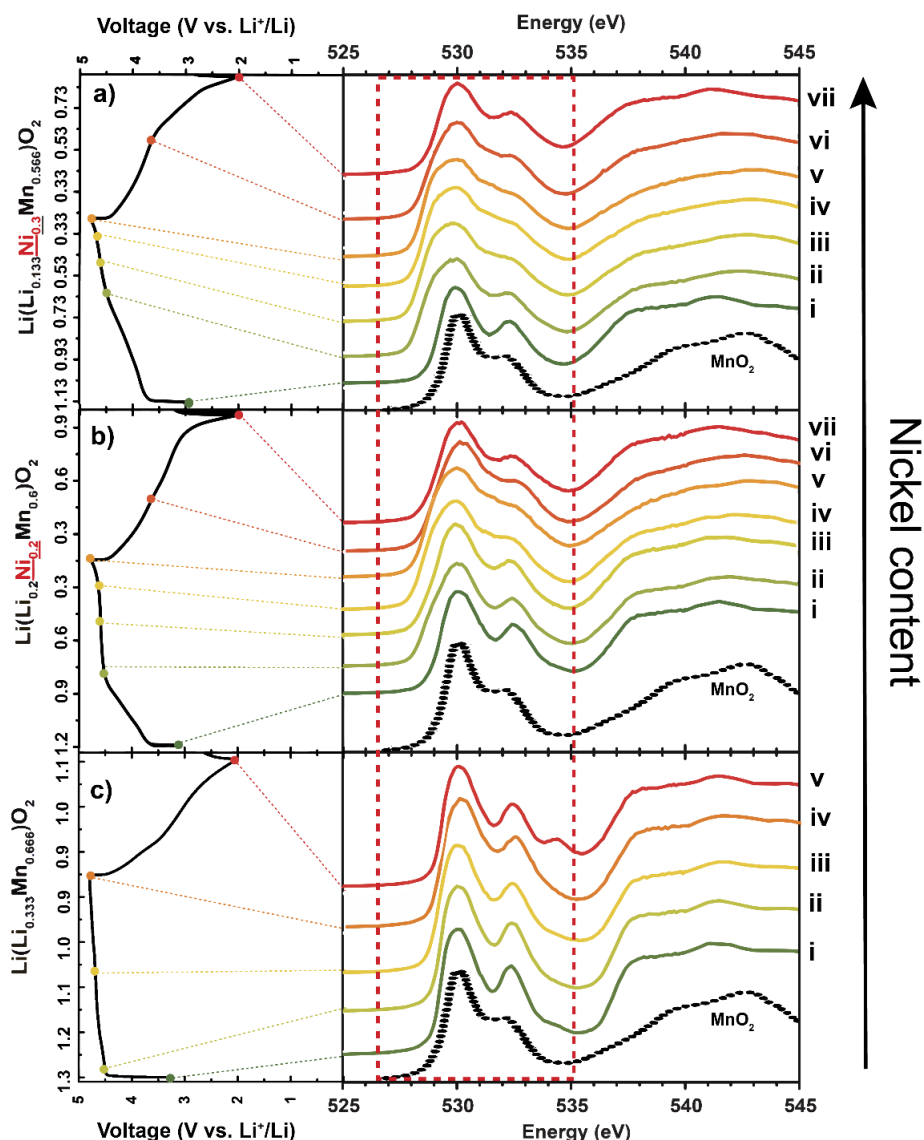


Figure 4.11 Oxygen K-edge spectra collected at different points over the first galvanostatic cycle for $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (panel a), $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (panel b) and $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (panel c). all the materials were cycled at 50 mAg^{-1} between 2 and 4.8 V vs. Li^+/Li

In fact, in the case of $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ no change should happen at the oxygen K-edge over the first cycle since all of the extracted charge can be accounted for oxygen-loss (Figure 4.9). At the same time, in the case of $\text{Ni} = 0.3$ material an even higher increase in the area of the pre-edge oxygen SXAS is expected with respect to the $\text{Ni} = 0.2$ material. Looking at the SXAS spectra for these three materials it is possible to observe that the forecasted behaviours of the absorption edges are confirmed in the experimental data. The pre-edge does not change over the first cycle in the case of $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (Figure 4.11c, spectra i-v) although a shoulder centred at 534.5 eV appears in spectrum v corresponding to the end of discharge in the first cycle. The shoulder, centred at 534 eV, can be associated with the presence of oxygen on the surface of the material as Li_2CO_3 as already reported in previous works^{25,26} and corresponds to the transition to the π^* (C=O) orbital. As it can be observed, the shoulder is not present in the spectra of the fully discharged nickel substituted materials.

In the case of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (Figure 4.11b, spectra i-vii) the pre-edge gradually changes in shape going from the pristine to the end of charge with a progressive decrease in the depth of the well between the pre-edge peaks centred at 530 and 532.5 eV. The trend is inverted in the discharge (spectra vi-vii) where the pre-edge decreases in area recovering at the end of the first cycle a similar shape to the pristine one

The overall trend respects and confirms the results presented in the previous chapter for the same material although in this case a higher number of points across the first cycle and so a more detailed characterisation of the absorption edge was collected.

As for $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (Figure 4.11a, spectra i-vii) a clear difference in the pre-edge trend is evident, with respect to the $\text{Ni} = 0.2$ substituted oxide. An important increase in the pre-edge area occurs passing from the pristine (i) to the end of sloped region (ii), suggesting the presence of more mixing between the oxygen and nickel valence orbitals in comparison to the $\text{Ni} = 0.2$ material. The pre-edge area continues to increase until the end of charge, spectrum v, to then reverse the trend as for the $\text{Ni} = 0.2$ case and recover

a similar shape and area to the one for the pristine material, at the end of the discharge (vii). Comparing the Ni = 0.2 and 0.3 materials (Figure 4.11b and a respectively) the latter one shows a higher increment in the pre-edge area over the charge (spectra i-v). This observation points towards a picture in which in the higher nickel substituted material is present a higher degree of covalence in of the bonding orbitals that would favour a stabilisation of the oxygen redox with respect to the oxygen loss, in good agreement with what expected from the OEMS results.

It is worth noticing that the results presented in this chapter were attained at Spring 8 synchrotron (Japan) facility whilst the ones presented in Chapter 3 had been collected at the ALS synchrotron facility (USA) demonstrating the substantial reproducibility of the data.

Mn-SXAS

In Figure 4.12 the manganese L-edges are reported for the same three materials presented above in the oxygen edge absorption data. In this case the collection of the L edge spectra was preferred to the more conventional metal K-edge (XANES) due to the higher sensitivity of the spectral weight and shape with respect to the oxidation state of the transition metal. The higher sensitivity is due to the longer lifetime of the states probed in the soft X-ray region which narrows down the line width in emission allowing for better resolved features in the measured spectrum²⁴. In a typical L-edge spectrum there are usually two peaks that can present fine features like shoulders or peak splitting. The peaks arise from the transitions between the metal 3p and 3d orbitals and their shapes is the result of multiplets interactions. The peak located at lower energy is due to the 3p^{3/2} to 3d transition and is denominated L_{III}, whilst the peak located at higher energies is due to the 3p^{1/2} to 3d transitions and is denominated L_{II}. Because of the high complexity of the interactions determining the peaks shape, to evaluate the oxidation states of the studied transition metal it is necessary to employ the spectra of standard materials in which the metal has known oxidation state.

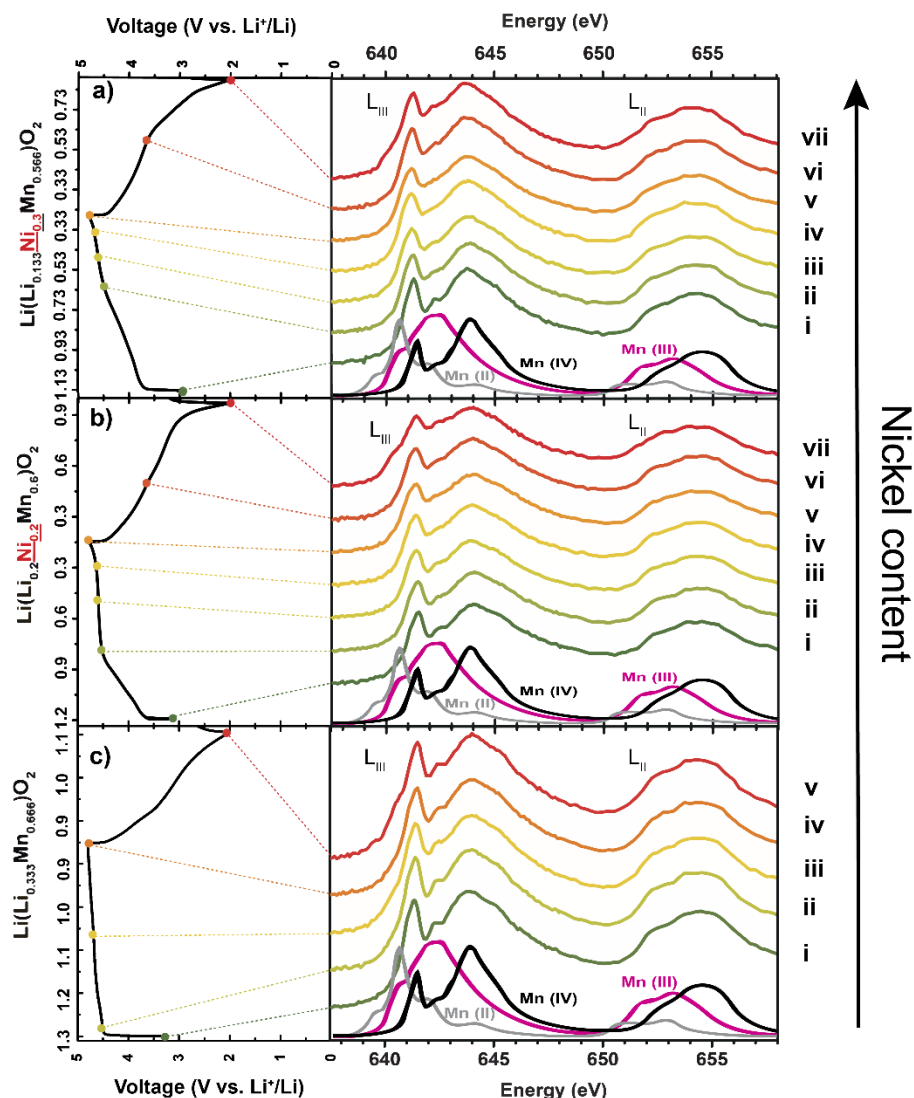


Figure 4.12 manganese L-edge spectra collected at different points over the first galvanostatic cycle for $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (panel a), $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (panel b) and $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (panel c). all the materials were cycled at 50 mA g^{-1} between 2 and 4.8 V vs. Li^+/Li

In the case of the manganese edges reported in Figure 4.12, the L_{III} peak is centred around 643 eV whilst the L_{II} peak is centred around 650/655 eV. For the analysed compounds the oxidation state of manganese is expected to be +4 over the full cycle, with the exception of $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ in which the comparison of manganese +3 at the end of the first discharge would confirm the idea of the activation of the redox couple Mn III/IV after the first charge, in which the charge is completely due to oxygen-loss. It is possible to observe that for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (Figure 4.12a) the manganese edge in the pristine

material (i) has the typical shape of the metal in the +4 oxidation state. The shape is maintained over the first cycle with the presence of an overall broadening of the L_{III} at the end of discharge (v) which may be indicative of the formation of some Mn^{3+} , although no dramatic change of the peaks shape is observed and the oxidation state appears to stay mostly +4 in the bulk of the material.

A similar trend is observed for the nickel substituted materials $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ and $Li_{1.13}Ni_{0.3}Mn_{0.56}O_2$ (Figure 4.12b and c) with no appearance of Mn^{3+} or Mn^{2+} confirming that manganese does not partake in the redox processes happening during the first cycle of these materials.

Ni-SXAS

The nickel L-edge was collected for $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ and $Li_{1.13}Ni_{0.3}Mn_{0.56}O_2$ at different points of charge over the first cycle between 855 and 875 eV. The spectra are reported in Figure 4.13, panels a and b. differently from manganese, nickel was expected to go from +2 in the pristine (i) to +4 oxidation state at the end of the sloped region (ii) present before the high voltage plateau in both materials. In both materials, it is possible to observe a dramatic change in the shape of the absorption edges going from spectrum i to spectrum ii but while spectrum i possess the typical shape of Ni^{2+} L-edge, spectrum ii does not match the shape of the reference Ni^{4+} edge. At point ii, nickel appears to have an oxidation state between +2 and +3 which keeps increasing across the whole charge, although never reaching a full +4 state in both materials. In the discharge, the edge shape reverses the trend going back to the pristine Ni +2 one (spectra vii).

Comparing the shapes of the spectra at the end of charge for the two materials, nickel looks to be more oxidized towards a +4 oxidation state in the case of Ni = 0.3 material (Figure 4.13, spectra v). This observation is in good agreement with what observed for the oxygen SXAS spectra (Figure 4.11), strengthening the idea of an increased stability of the lattice at high voltage values as the nickel content increases.

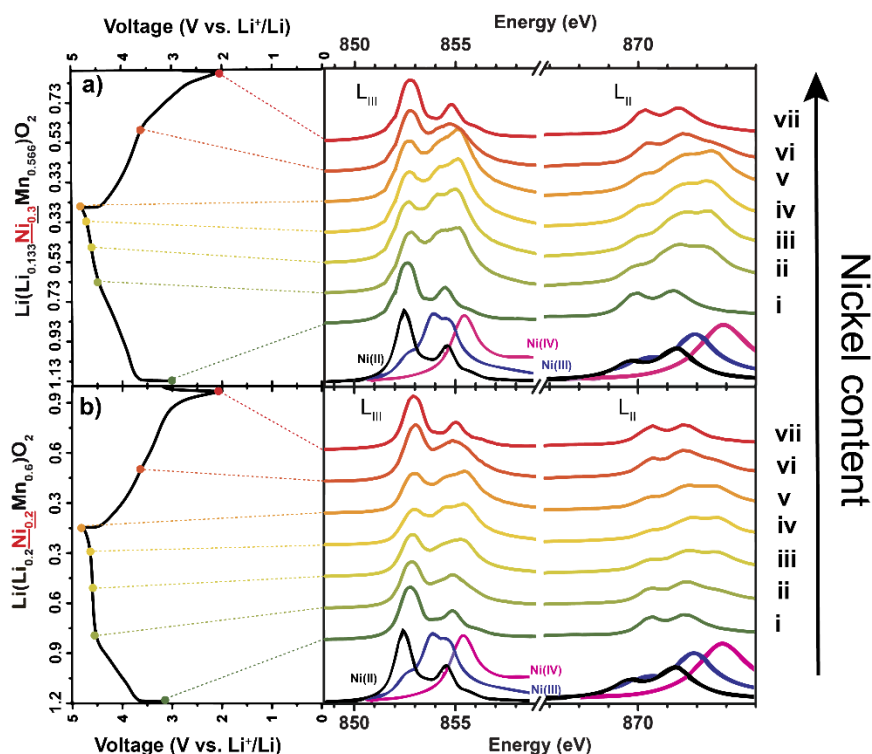


Figure 4.13 nickel L-edge spectra collected at different points over the first galvanostatic cycle for $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (panel a) and $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (panel b). All the materials were cycled at 50 mA g^{-1} between 2 and 4.8 V vs. Li^+/Li

Resonant inelastic X-ray spectroscopy

RIXS spectra were also collected on the samples measured in the SXAS experiment to get a better understanding on how $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ and $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ compared with respect to the already studied $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and whether the nature of the new states formed on oxygen in the case of the $\text{Ni} = 0.3$ substituted oxide had the same nature of the ones already observed for the $\text{Ni} = 0.2$ substituted material. As in the previous chapter, the RIXS experiment were performed with an excitation energy of 531.5 eV, corresponding to the top of the absorption peak in the pre-edge region for the oxygen K-edge.

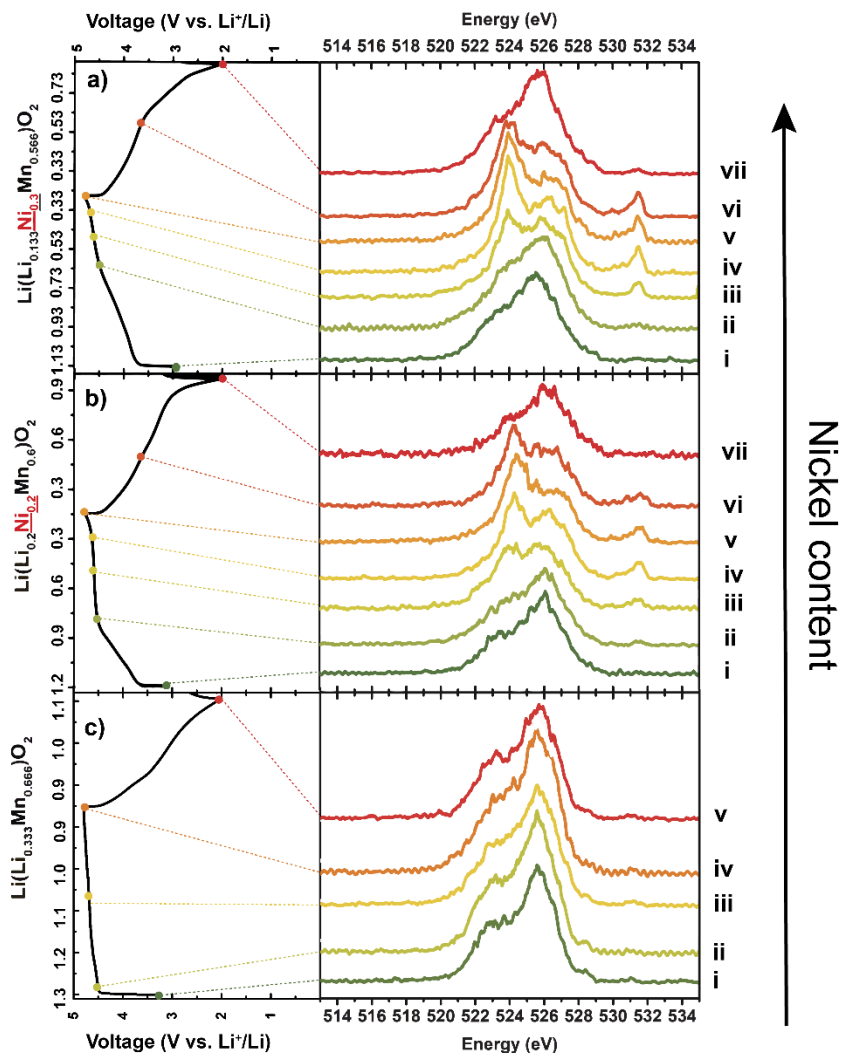


Figure 4.14 RIXS spectra collected ex-situ on $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (panel a), $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (panel b) and $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (panel c) at different states of charge with an excitation energy of 531.5 eV.

From Figure 4.14-b it is possible to observe that the behaviour of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ is in good agreement with what already presented in the previous chapter, confirming the good reproducibility of the data. The emission spectra do not appear to change in shape between the pristine and the end of the sloped region (spectra i and ii, panel b), whilst a substantial reshaping is observed over the plateau with the simultaneous appearance of the elastic peak centred at 531.5 eV (spectra iii to v). A very similar and even more pronounced behaviour is observed in the case of $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ (Figure 4.14a) confirming that for this material as well the nature of the new states observed over the plateau in the oxygen K-edge SXAS data is the same of the ones observed for

$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$. Hence new localized electron-hole states are formed on oxygen as $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ is charged over the plateau supporting the idea that oxygen redox activity is present in this material as it was for the $\text{Ni} = 0.2$. The RIXS spectra for both $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ and $\text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.56}\text{O}_2$ appear to recover a similar shape to the pristine ones during the discharge of the electrodes (spectra vi and vii, panels a and b) indicating the reversible nature of the localized electron-hole states.

The RIXS spectra for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ do not appear to change over the whole cycle with no comparison of elastic peak. This result is of high relevance as it demonstrates that $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ works through an oxygen-loss mechanism rather than an oxygen-redox one, without formation of localized holes on oxygens. As well, being RIXS a bulk sensitive technique for our materials, it confirms that the shoulder observed at the end of the discharge in the oxygen K-edge absorption spectra for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ is probably due to the formation of a carbonate layer at the surface of the particle during the discharge.

4.7 Discussion

The results attained from OEMS, SXAS and RIXS analyses evidenced the presence of oxygen redox activity in the nickel substituted samples whilst confirming that $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ works prevalently through oxygen loss over the first charge.

Trying to unravel the role of nickel in the working mechanisms of the materials investigated in this chapter STEM and ^6Li MAS-NMR analysis were performed on the parent compound $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ and on the most representative member of the nickel substituted series $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ to investigate the structural evolution in these samples during the charge.

STEM images in annular bright field mode and ^6Li MAS-NMR spectra were collected on both materials for the pristine and the charged to 4.8 V vs. Li^+/Li samples (Figure 4.15).

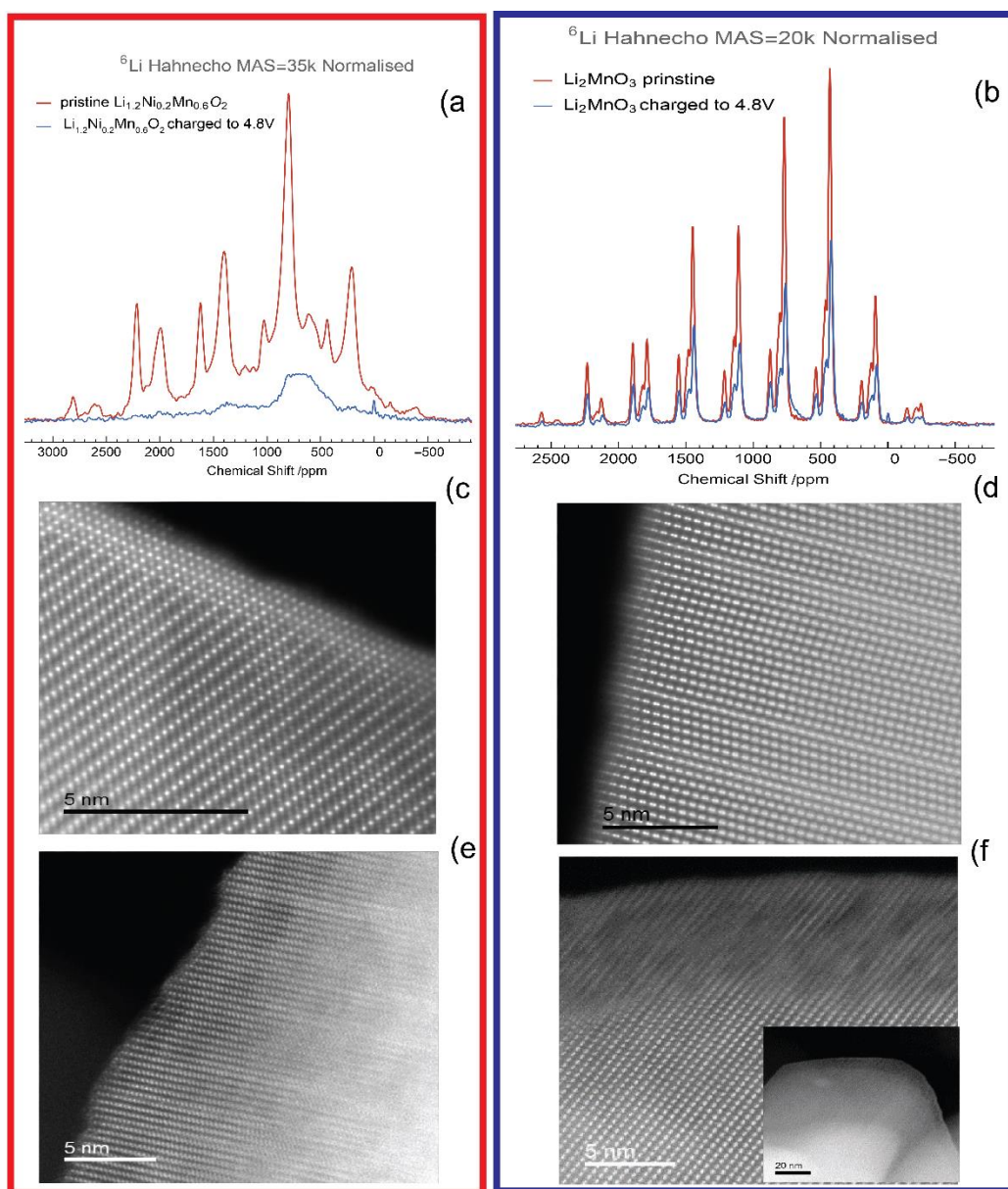


Figure 4.15 ^6Li -MAS NMR and TEM images for $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (red frame) and $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (blue frame). In panels (a) and (b) are reported the NMR spectra for the pristine (red lines) and charged to 4.8 V vs. Li^+/Li (blue lines) materials. Panels (c) and (d) show the TEM images for the pristine materials' particles whilst (e) and (f) the images for the charged to 4.8 V vs. Li^+/Li materials. TEM images were acquire with the help of Dr. Juan Lozano whilst MAS-NMR spectra were registered with the help of Dr Liyu Jin.

The NMR spectrum for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ (Figure 4.15-b) decreases in intensity between the pristine and the charged sample, as expected for a de-lithiated material in which less lithium ions will be present, although do not appear to change in shape with no presence of new peaks (i.e. new lithium environments). Conversely, the spectra for the nickel substituted $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ dramatically change passing from the pristine to the charged

sample with a decrease in intensity and a complete loss of peaks shape. As for the TEM images both the pristine materials show a uniform layered crystalline structure across the particles from the surface to the bulk whilst in the case of the charged samples it is possible to notice the formation of a 10-nanometer-thick disordered shell (Figure 4.15-f) surrounding the $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ sample particle whilst structural order is maintained (Figure 4.15-e) on the surface for the nickel substituted sample.

Since no new lithium environments are observed in the NMR spectrum for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ at the end of the charge it is reasonable to conclude that the amorphous shell formed around the particle is completely depleted of lithium ions and that the NMR signal is coming from the crystalline core that has remained intact pointing towards a core-shell structure model in which the amorphous de-lithiated shell is surrounding a crystalline core of the pristine material.

For the nickel substituted material a great change is observed in the NMR spectrum as the lithium is almost completely removed from the material resulting in a significant signal reduction. The remaining signal appears to contain no peaks from the pristine material suggesting that the charge product is a new phase and that the cathode material has homogeneously been involved in the reaction. The charged sample suggests that although at the surface some cation migration has occurred forming a spinel like structure at the surface a general ordered material is seen throughout.

This model suggest that not only would a much lower amount of charge extracted from $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ in comparison with the $\text{Ni} = 0.2$ material (Figure 4.7) but also the prevalent oxygen loss process over the oxygen redox observed in the case of the parent compound (Figure 4.8, Table 4.5 and Figure 4.9).

The highly lithium depleted shell in $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ would probably lead to an environment of under-coordinated oxygens as was recently reported in a similar material elsewhere²⁷.

The oxygen loss mechanism would be mitigated in the case of the nickel substituted materials compared to the oxygen redox process thanks to the presence of nickel that would form a percolating network for the conductivity of lithium ions across the bulk of the materials. This idea is partially backed by the observation made in the nickel L-edge SXAS spectra for the Ni = 0.2 and Ni = 0.3 materials (Figure 4.13) in which it appears that the nickel is not fully oxidized to a +4 oxidation state over the sloped region meaning that lithium ions could still surround the nickel ions over the charge in the plateau region maintaining at the same time the structural stability and forming a preferential channel for the conduction of lithium ions. The oxygen loss would then happen at the very end of charge in the Ni = 0.2 material (Figure 4.8) due to the high depletion of lithium from the structure resulting in the same under-coordinated oxygen environment postulated for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$.

4.8 Conclusions

The thorough characterisation of the $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$ series of materials (where x = 0, 0.06, 0.12, 0.2 and 0.3) through advanced techniques such as the OEMS analysis, SXAS and RIXS spectroscopies, allowed to demonstrate the crucial role of nickel in favoring the oxygen redox process over the oxygen loss one. The presence of oxygen redox with almost complete elimination of molecular oxygen loss was demonstrated for the Ni = 0.3 substituted material which also showed improved electrochemical performance and cycling stability with respect to the well-known Ni = 0.2 substituted material. Thanks to the combined use of OEMS, SXAS, RIXS, MAS-NMR and STEM was also possible to shine light on the differences in the working mechanisms of the nickel substituted samples with respect to the parent compound $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$. Thanks to a series of experimental evidence it is possible to postulate a model summarized in Figure 4.16

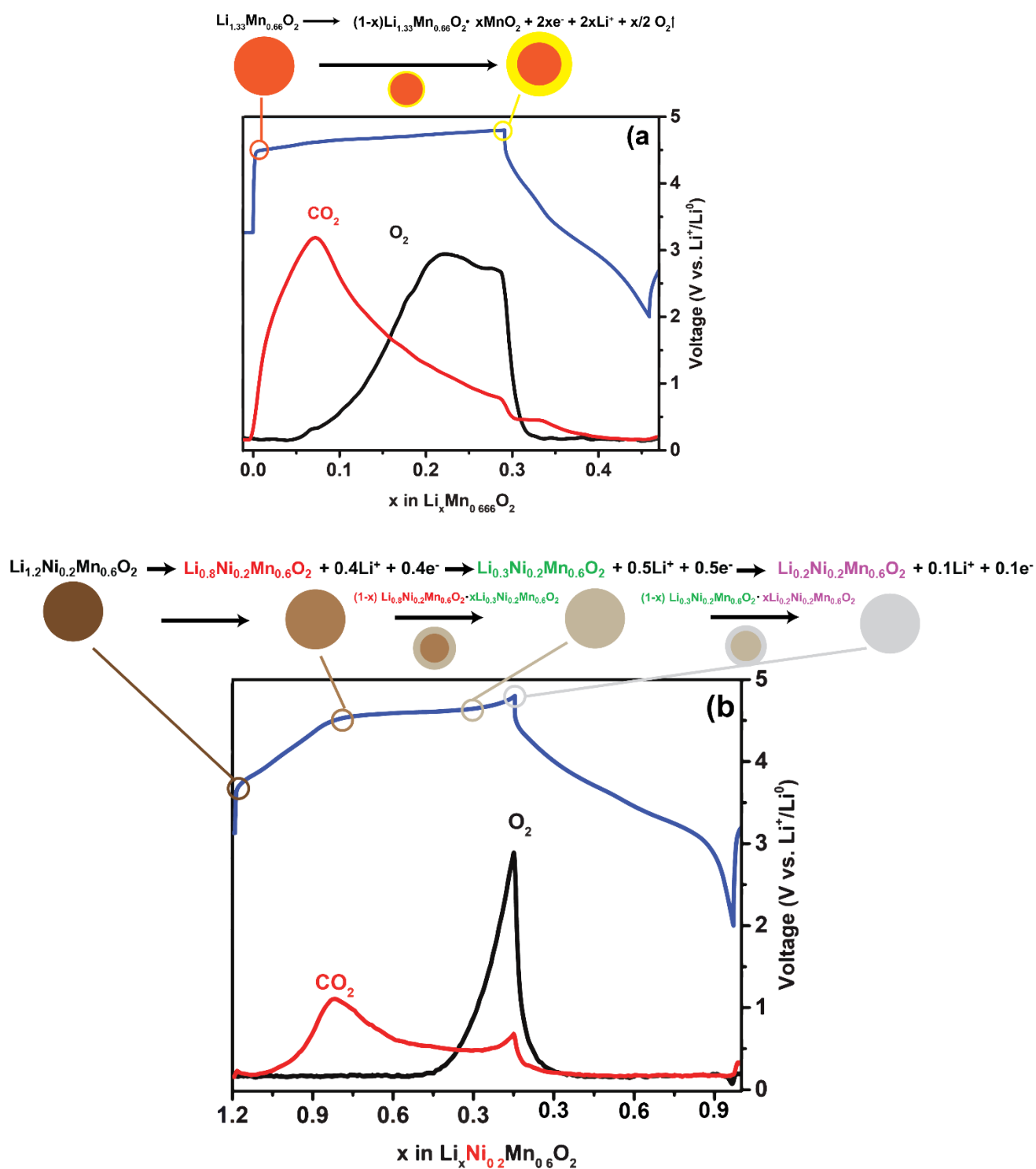


Figure 4.16 Schematics for the proposed working mechanisms of a) $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ and b) $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$.

As already mentioned in the previous paragraph the working mechanism proposed for $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$ is a core-shell model in which during the charge a two-phase system is

formed with the complete depletion of lithium from the surface layer and the loss of oxygen whilst the inner core should stay intact (Figure 4.16-a).

On the contrary, the proposed mechanism for the nickel substituted material is more articulated with the presence of three sequential processes happening over the charge. During the first part in the sloped region a one-phase process would happen with uniform depletion of lithium across the bulk of the material. In this process nickel would not be completely oxidized to +4 maintaining an environment of lithium ions that would constitute a preferential network for the conduction of lithium ions in the bulk. In the following plateau region a two-phase process would lead to the extraction of further lithium with the concomitant further oxidation of nickel towards +4 oxidation state and the oxidation of oxygen (oxygen redox) forming localized hole states appearing in the RIXS spectra (Figure 4.14).

The final process in which approximately 0.1 moles of lithium are extracted (Figure 4.16-b and Table 4.5) is prevalently due to the loss of molecular oxygen via a core-shell process similar to what observed in $\text{Li}_{1.33}\text{Mn}_{0.66}\text{O}_2$.

To conclude, it is noticed that differently from the Ni = 0.12 and 0.2 oxides, for the Ni = 0.3 substituted material it is removed less than one lithium per formula unit during the first charge. This might reduce the amount of under-bonded oxygens in the structure which we have recently shown²⁷ to play a central role in the formation of molecular oxygen that subsequently gets released from the lattice.

4.9 Appendix

BET surface area

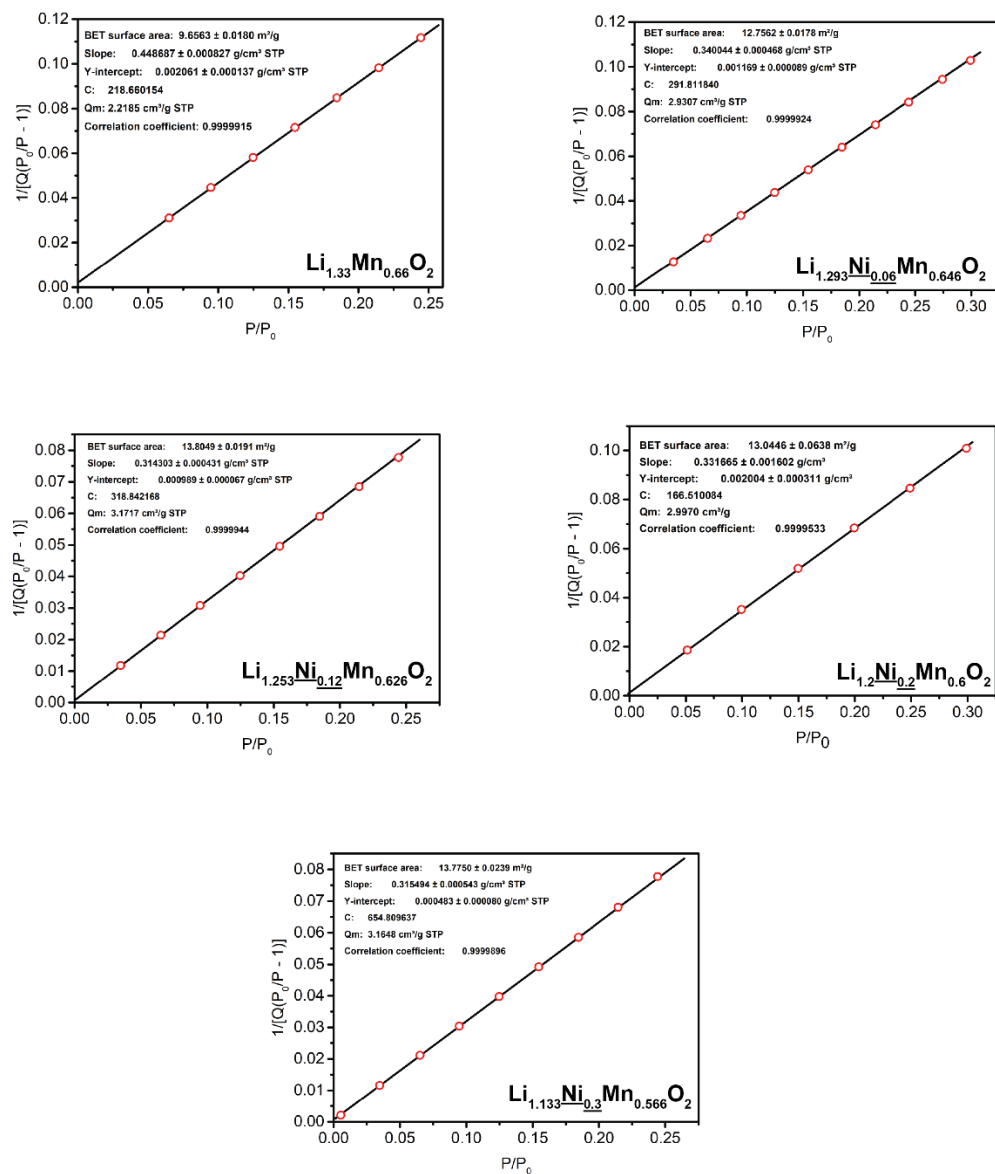


Figure 4.17 BET plots for the whole series of nickel substituted materials.

4.10 References

- 1 M. M. Thackeray, S. H. Kang, C. S. Johnson, J. T. Vaughey and S. A. Hackney, *Electrochem. commun.*, 2006, **8**, 1531–1538.
- 2 C. S. Johnson, *J. Power Sources*, 2007, **165**, 559–565.
- 3 C. S. Johnson, J. S. Kim, C. Lefief, N. Li, J. T. Vaughey and M. M. Thackeray, *Electrochem. commun.*, 2004, **6**, 1085–1091.
- 4 P. Kalyani, S. Chitra, T. Mohan and S. Gopukumar, *J. Power Sources*, 1999, **80**, 103–106.
- 5 A. D. Robertson and P. G. Bruce, *Chem. Mater.*, 2003, **15**, 1984–1992.
- 6 J. Lim, J. Moon, J. Gim, S. Kim, K. Kim, J. Song, J. Kang, W. Bin Im and J. Kim, *J. Mater. Chem.*, 2012, **22**, 11772.
- 7 T. X. T. Sayle, F. Caddeo, N. O. Monama, K. M. Kgatwane, P. E. Ngoepe and D. C. Sayle, *Nanoscale*, 2015, **7**, 1167–1180.
- 8 Z. Lu, L. Y. Beaulieu, R. A. Donabarger, C. L. Thomas and J. R. Dahn, *J. Electrochem. Soc.*, 2002, **149**, A778–A791.
- 9 M. Sathiya, G. Rousse, K. Ramesha, C. P. Laisa, H. Vezin, M. T. Sougrati, M. L. Doublet, D. Foix, D. Gonbeau, W. Walker, A. S. Prakash, M. Ben Hassine, L. Dupont and J. M. Tarascon, *Nat. Mater.*, 2013, **12**, 827–835.
- 10 D. H. Seo, J. Lee, A. Urban, R. Malik, S. Kang and G. Ceder, *Nat. Chem.*, 2016, **8**, 692–697.
- 11 K. Luo, M. R. Roberts, N. Guerrini, N. Tapia-Ruiz, R. Hao, F. Massel, D. M. Pickup, S. Ramos, Y.-S. Liu, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *J. Am. Chem. Soc.*, 2016, **138**, 11211–11218.
- 12 K. Luo, M. R. Roberts, R. Hao, N. Guerrini, D. M. Pickup, Y.-S. Liu, K. Edström, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *Nat. Chem.*, , DOI:10.1038/nchem.2471.
- 13 A. J. Achkar, T. Z. Regier, H. Wadati, Y. J. Kim, H. Zhang and D. G. Hawthorn, *Phys. Rev. B - Condens. Matter Mater. Phys.*, , DOI:10.1103/PhysRevB.83.081106.
- 14 H. Wadati, A. J. Achkar, D. G. Hawthorn, T. Z. Regier, M. P. Singh, K. D. Truong, P. Fournier, G. Chen, T. Mizokawa and G. A. Sawatzky, *Appl. Phys. Lett.*, , DOI:10.1063/1.4711801.
- 15 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65–71.
- 16 K. G. Gallagher, J. R. Croy, M. Balasubramanian, M. Bettge, D. P. Abraham, A. K. Burrell and M. M. Thackeray, *Electrochem. commun.*, 2013, **33**, 96–98.
- 17 C. P. G. and N. Dupré, *Chem. Rev.*, 2004, **104**, 4493–4512.
- 18 ‡ Y. S. Meng, †, † G. Ceder, § C. P. Grey, || W.-S. Yoon, § M. Jiang, § and J. Bréger and ⊥ Y. Shao-Horn*, *Chem. Mater.*, 2005, **17**, 2386–2394.
- 19 J.-K. Kim, J.-W. Choi, G. S. Chauhan, J.-H. Ahn, G.-C. Hwang, J.-B. Choi and H.-J. Ahn, *Electrochim. Acta*, 2008, **53**, 8258–8264.
- 20 A. R. Armstrong, A. D. Robertson and P. G. Bruce, in *Journal of Power Sources*, Elsevier, 2005, vol. 146, pp. 275–280.

- 21 P. Yan, L. Xiao, J. Zheng, Y. Zhou, Y. He, X. Zu, S. X. Mao, J. Xiao, F. Gao, J. G. Zhang and C. M. Wang, *Chem. Mater.*, 2015, **27**, 975–982.
- 22 F. M. F. De Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky and H. Petersen, *Phys. Rev. B*, 1989, **40**, 5715–5723.
- 23 M. Giorgetti, *ISRN Mater. Sci.*, 2013, 1–21.
- 24 M. L. Baker, M. W. Mara, J. J. Yan, K. O. Hodgson, B. Hedman and E. I. Solomon, *Coord. Chem. Rev.*, 2017, **345**, 182–208.
- 25 A. Augustsson, M. Herstedt, J.-H. Guo, K. Edström, G. V. Zhuang, J. P. N. Ross, J.-E. Rubensson and J. Nordgren, *Phys. Chem. Chem. Phys.*, 2004, **6**, 4185–4189.
- 26 R. Qiao, Y.-D. Chuang, S. Yan and W. Yang, *PLoS One*, 2012, **7**, e49182.
- 27 U. Maitra, R. A. House, J. W. Somerville, N. Tapia-Ruiz, J. G. Lozano, N. Guerrini, R. Hao, K. Luo, L. Jin, M. A. Pérez-Osorio, F. Massel, D. M. Pickup, S. Ramos, X. Lu, D. E. McNally, A. V Chadwick, F. Giustino, T. Schmitt, L. C. Duda, M. R. Roberts and P. G. Bruce, *Nat. Chem.*, 2018, **10**, 288–295.

5 Ion conducting binders for silicon anodes

5.1 Background

Silicon has been studied over the last four decades¹⁻⁴ as an attractive alternative anode material for lithium ion batteries instead of the commonly used carbonaceous materials, such as graphite.

At room temperature silicon can alloy⁵ with lithium up to $\text{Li}_{22}\text{Si}_5$ composition, with a theoretical gravimetric capacity above 4200 mAhg^{-1} , which together with the average working potential, 0.1-0.2 V vs. Li^+/Li , makes this material the most promising lithium battery anode system, in terms of energy density, after metallic lithium itself.

Despite its great potential performance though, silicon suffers from major structural strains and huge volume expansion ($\sim 300\%$)^{6,7} during the alloying process with lithium, leading to a progressive fragmentation of the electrode and definitive loss of electrical wiring upon electrochemical cycling.

Over the years several different strategies have been attempted trying to stem the progressive structural degradation of the electrodes during cycling. The different approaches to the problem can be divided into four main categories:

- Synthesis of composite^{8,9} materials with silicon particles embedded in a solid matrix able to buffer the volume expansion of Si particles over cycling.
- Use of nanosized particles¹⁰⁻¹² of silicon as an active material in order to sustain the strain and limit the fragmentation.
- Growth of silicon thin films^{13,14} on the current collector in the attempt to get a better adhesion of the active material.

- Utilization of selected binders^{15,16} able to maintain the integrity of the electrode and electrical contact with the current collector whilst accommodating the volume expansion.

Of the four approaches, the second and the last one have been so far the most successful in limiting a quick fade in performance for silicon-based anodes.

Aim of the chapter

In this chapter, four different kinds of binders, three of which are polymers employed for the first time as binders for silicon anodes to date, are tested with nanosized silicon. The electrodes preparation will be detailed together with the structural and morphological characterization by SEM and PXRD of the active material. The effect on the electrochemical performance for each binder will be investigated with galvanostatic cycling.

The final aim is to improve the electrochemical performance and cycling stability of the silicon-based anodes.

5.1.1 Tested Binders

The polymers chosen to be tested as binders were sodium-carboxymethylcellulose (Na-CMC), poly(3,4-ethylenedioxythiophene) (PEDOT), polystyrene sulfonic acid (PSSA) and the co-polymer PEDOT-PSS.

Na-CMC is a binder of choice for silicon and has already been employed in numerous works^{17–19}. In this chapter, the performance of Na-CMC is used as a benchmark to evaluate the results obtained with the other polymers. Originally PEDOT-PSS had been chosen because of its high electronic conductivities, with values that can widely range from 10^{-2} to 10^3 Scm,²⁰ depending on the synthetic conditions and post-synthesis treatments. In addition, the components of PEDOT-PSS, the p-type conductor PEDOT

and the n-type conductor PSS, were also tested to better understand how each component could affect the electrochemical performance.

Carboxymethylcellulose (sodium salt, Na-CMC)

sodium carboxymethylcellulose is a linear polymeric derivative of cellulose constituted by β -linked glucopyranose units in which the hydroxyl residues are substituted at different levels with sodium carboxymethyl ($-\text{OCH}_2\text{C}(\text{O})\text{O}^- \text{Na}^+$) residues (Figure 5.11). It is a stiff and brittle polymer which can be obtained with different molecular weights, although in this work only the 97 kDa weight was employed. Despite the poor mechanical properties Na-CMC has drawn much attention in the last decade as a good binder for silicon based anodes²¹ showing superior performance with respect to the established industry standard, polyvinylidene fluoride (PVDF) binder. In this work, Na-CMC has been used as a reference binder for evaluating a baseline of cycling performance of the silicon anodes.

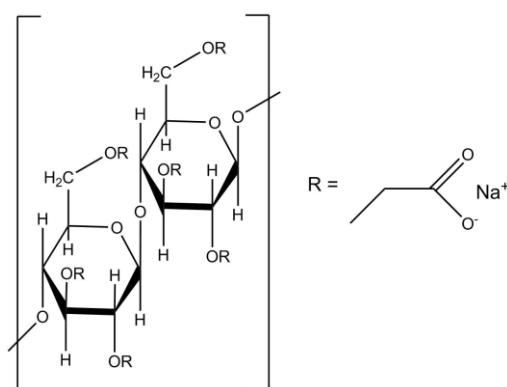


Figure 5.1 Na-CMC molecular structure.

Poly(3,4-ethylenedioxythiophene) (PEDOT)

PEDOT (Figure 5.22) is a conductive and stable polymer with a moderate band gap and a low redox potential²² based on 3,4-ethylenedioxythiophene monomers. PEDOT is a conjugated p-type conductor with poor solubility in protic solvents.

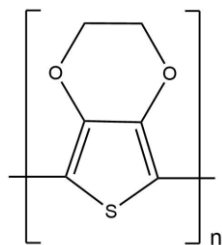


Figure 5.2 PEDOT molecular structure.

Polystyrene sulfonic acid (PSSA)

PSSA is one of the large family of polystyrene sulfonate-based polymers (Figure 5.3). Similar to PEDOT, PSS-based polymers have a relatively low band gap and can be conductive even though they are used mainly in water softening applications, thanks to the great number of sulfonic groups that can easily coordinate metallic ions such as Na^+ , K^+ or Ca^+ .

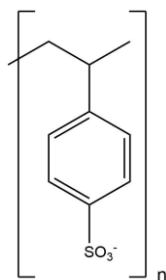


Figure 5.3 PSS molecular structure.

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS)

PEDOT-PSS is an ionomeric mixture based on the two ionomers PEDOT and PSS (Figure 5.4). Despite both components being conductive polymers themselves, in PEDOT-PSS the PSS polymer is employed mainly due to its high solubility in water, hence acting as a surfactant for PEDOT in water solutions. As already mentioned PEDOT-PSS presents a wide range of conductivity values and is characterised by a high work function of around 5 eV as well as being almost transparent when deposited as a

film. These unique characteristics have resulted in PEDOT-PSS being widely employed in the fields of energy conversion (e.g. solar) and storage (e.g. Li-ion/air battery cathodes)^{23,24}. To the best of our knowledge, PEDOT-PSS has never been previously employed as a binder for silicon-based anodes and this work probably represents one of the first attempts.

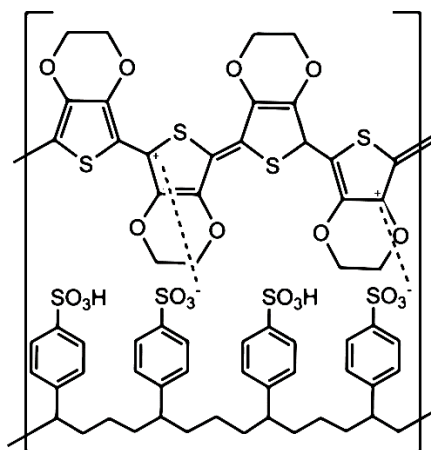


Figure 5.4 PEDOT-PSS ionomeric structure.

5.2 Experimental Methods

Here follows a summary of the procedures and conditions used for these experiments.

For further details, see: Chapter 2.

5.2.1 Electrodes Preparation

The silicon employed as active material for the preparation of the electrodes is commercially available silicon nanopowder which was purchased from Nanostructure and Amorphous Material Inc. ($\varnothing = 20\text{-}30$ nm particles). Carbon super-P (Timcal) was used as a conducting additive to guarantee homogeneous electronic conductivity within the electrodes. Regarding the binder, different types have been used to obtain different composite materials such as:

- Carboxymethyl cellulose (CMC, Sigma Aldrich, average weight 90 kDa)

- Poly(styrene sulfonic acid) (PSSA, Sigma Aldrich, average weight 75 kDa, 18 % solution in water)
- Poly(3,4-ethylenedioxythiophene) (PEDOT, Sigma Aldrich, nanoparticles dispersion in water)
- Poly(3,4-ethylenedioxythiophene) Poly(styrene sulfonate) (PEDOT-PSS, Sigma Aldrich, re-dispersible pellets)

A 500 mg mixture of the composite's forming powders (silicon powder, carbon super-P and binder) were placed in a 1:1:1 weight ratio in a stainless steel ball mill (20 cm³) with 3.5 mL of distilled water and 2 stainless steel spheres ($\varnothing = 0.5$ cm) and milled in a planetary mill (Retsch, mod. PM100) for 60 minutes at 450 rpm to attain a slurry (Figure 5.55).

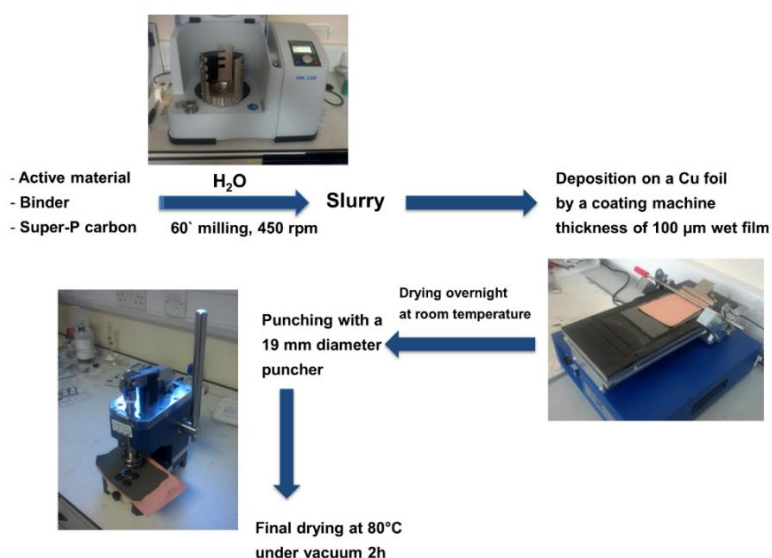


Figure 5.5 Electrodes Preparation Schematic

Once obtained, the slurry was cast using a casting bar on a copper current collector (Advent Research Material, 17 μ m thickness) with an average wet film thickness of 100 μ m as determined by the depth of the thread on the casting bar. The cast material was left to dry overnight in air and then 20 mm diameter electrodes were punched and further dried in a vacuum oven at 80 °C for 2 h.

5.2.2 Cell Preparation

Once dry, the electrodes were assembled into coin-cells from CR2325 coin-cells parts, provided by the National Research Council of Canada, under an inert Ar atmosphere inside a glove box (*MBraun LABmaster sp*, O_2 and $H_2O < 0.1$ ppm). A lithium metal disc ($\varnothing = 18$ mm, 0.1 mm thick) was used as counter electrode with two glass fibre discs ($\varnothing = 22$ mm, *Whatman GF-D*) as separator, soaked with 0.2 mL of a 1M solution of $LiPF_6$ in a mixture of EC/DMC (1:1 weight ratio, 87 % wt/wt), Vinylene Carbonate²⁵ (VC; 3 % wt/wt, Sigma Aldrich) and Fluoroethylene Carbonate (FEC, 10 % wt/wt, Sigma Aldrich).

5.2.3 Analyses and Characterisation

PXRD data was preliminarily collected on the silicon nanopowders on a Rigaku SmartLab powder diffractometer equipped with a 3 kW Cu rotating anode. Morphological studies were conducted on the silicon powder using a Zeiss Merlin scanning electron microscope equipped with an EDX detector. The electrochemical behavior and performance of the electrodes made with different binders were characterized through galvanostatic cycling versus lithium, between 0.01 V and 2 V vs. Li^+/Li , employing a BioLogic VMP3 potentiostat at a rate of 1800 mA g^{-1} (roughly C/2 for silicon) and the electrolyte employed was

Results

5.2.4 Silicon Characterisation

Powder X-ray diffraction

The PXRD pattern collected on the nanometric silicon powder (Figure 5.66) is compared with a theoretical pattern for pure silicon, obtained from the ICSD database. It is possible to observe that the peaks positions and their relative intensities ratios are the same in both patterns. This suggests that the powder used as an active material in the electrodes was pure crystalline silicon assuming that no amorphous impurities are present. Despite

the nanosized dimensions of the silicon employed, the peak broadening in the experimental pattern is little if compared with the reference one. This can be attributed to the high crystallinity of the nanoparticles employed and the presence of large crystallites within the particles. In fact, in almost ideal experimental conditions (e.g. synchrotron light source) the peak broadening can be detected at high angles for crystallites smaller than 200 nm, although for a lab-based X-ray diffractometer the broadening starts to be visible when the crystallites size is reduced to 5-10 nm. Being the samples employed highly crystalline and the particles dimensions 20-30 nm, it is reasonable to conclude that little peak broadening is expected for the peaks in the XRD pattern.²⁶

To get a deeper insight on the structural behaviour of the silicon during cycling an in-situ XRD analysis was performed on one of the prepared silicon-CMC-carbon electrodes during the galvanostatic cycling versus metallic lithium, with the help of a specially built electrochemical cell. The results of the in-situ analysis are reported in the appendix at the end of the chapter.

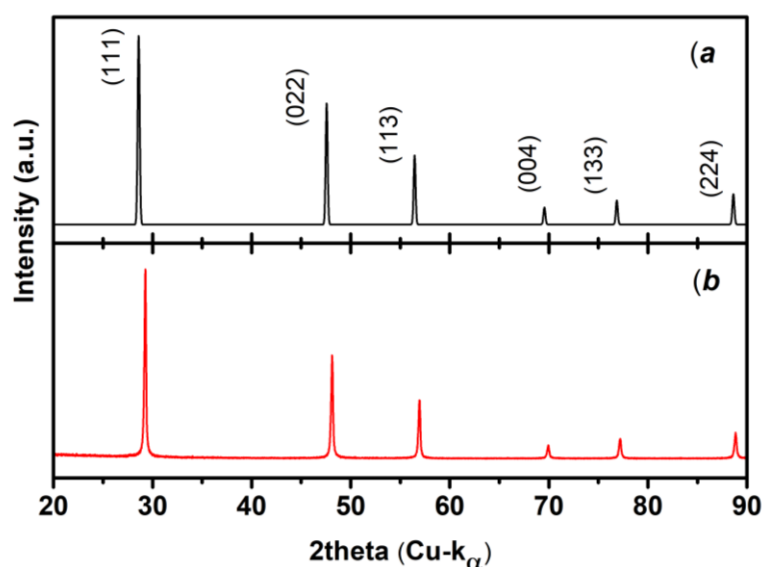


Figure 5.6 Calculated PXRD diffraction pattern for pure silicon (panel a) and experimentally measured pattern on the silicon nanopowder employed as active material (panel b). All reflections have been indexed with their relative Miller indices. The experimental data appears to be in perfect agreement with the calculated pattern on both position and relative intensities of the peaks, indicating that the material is pure.

Scanning electron microscopy

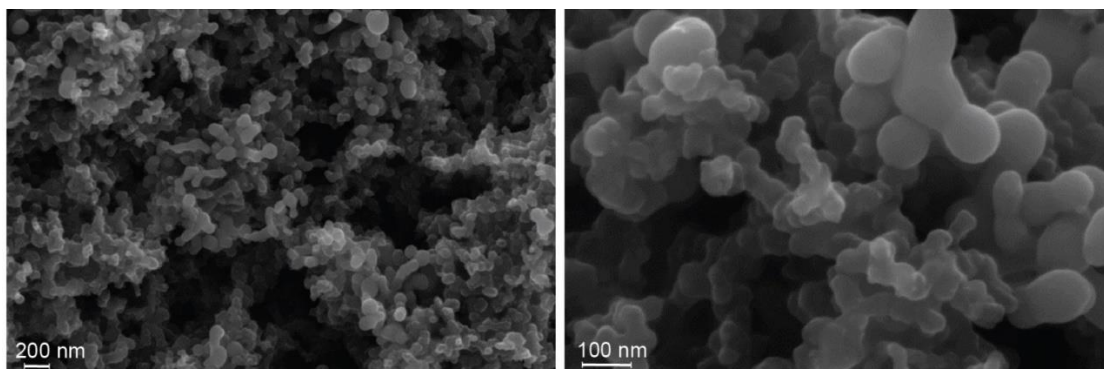


Figure 5.7 SEM images of the nanometric silicon powder employed as active materials in the electrodes tested with different binders. The images were collected with a voltage of 5 kV and an enlargement of 28000x and 60000x for the left and right image respectively.

In Figure 5.7, SEM images at different magnifications are presented of the employed silicon powder. From the images, it is possible to observe that the average dimension of the particles is between 20 and 30 nanometers, with the presence of local agglomerates. The particles' shape appears sphere-like with a smooth surface and a uniform and narrow dimensional distribution.

5.2.5 Electrochemistry

The electrochemical performance of the different binders were measured through galvanostatic cycling of composite electrodes, made from slurries with the same weights ratios (1;1;1 wt/wt, Si;C super P;binder), one for each binder (see Electrodes Preparation). In Figure 5.88, the cycling performance is reported of silicon electrodes made with the different binders together with the coulombic efficiencies of each cycle.

The Na-CMC based electrode (panel i) shows initial capacity values around 2500 mAhg^{-1} that constantly drop over cycling until the 300th cycle in which the capacity is reduced to 1000 mAhg^{-1} , corresponding to a 60% loss in performance. The coulombic efficiency for the Na-CMC electrode keeps increasing over cycling, although it reaches 99% only around the 150th cycle and presents a first cycle efficiency of 85.2%.

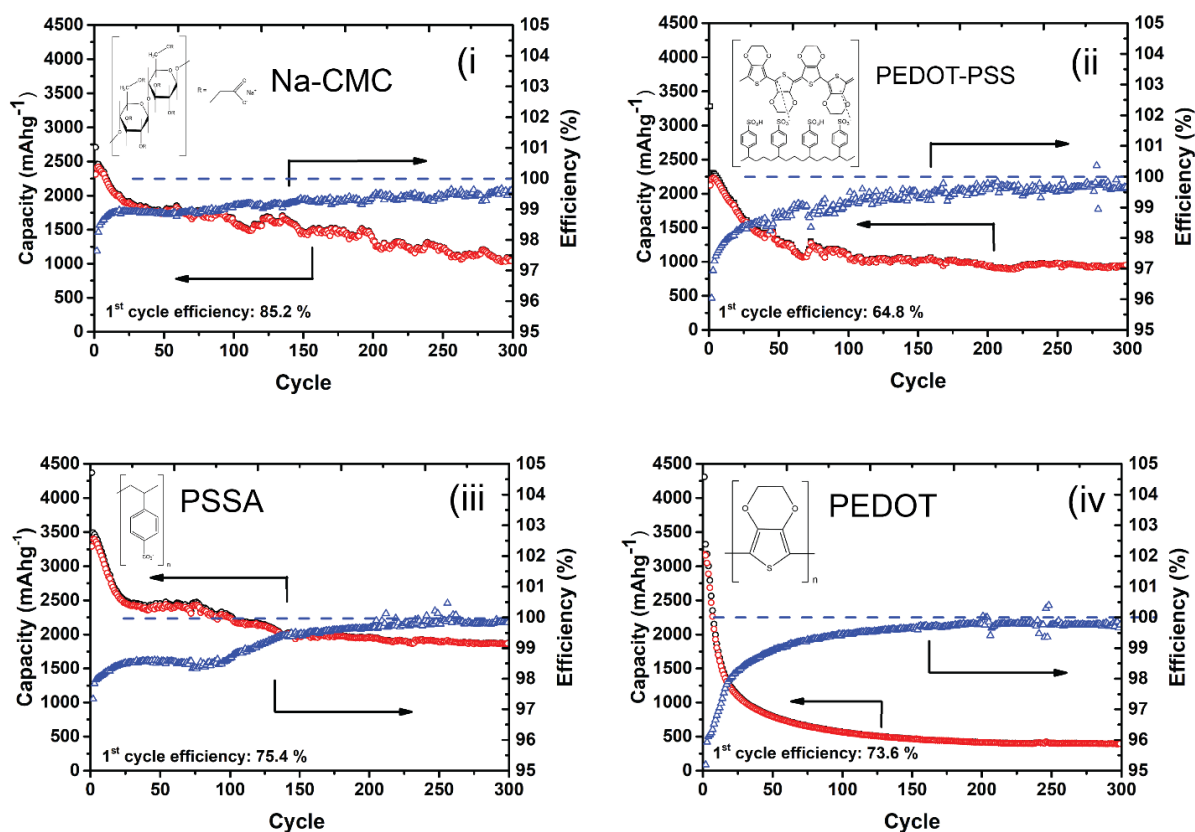


Figure 5.8 Galvanostatic cycling of the silicon based anodes prepared with different binders: i) CMC; ii) PEDOT-PSS; iii) PSS; iv) PEDOT. The arrows indicate respectively the capacity delivered upon lithiation and de-lithiation per each cycle (left Y-axis, red and black circles) and the coulombic efficiency of lithiation/de-lithiation (right Y-axis, blue triangles). All the electrodes were cycled at 1800 mA g^{-1} ($\sim C/2$) between 0.01-2 V vs. Li^+/Li .

In panel ii the PEDOT-PSS electrode starts lower than Na-CMC with a capacity of 2250 mAhg^{-1} and an efficiency of 64.9% in the first cycle. The capacity fades quickly for PEDOT-PSS in the first 70 cycles after which it appears to plateau losing less than 500 mAhg^{-1} between the 80th and the 300th cycle. Higher values of capacity are displayed by the PSS based electrode (panel iii) with an initial capacity around 3500 mAhg^{-1} . The capacity drops very quickly in the first 20 cycles of the PSS electrode to less than 2500 mAhg^{-1} although between the 120th and 300th very little fade is noticed in capacity with values around 2000 mAhg^{-1} displayed at the end of cycling.

It is worth noting that the capacity loss for PSS over the 300 cycles is about 40% of the first cycle capacity meaning that the overall charge loss is 20% lower than for Na-CMC.

Additionally, the efficiency of the PSS electrode does not show a monotonic growth over cycling but rather an oscillatory behaviour in the first 120 cycles, to then grow constantly until almost 100% for the last 100 cycles. Regarding the PEDOT based electrode in panel iv, it shows comparable values of capacity to the PSS one in the first cycles and similar values of efficiency although it appears to steeply drop in capacity over the first 50 cycles to then plateau out around 500 mAhg⁻¹.

Hence the electrode with PEDOT seems to display a lower specific capacity with respect to that fabricated with PEDOT-PSS. However, the electrode with PSS appears to show even higher performance with respect to the electrode made with Na-CMC. The electrode with PSS still displays about 2000 mAhg⁻¹ after 300 cycles with a good capacity retention while the one with Na-CMC gradually decreases in performance until it arrives to a comparable performance to that of PEDOT-PSS at the end of cycling displaying a specific capacity of 1000 mAhg⁻¹. A different behaviour is observed in the efficiencies trends (Figure 5.88), where the CMC still appears to be the most reliable binder in terms of efficiency especially at the beginning of cycling with a first irreversible capacity much lower (15 % of the intercalated lithium ions) respect to the other binder (30-35 % of intercalated ions). In particular, the electrode with PSS seems to suffer from the worst efficiency behaviour at the beginning with respect to the one with PEDOT-PSS and Na-CMC even though it recovers with cycling, ending up to have a comparable coulombic efficiency to Na-CMC after 150 cycles. In Figure 5.9, the galvanostatic curves for the silicon anodes cycled with different binders are compared after the 1st, 10th, 50th, 100th, 200th and 300th cycle. In the curves, it is possible to observe the presence of the lithiation/de-lithiation plateaus of Li⁺ ions respectively during the lithiation process around 0.1-0.2 V vs. Li⁺/Li and during the de-lithiation one around 0.3-0.5 V vs. Li⁺/Li. The extension of the plateaus decreases with cycling probably due to the increasing in SEI layer thickness trapping lithium ions, or from the fragmentation of the electrode due to the large volume changes of silicon leading to electronic disconnection.

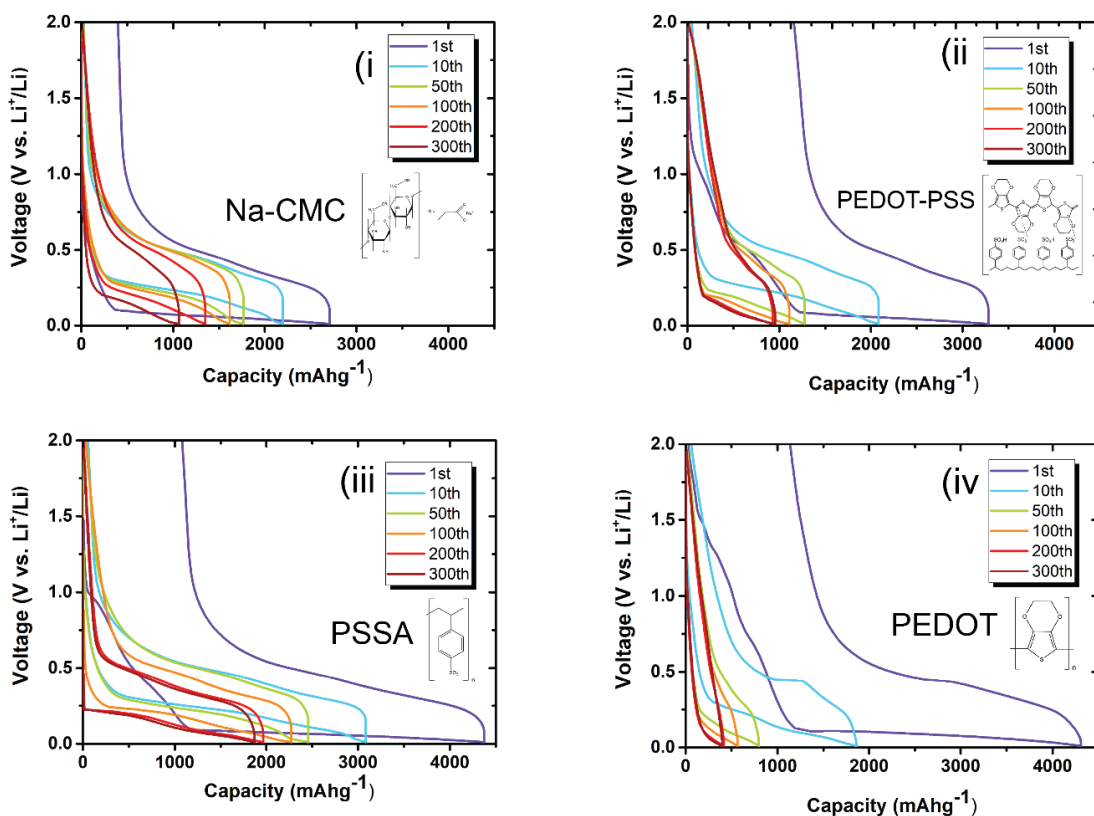


Figure 5.9 Galvanostatic curves at the 1st, 10th, 50th, 100th, 200th and 300th cycle for the silicon electrodes fabricated with different binders: i) Na-CMC; ii) PEDOT-PSS; iii) PSS; iv) PEDOT. All the electrodes were cycled at 1800 mA_g⁻¹ (~C/2) between 0.01-2 V vs. Li⁺/Li.

It is interesting to notice how the PEDOT binder (Figure 5.9-iv) shows very good performance at the beginning of cycling with a displayed capacity comparable to the one of PSS (Figure 5.9-iii); however, this fails quite rapidly at higher cycles. The electrodes fabricated with the PSS binder (Figure 5.9-iii) present an interesting shape of the galvanostatic curves at after 200 cycles with a vertical fall in voltage values at the beginning of the lithium insertion process from 2 to 0.2 V vs. Li⁺/Li. This is particularly interesting as it suggests that there is no other phenomenon than lithium insertion taking place. As opposed to the commonly used Na-CMC, PSS appears to favour the formation of a very stable and conductive SEI at high cycle values. This very stable SEI gives the PSS electrode an exceptional stability over cycling, with a loss of just 8% capacity between the 150th and 300th cycle (Figure 5.8-iii), which implies a coulombic efficiency very close to 100%.

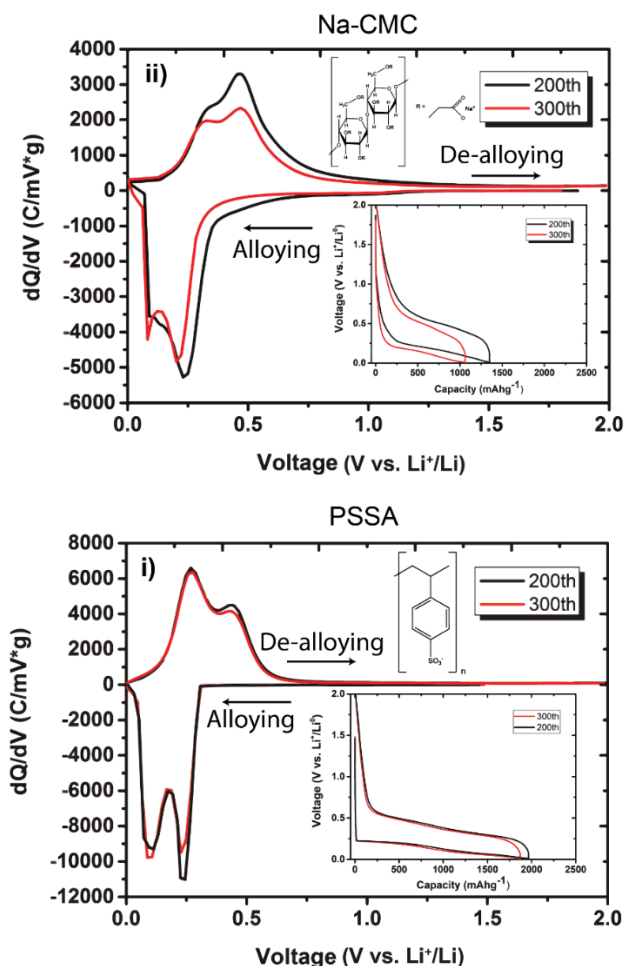


Figure 5.10 Differential capacity plots at the 200th (black line) and 300th cycle (red line) for (i) the PSS based electrode and (ii) the Na-CMC based electrode. The galvanostatic curves for the corresponding cycles have been reported together with the differential capacity plots in the small insert graphs.

The improved long-cycling performance of the silicon anode fabricated with the innovative PSS binder over the more traditional Na-CMC is also confirmed by the comparison of the differential capacity plots of the 200th and 300th cycles (Figure 5.10). The differential plot for Na-CMC (Figure 5.10-a) appears to substantially change between the 200th and 300th cycle with a shift towards lower potential values for the main peaks on insertion and extraction of the alkali ions. This is indicative that in the electrode rearrangement processes are still ongoing, probably due to the continuous evolution of the SEI layer. In contrast, in the plot for the PSS silicon electrode (Figure 5.10-b), the 200th and 300th cycles curves are almost superimposable showing no change in shape or appreciable

shift in the peaks positions. This result is consistent with the observed behaviour in the galvanostatic cycling and confirms the high stability gained in the silicon electrode with PSS.

5.3 Conclusions

Three conductive polymers, PEDOT-PSS, PSS and PEDOT, have been tested for the first time as binders in silicon-based anodes. The electrochemical performance and cycling stability were carefully investigated through galvanostatic cycling and the study of the load curves behaviour together with the differential capacity plots. The performance of the binders was compared to that of Na-CMC that is one of the standard binders of choice for silicon.

The results obtained showed that PEDOT-PSS and PSS can compete with the well-renowned Na-CMC showing even higher reversible capacity values after 300 cycles at C/2 in the case of PSS. Additionally, PSS showed excellent reversibility after 200 cycles with no appreciable change in the differential capacity plot of the cycles 200 and 300. The high stability reached by the PSS is also confirmed by the coulombic efficiency behaviour between the 200th and 300th cycle, with values close to 100%. The explanation of the superior performance of PSS with respect to Na-CMC, PEDOT and PEDOT-PSS might be related to two main reasons. The first one is that PSS could be determinant in controlling the strong volume expansion and contraction of silicon upon lithiation/delithiation which is a major cause of particle disconnection and electrode failure. The second is that the sulfonate groups along the polymeric chain of PSS could be able to coordinate and conduct lithium ions, hence providing improved ionic conductivity through the bulk electrode and to the silicon particles.

These two properties of PSS may act in synergy to guarantee a highly stable electrode with excellent ionic conductivity.

An important point that shall need further research and improvement concerns the coulombic efficiency of PSS in the first 100 cycles that still appears to be lower than that of Na-CMC and surely too low to consider PSS as a commercially viable binder.

5.4 Appendix

In-situ XRD of silicon anodes

An in-situ X-ray diffraction measurement was performed on a silicon-based electrode in order to investigate the evolution of the active material particles during galvanostatic cycling. The electrode was made up of a 1:1:1 weight ratio of silicon nanoparticles, carbon super-P and Na-CMC as a binder. The measurement was performed in a specially fitted cell (Figure 5.11) employing LP30 as electrolyte and lithium foil as counter electrode.

A rate of 180 mA g^{-1} between 0.01 and 2 V vs Li^+/Li was employed to cycle the material.

Diffraction patterns were collected between 20 and 60 degrees of 2θ continually during the electrode galvanostatic cycling, as shown in Figure 5.12. The evolution of three peaks centred at 30, 48.5 and 57.5 2θ degrees respectively corresponding to the indexed reflections 111, 022 and 113.

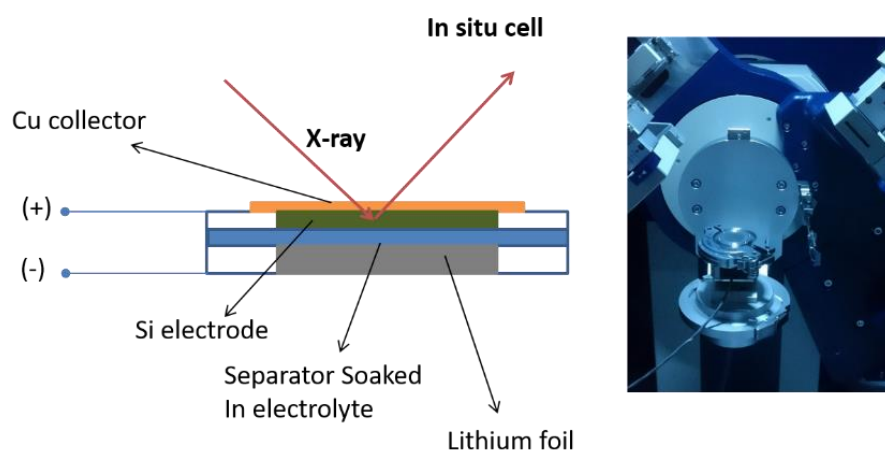


Figure 5.11 In situ PXRD cell schematic

Figure 5.12 shows all three peaks, monitored during the experiment, progressively decreasing in intensity while the lithium ions alloy with silicon. This means that the silicon lattice gradually loses its crystallinity, becoming amorphous in good agreement with that

reported in literature^{5,27}. Additionally, the reflection 111 appears to slightly shift towards lower angles, indicating an expansion of the lattice parameters

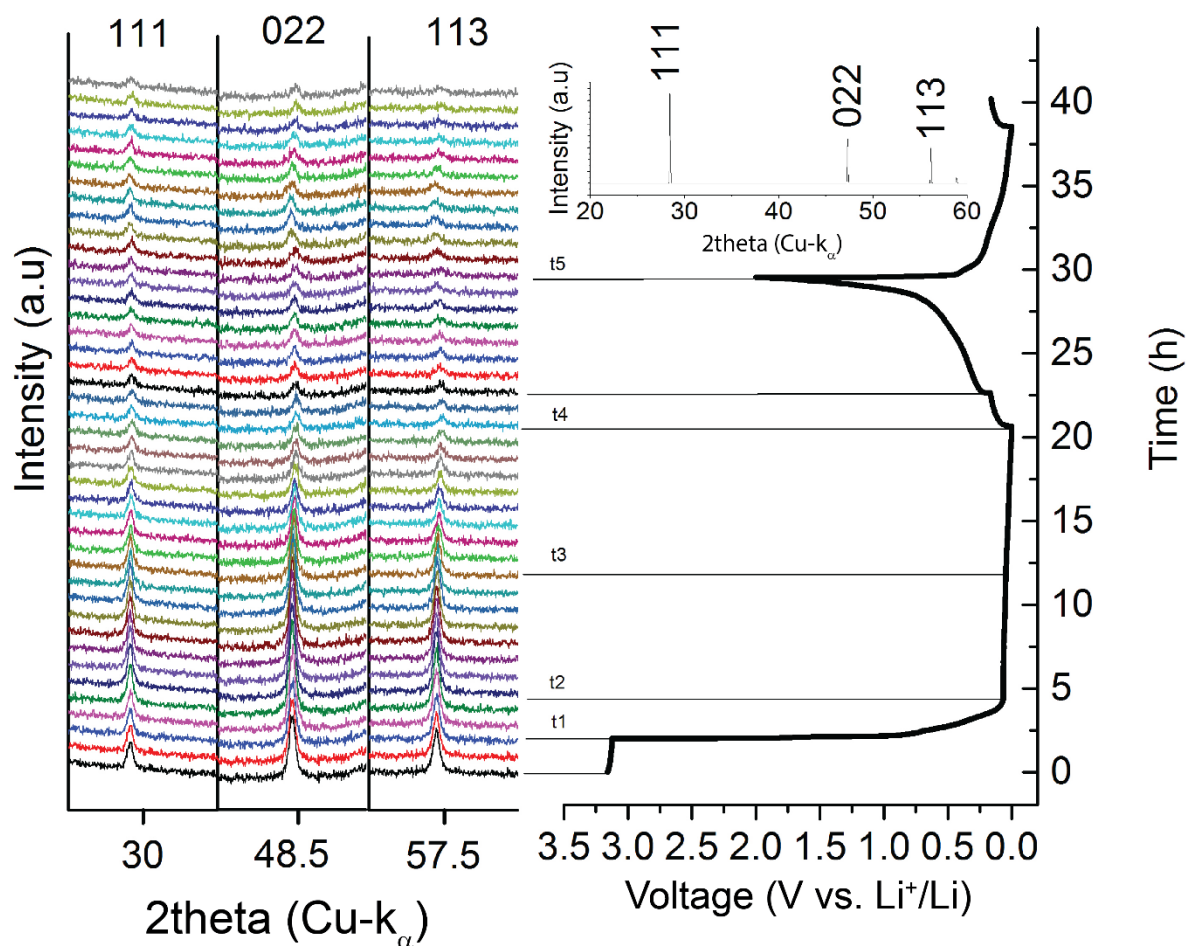


Figure 5.12 Evolution of the 111, 022 and 113 reflections (top right panel) in the silicon PXRD diffraction pattern during galvanostatic cycling. On the right-hand side the evolution of the potential reported vs. time is shown.

. Over the subsequent process of extraction of the alkali ions from the material the peaks do not appear to reversibly recover the original shape indicating that the silicon stays amorphous. This behaviour is in good agreement with that expected for silicon, where a dramatic volume expansion is observed during lithiation.

5.5 References

- 1 C. J. Wen and R. A. Huggins, *J. Solid State Chem.*, 1981, **37**, 271–278.
- 2 C. K. Chan, H. Peng, G. Liu, K. Mcllwraith, X. F. Zhang, R. a Huggins and Y. Cui, *Nat. Nanotechnol.*, 2008, **3**, 31–5.
- 3 M. T. McDowell, S. W. Lee, W. D. Nix and Y. Cui, *Adv. Mater.*, 2013, **25**, 4966–4985.
- 4 S. Bourderau, T. Brousse and D. . Schleich, *J. Power Sources*, 1999, **81–82**, 233–236.
- 5 M. N. Obrovac and L. Christensen, *Electrochem. Solid-State Lett.*, 2004, **7**, A93.
- 6 L. Y. Beaulieu, K. W. Eberman, R. L. Turner, L. J. Krause and J. R. Dahn, *Electrochem. Solid-State Lett.*, 2001, **4**, A137.
- 7 L. Y. Beaulieu, T. D. Hatchard, A. Bonakdarpour, M. D. Fleischauer and J. R. Dahn, *J. Electrochem. Soc.*, 2003, **150**, A1457.
- 8 H. Li, *Electrochem. Solid-State Lett.*, 1999, **2**, 547.
- 9 Y. Zhang, X. G. Zhang, H. L. Zhang, Z. G. Zhao, F. Li, C. Liu and H. M. Cheng, *Electrochim. Acta*, 2006, **51**, 4994–5000.
- 10 H. Kim, M. Seo, M. H. Park and J. Cho, *Angew. Chemie - Int. Ed.*, 2010, **49**, 2146–2149.
- 11 M.-H. Park, M. G. Kim, J. Joo, K. Kim, J. Kim, S. Ahn, Y. Cui and J. Cho, *Nano Lett.*, 2009, **9**, 3844–7.
- 12 H. Wu and Y. Cui, *Nano Today*, 2012, **7**, 414–429.
- 13 C. Yu, X. Li, T. Ma, J. Rong, R. Zhang, J. Shaffer, Y. An, Q. Liu, B. Wei and H. Jiang, *Adv. Energy Mater.*, 2012, **2**, 68–73.
- 14 J. P. Maranchi, a. F. Hepp and P. N. Kumta, *Electrochem. Solid-State Lett.*, 2003, **6**, A198.
- 15 J. Song, M. Zhou, R. Yi, T. Xu, M. L. Gordin, D. Tang, Z. Yu, M. Regula and D. Wang, *Adv. Funct. Mater.*, 2014, **24**, 5904–5910.
- 16 C. Erk, T. Brezesinski, H. Sommer, R. Schneider and J. Janek, *ACS Appl. Mater. Interfaces*, 2013, **5**, 7299–7307.
- 17 J.-S. Bridel, T. Azaïs, M. Morcrette, J.-M. Tarascon and D. Larcher, *Chem. Mater.*, 2010, **22**, 1229–1241.
- 18 N. Ding, J. Xu, Y. Yao, G. Wegner, I. Lieberwirth and C. Chen, *J. Power Sources*, 2009, **192**, 644–651.
- 19 N. S. Hochgatterer, M. R. Schweiger, S. Koller, P. R. Raimann, T. Wöhrle, C. Wurm and M. Winter, *Electrochem. Solid-State Lett.*, 2008, **11**, A76.
- 20 X. Crispin, F. L. E. Jakobsson, A. Crispin, P. C. M. Grim, P. Andersson, A. Volodin, | C Van Haesendonck, | M Van Der Auweraer, W. R. Salaneck and M. Berggren, *Chem. Mater.*, 2006, **18**, 4354–4360.
- 21 J. Li, R. B. Lewis and J. R. Dahn, *Electrochem. Solid-State Lett.*, 2007, **10**, A17.
- 22 M. Dietrich, J. Heinze, G. Heywang and F. Jonas, *J. Electroanal. Chem.*, 1994, **369**, 87–92.
- 23 P. R. Das, L. Komsiyiska, O. Ostera and G. Wittstock, *J. Electrochem. Soc.*, 2015,

162, A674–A678.

- 24 D. H. Yoon, S. H. Yoon, K.-S. Ryu and Y. J. Park, *Sci. Rep.*, 2016, **6**, 19962.
- 25 A. L. Michan, B. S. Parimalam, M. Leskes, R. N. Kerber, T. Yoon, C. P. Grey and B. L. Lucht, *Chem. Mater.*, 2016, **28**, 8149–8159.
- 26 A. R. West, *Solid State Chemistry and Its Applications*, 1984.
- 27 M. T. McDowell, S. W. Lee, W. D. Nix and Y. Cui, *Adv. Mater.*, 2013, **25**, 4966–4985.

6 Pre-treatment of silicon and hard carbon-based anodes to reduce the first cycle irreversible capacity

6.1 Background

As seen in the previous chapter, silicon appears to be one of the most promising active materials to be employed at the anode electrode in Lithium Ion Batteries (LIB)^{1–3}. Thanks to the alloying mechanism with lithium, very high theoretical specific capacities above 4000 mAhg⁻¹ can be anticipated from silicon-based anodes. Additionally, much attention has been drawn by disordered carbons, commonly denominated hard carbons, obtained from the pyrolysis^{4–7} of organic precursors⁸ such as phenolic resins and sugars. The hard carbons, thanks to their structure, in which large domains of single graphene sheets are stacked in a ‘house of cards’ fashion, are able to intercalate both lithium and sodium ions. They display capacities higher than either of the two respective commercially relevant graphite and sodium titanium oxides⁹ systems. Despite the great scientific and industrial interest around silicon and hard carbon, these materials are affected by poor cycling efficiencies that prevent their use in commercial lithium/sodium-ion batteries. Whilst it is not always the case, the efficiencies on the cathode side will be considered minimal in the following discussion. If this is the case and the anode has a cycling efficiency of only 99% then every cycle a fraction of the lithium extracted from the cathode will be lost; over continued cycling this will result in capacity fading as shown in Figure 6.1.

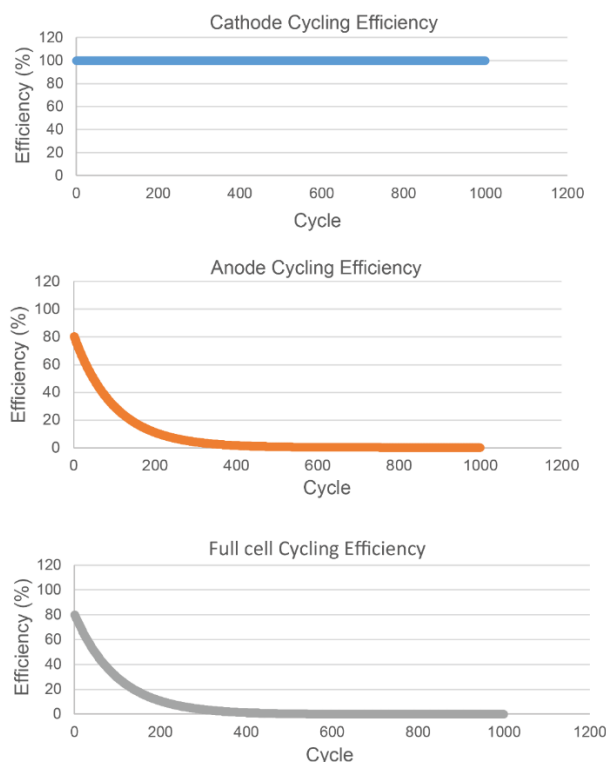


Figure 6.1 Simulated trend for the cycling efficiency versus cycle number in which the efficiency on the cathode (top panel) is assumed constant to 100% whilst the efficiency on the anode (middle panel) is assumed to present a first cycle efficiency of 80% and a 99% efficiency in all the subsequent ones. The trend for the full cell case (bottom panel) follows the anode one.

This effect is even more dramatic on the first cycle where much lower cycling efficiencies are seen on anode materials. To have a better idea of the importance of having high cycling efficiency it can be considered an ideal silicon electrode performing the same way of the anode in Figure 6.1 with 80% efficiency in the first cycle and 99% in the following ones. If the electrode delivers the theoretical capacity of 4200 mAhg^{-1} in the first insertion process the performance trend can be evaluated and is shown in figure where it can be seen that a dramatic performance fade occurs in the first cycles with the anode delivering only 12% of the original capacity after 200 cycles.

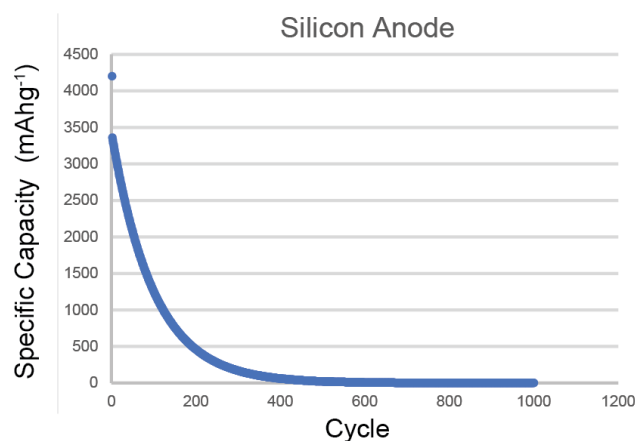


Figure 6.2 Simulated capacity fade of an ideal silicon-based anode delivering the theoretical capacity over the first alloying process.

The First Cycle Irreversible Capacity^{5,10,11} (FIC), Figure 6.3, is the highest among the capacity losses experienced in the electrodes during cycling, with values that reach up to 50% and 20% of the charge intercalated during the first lithium insertion process by hard carbon and silicon respectively. The FIC is mostly due to 4 factors:

- Formation of the Solid Electrolyte Interphase layer (SEI)
- Reduction of functional groups adsorbed on the anode's surface (e.g. hydroxyl groups)
- Parasitic reactions
- Irreversible trapping of lithium ions in the anode structure during the first lithiation

The formation of the Solid Electrolyte Interphase (SEI) is the dominant process that determines the FIC although several parasitic reactions and the reduction of the anode surface play a relevant role.

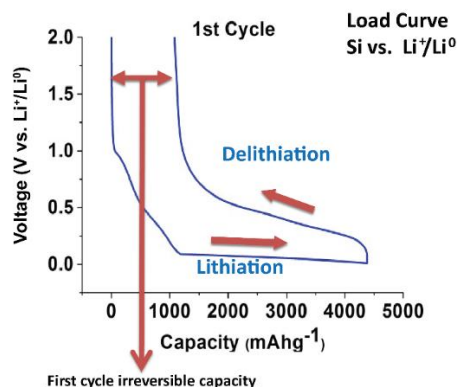


Figure 6.3 Typical load curve for the first cycle of a silicon electrode. In this case it appears that the first cycle irreversible capacity accounts for about 25% of the first discharge capacity.

The reduction or even the elimination of the FIC would then be a crucial step to avoid excessive consumption of alkali ions in a full cell during the first cycles, allowing for improved performance and longer cycle life.

Aim of the chapter

The main aim of this chapter is to find a way to reduce the first cycle irreversible capacity of silicon and hard carbon anodes for application in both lithium and sodium ion batteries. To reach the final aim, a series of smaller objective will be pursued. First, hard carbon with typical performance, as reported in the literature, will be prepared and characterised. Subsequently, a highly reducing treatment of the hard carbon and silicon electrodes will be performed to ascertain its effect on the first cycle efficiencies of the anode cycling. The hope is to reduce the electrodes FIC either by reducing the surface-adsorbed species or to partially lithiate/sodiate the active materials^{12,13} prior to the electrochemical cycling. The treated materials will be assembled into coin cells and characterised through galvanostatic cycling and X-ray Photoelectron Spectroscopy to investigate the differences between the treated and untreated electrodes.

6.2 Experimental Methods

The following is a summary of the materials synthesis procedures and conditions used in the experiments.

For more details on the techniques employed, see: Chapter 2 Experimental techniques.

6.2.1 Synthesis of the Hard Carbon

Hard carbon was synthesised following a previously reported procedure¹⁴.

5 grams of sucrose ($C_{12}H_{22}O_{11}$, >99.5%, Sigma Aldrich) was dispersed in 20 mL of concentrated sulfuric acid (H_2SO_4 , >95%, Fisher) and left in the acid bath for overnight.



The dehydrated product, obtained from the above reaction in Equation (6.1), was drained out from the acid excess and repeatedly centrifuged with distilled water until the washings had a neutral pH. The precursor was then dried overnight at 80 °C under dynamic vacuum and subsequently treated at 900 °C under vacuum for 1 h.

Finally, the obtained product was thoroughly milled into fine powder using a mortar and pestle.

6.2.2 Electrodes Preparation

Silicon based anodes

The silicon electrodes were prepared in an analogous way to those employed in the previous chapter for the investigation of binder effect. The electrodes employed were 1:1:1 wt./wt. ratio of active material, carbon super-P and Na-CMC (Sigma Aldrich, average weight 90 kDa) as a binder.

Hard carbon-based anodes

The synthesised hard carbon was mixed with carbon super-P ($\varnothing = 40$ nm particles, Timcal) and sodium carboxymethyl cellulose (Na-CMC, Sigma Aldrich, average weight 90 kDa) in a weight ratio of 7:2:1 active material, carbon super-P and binder for a total of 600 mg of solids per mixture. A slurry was obtained from the powders through the same

milling procedure employed in the case of silicon although a smaller amount of water (1.5 mL).

Identical casting conditions to silicon were used to coat the copper current collector foil (Advent Research Material, 17 μm thickness). Once prepared, the slurry was dried in air overnight. 19 mm diameter electrodes were punched and further dried in a vacuum oven at 80 $^{\circ}\text{C}$ for 2 h.

6.2.3 Electrodes Treatment With Na- and Li-naphthalenide

The solutions of lithium and sodium naphthalenide employed to treat the silicon and hard carbon anodes before cycling were prepared following previous works¹⁵.

A 1 M solution of naphthalene in completely anhydrous tetrahydrofuran (THF, <100 ppm water content, Sigma Aldrich) was prepared inside a glovebox under an inert atmosphere of Argon. Once the naphthalene was completely dissolved an equimolar quantity of lithium/sodium metal with respect to the naphthalene was immersed into the solution which was continuously stirred with a glass coated magnetic spinner. In both cases when the lithium or sodium was added to the solution it assumed a dark green colour due to the oxidation of the alkali metals by the naphthalene to form the anion naphthalenide (Figure 6.4).

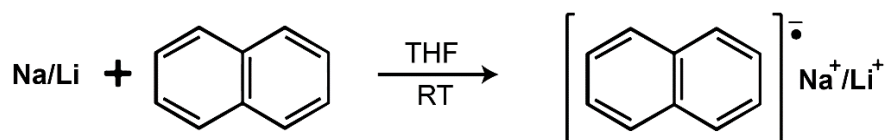


Figure 6.4 Schematic for the synthesis of Na/Li-naphthalenide.

The solutions were left under vigorous stirring overnight inside the glovebox to guarantee a complete reaction of the alkali metals with the naphthalene.

Due to the extreme reactivity of the naphthalenide anions all the treatments were carried out inside the glovebox. The anodes (silicon or hard carbon based) were treated by immersion in the naphthalenide solutions overnight. The ratio employed was 1 mL of

solution per electrode to ensure a large excess of reducing agent with respect to the loading of the electrodes that was around 3 mg of active material for silicon and 5 mg for hard carbon. Once treated the electrodes were repeatedly washed with THF to remove any residue of the naphthalenide solution and subsequently dried under vacuum for 2 h.

6.2.4 Evaluation of the Reduction Potential of Lithium and Sodium Naphthalenide

The determination of the redox potential of the Li-naphthalenide solution was carried inside an argon filled glovebox and the setup employed is shown in Figure 6.5

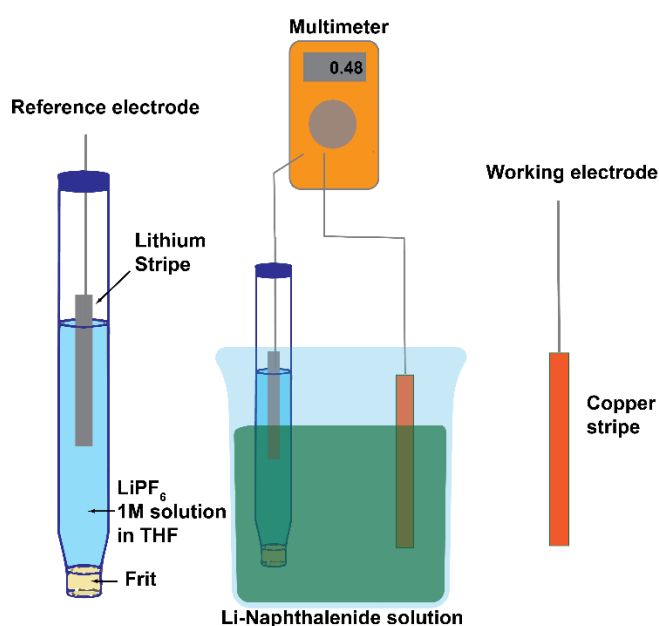


Figure 6.5 Experimental setup for the determination of the redox potential of Li/Na-naphthalenide solutions employed to treat the anodes.

The potential was measured with respect to the redox couple Li^+/Li . To do so a reference electrode was built using a glass pipette with an ionically conductive frit stuck at the bottom that had been soaked in the solvent, THF, for overnight to allow a complete soaking. Inside the pipette a strip of metallic lithium was immersed in a 1 M solution of LiPF_6 in THF. The working electrode was made of a metallic strip of copper.

The two electrodes were connected to a multimeter and immersed in a freshly prepared solution of Li-naphthalenide and naphthalene (1:1 molar ratio) in THF with a 1M concentration of LiPF_6 dissolved in it. The potential reading was left to stabilize for a few seconds and the value obtained was 0.48 V which corresponds to the difference of redox potential ΔE between the lithium metal and the naphthalenide solution. In the case of Na-naphthalenide the same procedure was repeated employing a reference electrode made of metallic sodium immersed in a 1 M solution of NaPF_6 in THF. The potential obtained for sodium naphthalenide was 0.25 V vs. Na^+/Na .

6.2.5 Cell Preparation

Silicon and hard carbon vs. lithium

The electrodes were assembled into CR2325 coin cells following the same procedure employed for the silicon electrodes in the previous chapter.

Hard carbon vs. sodium

The electrodes were assembled the same way that was employed for the silicon ones. The only differences were the use of a metallic sodium foil as counter electrode and the composition of the electrolyte that in this case was made from a 1 M solution of NaPF_6 (Kishida Chemicals) in propylene carbonate (PC, anhydrous, 99.7%, Sigma Aldrich).

6.3 Results and Discussions

Both the active materials employed, i.e. silicon powder and hard carbon were characterised by SEM and PXRD prior to the preparation of the electrodes and their subsequent treatment with lithium/sodium naphthalenide. Once assembled into coin cells the treated electrodes were tested by galvanostatic cycling and their performance compared with the non-treated materials. X-ray Photoelectron Spectroscopy analysis of the treated and non-treated materials was carried out to investigate the changes induced on the surface of the anodes by the treatment.

6.3.1 Analyses and Characterisation of the Active Materials

The SEM and PXRD characterisation performed on the silicon nanopowder resulted in analogous results to the ones shown in the previous chapter 5 and will not be repeated here.

Powder X-ray diffraction of hard carbon

The PXRD of hard carbon was collected on the synthesized material between 10 and 70 2θ degrees. The pattern obtained is reported in Figure 6.6 where it is possible to observe the presence of two broad peaks centred around 20 and 43 2θ degrees.

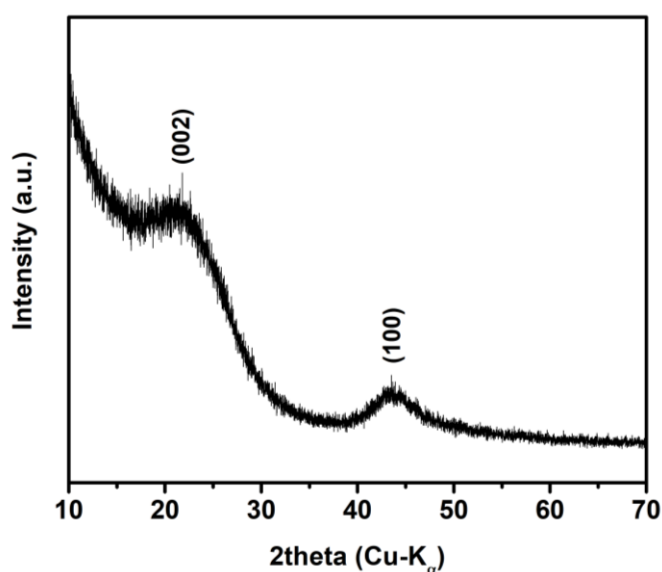


Figure 6.6 Powder X-Ray Diffraction pattern of the synthesized hard carbon.

The peaks have been indexed following previous works and their respective ratios and positions appeared to be in good agreement with that reported in literature previously for the material^{6,14}. Moreover, the positions and FWHM values of the (002) and (100) peaks are closely related respectively to the number of stacked graphic layers and their surface extension. Both these parameters can be tuned by varying the temperature of pyrolysis.

Scanning electron microscopy of hard carbons

In Figure 6.7 the SEM images are reported for the prepared hard carbons collected at different magnifications.

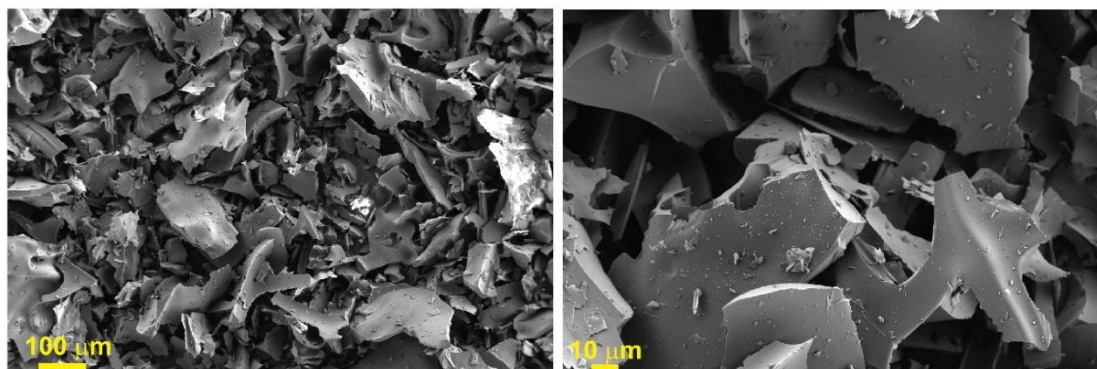


Figure 6.7 SEM images of the synthesized hard carbon. The images were collected with magnifications of 100x (left) and 500x (right) and an operating voltage of 5 kV.

It is possible to notice that the particles possess an irregular flake-like appearance with a relatively large distribution in dimensions, ranging between 5 and 100 μm in diameter.

The peculiar shape assumed by the particles might be associated with the pyrolysis step in which the dehydrated sucrose is heated up to 900 $^{\circ}\text{C}$ under inert atmosphere. During the heating process the acid treated sugar melts down and all the residual oxygen and hydrogen not removed with the acid washing boils off in the form of H_2O and CO_2 . The vapours extracted leave a highly porous and brittle hard carbon structure that once milled yields the final particles observed in the SEM images.

6.3.2 Comparison of the Electrochemical Performance on the Treated and Non-Treated Electrodes

The results below show the effect of the naphthalenide treatment in improving the coulombic efficiency of the electrodes during the first cycle. It should be noted that all the electrodes compared possessed an identical diameter and comparable loading (3-5 mg) of active material.

Silicon

In Figure 6.8 a comparison of the electrochemical performance during cycling for silicon electrodes with (treated) and without (pristine) a lithium naphthalenide treatment is shown. In the first instance, it is important to notice that the treatment does not appear to have affected the overall performance of the electrodes. The galvanostatic cycling data are presented in Figure 6.8-a for the two electrodes. The behaviour appears almost identical with a gradual fade in capacity over 150 cycles from 2500 to 1700 mAhg⁻¹, although the non-treated silicon electrode, pink triangles, delivers a higher specific capacity between 30 and 100 cycles. In panel (b and (c) are reported the coulombic efficiencies and the load curves for the first cycle of the treated and non-treated electrodes.

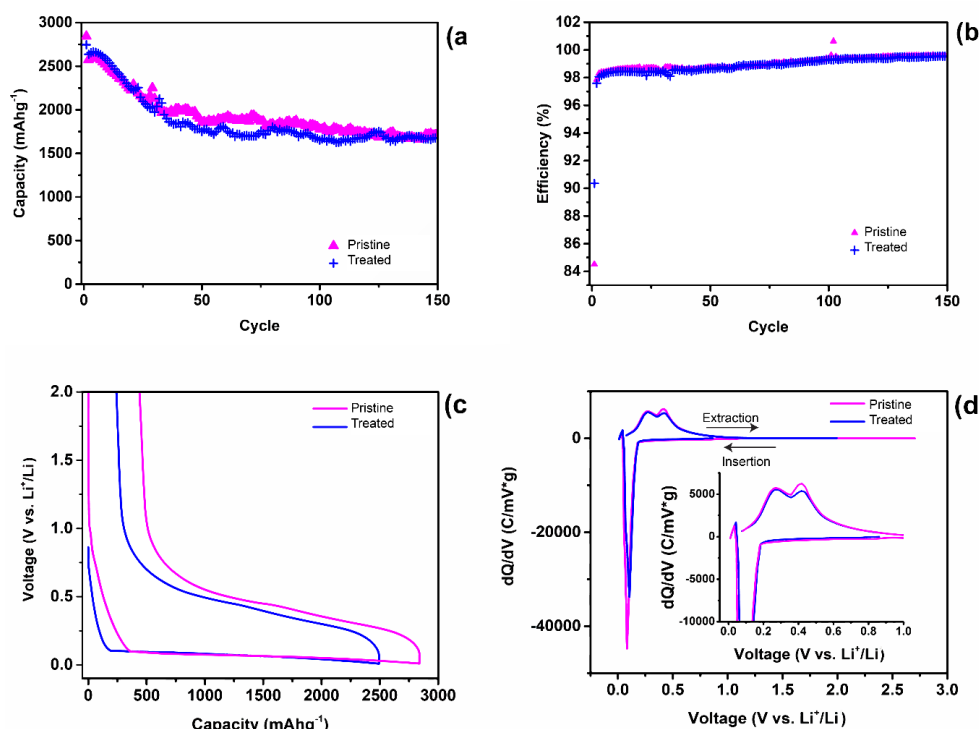


Figure 6.8 Comparison of the electrochemical performance of the silicon anodes before (pink) and after (blue) the treatment with Li-naphthalenide. Both the electrodes were cycled galvanostatically at 1800 mA g⁻¹ in a 0 to 2 V vs. Li⁺/Li voltage range. In the panels are reported the galvanostatic cycling vs. cycle number (a), the coulombic efficiency vs. cycle number (b), the load curves for the first cycles vs. capacity (c) and the differential capacity plots vs. voltage (d).

In panel (c) for the pristine electrode the observed OCV is above 2 V vs. Li^+/Li that during the lithium insertion process fades after 250 mAhg^{-1} to a plateau region centred around 0.1 V vs. Li^+/Li resulting from the two-phase alloying of lithium with the silicon particles. A charge of about 2800 mAhg^{-1} is inserted in the electrode. In the subsequent de-alloying process an hysteresis of 0.3 V is present and about 2300 mAhg^{-1} are extracted with a FIC of about 500 mAhg^{-1} . In the case of the treated electrode the shape of the first cycle load curve is very similar to the pristine one although the OCV is 0.8 V vs. Li^+/Li and the 0.1 V plateau is reached after 100 mAhg^{-1} where the insertion of lithium continues up to a value of 2500 mAhg^{-1} . The lithium extraction process in the treated material shows the same hysteresis as the pristine one although the irreversible capacity drops from 500 to 200 mAhg^{-1} . It appears clear the beneficial effect of the treatment in reducing the first-cycle irreversible capacity with an efficiency gain higher than 6% during the first cycle, allowing for a reduction of the FIC to less than 10% of the overall charge inserted in the anode.

Over the remaining cycles the coulombic efficiencies do not appear to be affected (Figure 6.8-b) by the treatment in good agreement with what is shown in panel (a) for the specific capacity delivered. The differential capacity plots shown in Figure 6.8-d appear almost identical in shape confirming that no parasitic process is affecting the treated anode with a shallower peak corresponding to the insertion of lithium at 0.1 V vs. Li^+/Li for the treated material (less charge stored).

Hard carbon vs. lithium

The electrochemical cycling obtained from a naphthalenide treated electrode of the synthesized hard carbon (HC) anode cycled against metallic lithium are reported in Figure 6.9 together with the performance of a pristine electrode. In Figure 6.9-c the load curves for the treated and pristine electrodes are shown. In the case of the pristine electrode the starting OCV is about 3.2 V vs. Li^+/Li and as the lithium ions are inserted in the material a gradual fade in voltage, probably due to a one-phase insertion process in the disordered carbon matrix, is observed until 600 mAhg^{-1} .

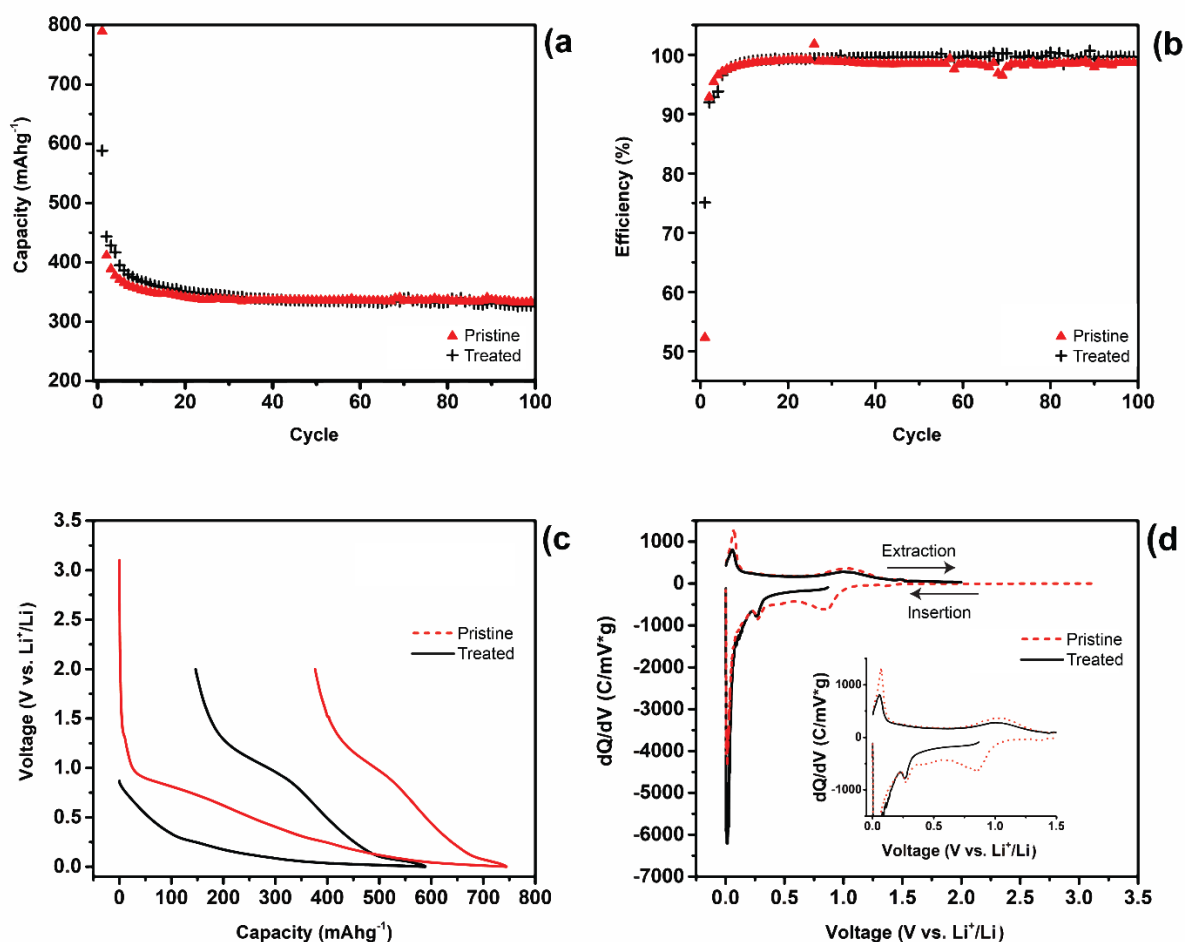


Figure 6.9 Comparison of the electrochemical performance of the hard carbon anodes before (red) and after (black) the treatment with Li-naphthalenide. Both the electrodes were cycled galvanostatically at 20 mA g⁻¹ in a 0 to 2 V vs. Li⁺/Li voltage range. In the panels are reported the galvanostatic cycling vs. cycle number (a), the coulombic efficiency vs. cycle number (b), the load curves for the first cycles vs. capacity (c) and the differential capacity plots vs. voltage (d).

A short plateau region then appears centred around 0.05 V vs Li⁺/Li that could be assigned to the two-phase insertion process of lithium in the small graphitic domains dispersed in the highly disordered carbon matrix. An overall capacity of 750 mAhg⁻¹ is stored in the pristine material and upon lithium extraction only about half of that capacity is recovered, with an FIC of almost 50% (Figure 6.9-b). As for the treated electrode a much lower starting OCV of 0.7 V vs. Li⁺/Li and a smooth and uniform curve shape during lithium insertion are observed. A lower amount of charge is stored in the treated material of approximately 600 mAhg⁻¹, with respect to the pristine, but a comparable amount of

charge is recovered upon lithium extraction ($\sim 350 \text{ mAhg}^{-1}$), hence reducing the FIC to 25%.

In Figure 6.9-a are reported the cyclabilities for both the electrodes and where the specific capacity appears to steeply drop at the beginning of cycling for both the pristine and treated although subsequently it becomes stable with values well over 300 mAhg^{-1} for 100 cycles.

The change in the electrochemical behaviour of the treated HC with respect to the pristine one is even more evident in Figure 6.9-d where the differential capacity plots appear to differ. For the lithium insertion curve, a peak centred at 0.8 V vs. Li^+/Li is present for the pristine material but completely disappears in the curve of the treated one.

The elimination of the 0.8 V step after the treatment indicates that the process happening at the anode during the lithium insertion at this potential has been suppressed in the treated electrodes.

The mitigation of the FIC in the treated hard carbon electrodes could be explained through the idea that a large amount of surface-adsorbed species, which would be reduced electrochemically at low voltage values, are chemically reduced in the case of the naphthalenide treatment prior to the electrochemical cycling.

As well the contact between the highly reduced electrode surface after the treatment and the electrolyte in the coin-cell might lead to spontaneous reduction of the electrolyte on the electrode surface to form an SEI layer before the electrochemical cycling.

Hard carbon vs. sodium

The same kind of hard carbon-based electrodes washed with lithium naphthalenide were treated with sodium naphthalenide and cycled against metallic sodium. As already discussed hard carbon still represents one of the materials of choice for anodes in sodium-ion batteries.

As for the previous cases in Figure 6.10-c are shown the load curves for the first cycles of the treated and pristine electrodes. The first cycle load curve for the pristine material shows a starting OCV of 2.4 V vs. Na^+/Na with the voltage initially dropping to around 1 V Na^+/Na and subsequently fading with the insertion of sodium ions.

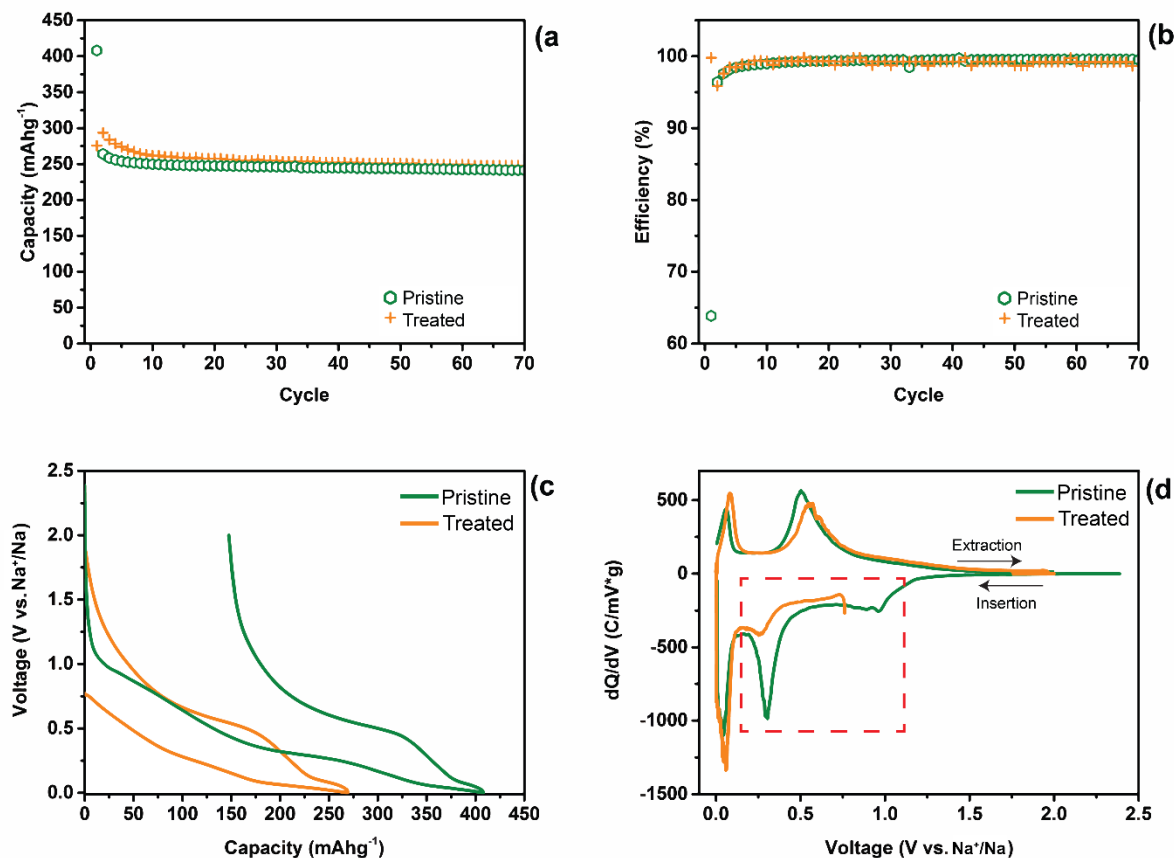


Figure 6.10 Comparison of the electrochemical performance of the hard carbon anodes before (green) and after (orange) the treatment with Na-naphthalenide. Both the electrodes were cycled galvanostatically at 20 mA g⁻¹ in a 0 to 2 V vs. Na^+/Na voltage range. In the panels are reported the galvanostatic cycling vs. cycle number (a), the coulombic efficiency vs. cycle number (b), the load curves for the first cycles vs. capacity (c) and the differential capacity plots vs. voltage (d).

The lower voltage cut-off is reached after 410 mAhg⁻¹ of charge has been passed. The process of insertion of sodium ions in the hard carbon appears to be articulated into at least three different steps as shown in Figure 6.10-d where the differential capacity plot for the pristine presents three peaks centred at 1, 0.3 and 0.05 V vs. Na^+/Na . In the sodium extraction process, only two peaks appear in Figure 6.10-d at 0.1 and 0.5 V vs. Na^+/Na with about 260 mAhg⁻¹ extracted from the material, accounting for a FIC of 36%.

The treated electrode's load curve shows a much lower starting OCV of 0.75 V vs. Na⁺/Na with an immediate and gradual fade of the voltage as the sodium ions are inserted with a total charge stored of 260 mAhg⁻¹. The treated material differential capacity plot (Figure 6.10-d) in the sodium insertion branch shows a complete elimination of the 1 V peak and a much smaller 0.5 V one with maintenance of the 0.05 V peak. As for the extraction process the load curve of the treated material resembles the one of the pristine with a similar value of charge extracted from the HC (~250 mAhg⁻¹). This implies a dramatic reduction of the FIC to about 1% and a coulombic efficiency in the first cycle of 99% for the treated material.

Once again, the sodium naphthalenide treatment did not affect the overall performance of the electrode which displays a stable capacity above 250 mAhg⁻¹ for over 50 cycles (Figure 6.10-a).

The striking difference in the coulombic efficiency and FIC reduction observed between the first cycle for the two electrodes (Figure 6.10-b) could be not only to surface reducing effect exerted by the naphthalenide but also to a partial insertion of sodium ions in the HC during the treatment. These results would be consistent with the potential of the Na-naphthalenide solution measured earlier of 0.25 V vs. Na⁺/Na, allowing for the partial intercalation of the alkali metal ions.

6.3.3 Comparison of the Electrode Components by X-ray Photoelectron Spectroscopy Before and After the Reducing Treatment

XPS analysis was carried out on the different electrode components before and after the treatment with Li/Na-naphthalenide to get a better understanding of the mechanisms happening at the electrode surface during the treatment, which lead to a performance improvement. The spectra were collected at the departmental in-house XPS facility with an incident energy of 1486.6 eV and fitted with the help of Dr. Andy Naylor using the

software suite CasaXPS. The purpose of the XPS in this case it is more qualitative rather than quantitative. The main goal was to observe whether the naphthalenide treatment had successfully reduced the species adsorbed on the surface of the electrodes and whether, especially in the case of hard carbon, alkali metal ions had been inserted in the active material.

Figure 6.11 to Figure 6.14 summarize the spectra measured on silicon (Figure 6.11), hard carbon (Figure 6.12), carbon super-P (Figure 6.13) and Na-CMC (Figure 6.14). On the top left corner of each panel is indicated the orbital probed: Si 2p and O 1s for silicon, C 1s and O 1s for the other components.

The spectra relative to the non-treated materials are labelled with the letter P (Pristine), while the treated ones with the letter T (Treated). The subscript specifies the alkali-metal cation dissolved in the naphthalene solution. The data are plotted with decreasing binding energy from left to right in the graphs in the x-axis. All the spectra were calibrated to the C 1s peak for hydrocarbon occurring at 284.8 eV and were not normalised to be able to see changes in intensities after the reducing treatments.

Silicon:

The Si 2p spectrum for the pristine silicon powder was fitted with 6 components centred respectively at 99, 100, 100.8, 102.5, 104 and 106 eV. The first two at 99 and 100 eV belong to elemental silicon, the double component is due to the spin-orbit coupling effect for which it possible to discriminate between the states Si 2p^{1/2} and Si 2p^{3/2}. The 100.8 eV component is associated with Si-C bond and the presence of carbon contamination on the pristine silicon surface could be related to the nanoparticles synthetic process. The other three components were associated with the Si-O_x bond, in which silicon has different oxidation number respectively 102.5 and 104 eV correspond to $x \leq 2$ and 106 eV corresponds to $x \geq 2$.

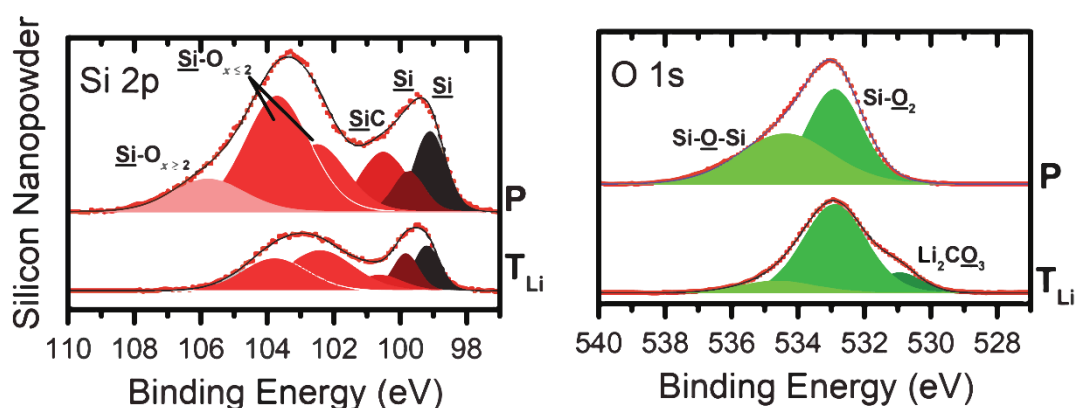
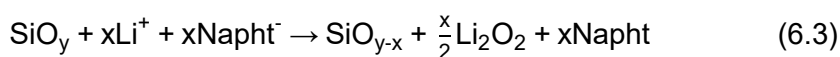


Figure 6.11 Fitting for the XPS spectra acquired on the silicon pristine nanopowder. In the left panel are reported the spectra for the Si 2p excitation energy whilst in the right one are reported the spectra for the O 1s excitation energy. In both cases the spectra on the top belong to the pristine powder (indicated with the letter P) and the spectra at the bottom belong to the Li-naphthalenide treated one (indicated with the letter T_{Li}).

In the treated material the peaks in the Si 2p spectrum appear to get broader with a significant loss in intensity. The peaks associated with highly oxidized silicon (binding energy >101 eV) appear to decrease in intensity and the ratio between the peaks centred at 102.5 and 104 eV is inverted. Moreover, the peak relative to the highest oxidation number for silicon $\text{Si-O}_{x>2}$ (106 eV) completely disappears after the reducing treatment. The components at lower binding energies relative to elemental silicon and Si-C are still present in the treated material although the intensity ratios vary. The evolution of the components for the highly oxidized silicon with the treatment could be explained considering that the native thin layer of silicon oxide present on the particles surface might be reduced during the treatment through reactions with the lithium naphthalenide such as,



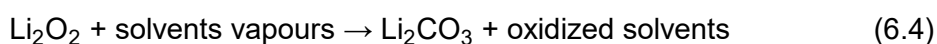
Or



As for the oxygen 1s spectra (Figure 6.11), the pristine material one has been fitted with two main components at 535 and 533 eV are associated with the highly oxidized oxygen

Si-O-Si and Si-O₂ respectively. After the treatment the peak at 535 eV is strongly attenuated confirming the reduction of the oxygen whilst the SiO₂ peak gets broader.

A new peak at 531 eV associated with Li₂CO₃ appears in the treated silicon powder. The generation of lithium carbonate could be justified through the reaction of the highly reduced surface of the treated material with the probable presence in the glovebox atmosphere of small amounts of electrolyte's solvents vapours such as DMC and PC that would be adsorbed on the material surface as lithium carbonate by reaction with the lithium peroxide formed during the treatment Equation (6.4)



Hard carbon

In the hard carbon the C 1s spectra of the pristine powder (Figure 6.12) were fitted with 4 peaks associated with C=C (284 eV), C-C (284.8 eV), C-O (286 eV) and C=O bond (288.5 eV) respectively.

The treatments with both Li- and Na-naphthalenide solutions seem to have a similar effect with the intense peak of C=C at 284 eV completely disappearing and the other three peaks rising in intensity although their intensity ratios are maintained. This implies that the graphitic sp² carbon on the surface is apparently oxidized to an sp³ hybridized carbon which would be in contrast with the highly reductive potential of the naphthalenide solutions. Another possible explanation could be related to the formation of a surface layer that would screen the graphic carbon signal.

This hypothesis would be backed from the O 1s spectra of the HC. In the pristine material three peaks centred at 531, 533 and 535 eV were used to fit the O 1s spectrum that were associated with C-O, C=O and Na KLL Auger.

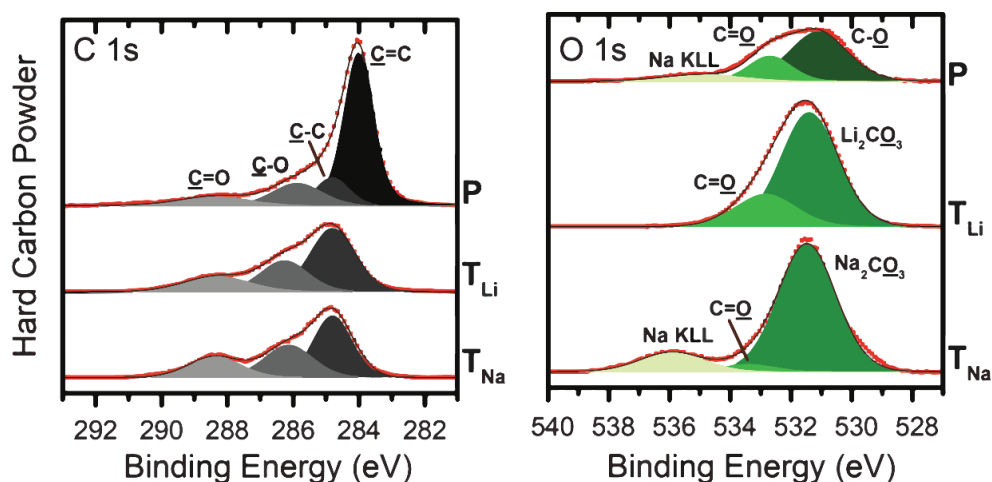


Figure 6.12 Fitting for the XPS spectra acquired on the hard carbon pristine powder. In the left panel are reported the spectra for the C 1s excitation energy whilst in the right one are reported the spectra for the O 1s excitation energy. In both cases the spectra on the top belong to the pristine powder (indicated with the letter P) and the spectra in the middle and at the bottom belong respectively to the Li-naphthalenide (indicated with T_{Li}) and to the Na-naphthalenide (indicated with T_{Na}) treated powders.

The presence of sodium in the pristine material might be due to partial contamination of the sample surface during the synthetic step at high temperatures in the furnace. The C-O peak (531 eV) after the treatments with either Na or Li naphthalenide is completely covered by a strong overlapping peak corresponding to the presence of Li₂CO₃ and Na₂CO₃. The formation of a rather thick layer of alkali metal carbonates on the HC surfaces after the reducing treatments would have the same origins of the lithium carbonate observed in the silicon powder being formed through reaction of solvents vapours present in the glovebox atmosphere with alkali metals peroxides and oxides on the HC surface.

The C=O peak at 534 eV seems to behave differently for the two treatments, increasing after the treatment with Li-naphthalenide and decreasing after the Na one. This difference in intensity might be related to the presence of rather intense peak for Na-KLL in the Na-naphthalenide treated HC or to the different redox potential of the two solutions that could lead to different processes happening at the electrodes surfaces. The overall increase of the O 1s signal with respect to the pristine hard carbon is indicative of the deposition of

oxygenated species on the surface due to the treatments. It has to be noticed as well that the Na KLL signal completely disappears after the Li naphthalenide treatment whilst it increases after the Na-naphthalenide one. The clear increase in the Na KLL signal for the Na-naphthalenide treated HC supports the hypothesis that sodium gets partially intercalated in the HC structure during the reducing treatment thanks to the low redox potential of the naphthalene/Na-naphthalenide couple.

Carbon super-P

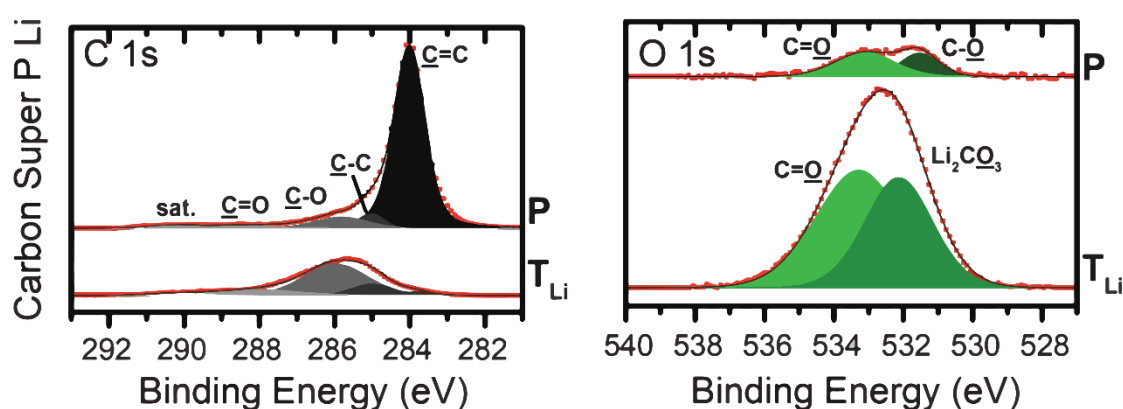


Figure 6.13 Fitting for the XPS spectra acquired on the carbon super-P pristine powder. In the left panel are reported the spectra for the C 1s excitation energy whilst in the right one are reported the spectra for the O 1s excitation energy. In both cases the spectra on the top belong to the pristine powder (indicated with the letter P) and the spectra at the bottom belong to the Li-naphthalenide treated one (indicated with the letter T_{Li}).

The C 1s and O 1s spectra (Figure 6.13) for the pristine super-P carbon were fitted with the same components used in the HC. As for the hard carbon the C sp² peak at 284 eV is no more visible after the treatment with Li-naphthalenide whilst the other peaks do not maintain the pristine ratios with intensity increase of the C-O peak at 286 eV that could be due to the C-O bond present in the carbonate anion. The O 1s spectrum of the super P behaves in a similar way to the HC one with the C-O component at 531 eV completely covered by a strong signal due to the C-O bond in Li₂CO₃ (531.5 eV) formed at the carbon super-P surface.

Na-CMC binder

The C 1s XPS spectrum of the pristine Na-CMC (Figure 6.14) binder was fitted with 4 components relative to C-C (284.8 eV), C-O (286 eV), C=O (288.5 eV) and O-C=O (290 eV) respectively.

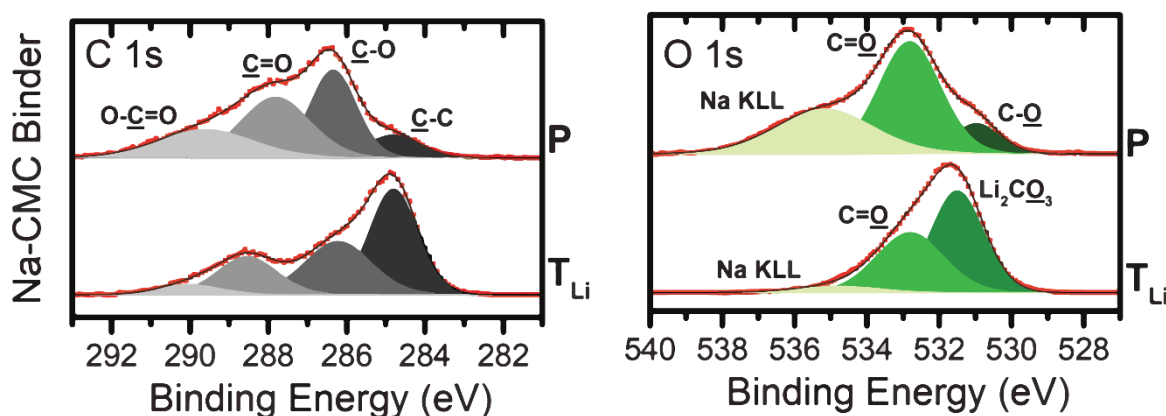


Figure 6.14 Fitting for the XPS spectra acquired on the Na-CMC binder pristine powder. In the left panel are reported the spectra for the C 1s excitation energy whilst in the right one are reported the spectra for the O 1s excitation energy. In both cases the spectra on the top belong to the pristine powder (indicated with the letter P) and the spectra on the bottom belong to the Li-naphthalenide treated one (indicated with the letter T_{Li}).

After the treatment with Li-naphthalenide the O-C=O groups (peak at 290 eV) are reduced and the intensity of the peak significantly decreases, at the same time the C sp^3 peak intensity at lower binding energies (285 eV) raises, whilst the C-O (286 eV) and C=O (288.5 eV) peaks do not appear to change their intensity ratios although their intensities is decreased with respect to the pristine powder. The Na-CMC C 1s spectrum after the reducing treatment resembles the treated HC C 1s spectrum (Figure 6.12) showing the formation of a reduced surface layer.

The O 1s spectrum for the pristine Na-CMC was fitted with the same C-O (530 eV) and C=O (533 eV) used for the carbons O 1s spectra although this time a strong Na-KLL signal is present as well, which is due to the sodium counterion in the Na-CMC salt. The sodium KLL signal in the O 1s spectrum of the treated binder is strongly decreased due to either the formation of a lithium carbonate surface layer or to the cationic substitution of

sodium with lithium in Na-CMC. As observed previously a strong signal due to the formation of Li_2CO_3 (531.5 eV) appears in the treated material, covering the 531 eV peak associated with C-O.

XPS discussion

Overall the XPS analysis suggests the formation of a blocking layer passivating the surfaces of all the tested powders, after the reducing treatments, that is rich in oxygenated species such as Li_2CO_3 and Na_2CO_3 .

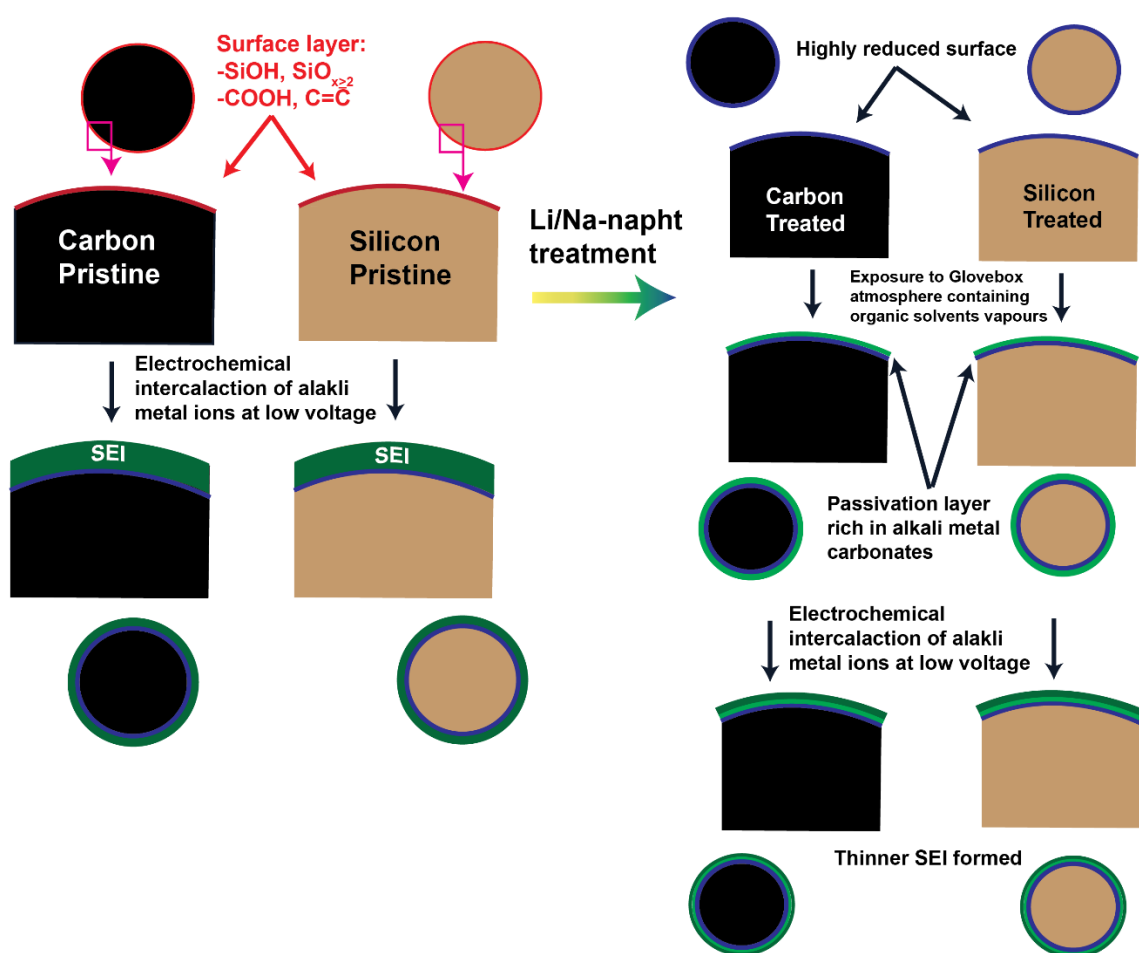


Figure 6.15 Schematic of the proposed working mechanisms of the naphthalenide solutions and their effects on particle interfaces during the first lithiation of the pristine silicon and hard carbon electrodes.

In Figure 6.15 is schematically represented a plausible way in which the treatment may work to improve the electrodes coulombic efficiency. As shown in the figure, the pristine particles of hard carbon and silicon present native surface layers rich in hydroxyl groups

and unsaturated bonds. Without naphthalenide treatment the surface species would be reduced over the first electrochemical cycle, during the alkali metal ion intercalation, at low potential values with the concomitant formation of the SEI layer from the electrochemical reduction of the native surface species and partial decomposition of the electrolyte. This mechanism leads to a loss of capacity known as First cycle Irreversible Capacity (FIC). Treatment with the Li/Na-naphthalenide solutions reduces the surface species in the pristine materials with presence of highly reactive species such as Li/Na₂O₂. Once the treated surfaces are exposed to the electrolyte's solvents traces in the glovebox atmosphere immediately react to form a passivating SEI-like layer rich in alkali metal carbonates species. This layer would prevent the electrolyte decomposition during cycling to the same extent as in the untreated samples improving the coulombic efficiency of the first cycle. Additionally, the presence of species like Li₂CO₃ and Na₂CO₃ in the passivating layer formed during the treatment could contribute to increase the coulombic efficiency acting as an alkali metal ions reservoir. It must also be noted that the O 1s spectrum for the Na-naphthalenide treated HC (Figure 6.12) showed the presence of elemental sodium (Na-KLL peak) on the material surface partially confirming the idea that, due to its low redox potential (0.25 V vs. Na⁺/Na), the Na-naphthalenide solution would be able to insert sodium in the HC, although due to the surface sensitivity of XPS no further speculations can be made in these regards.

6.4 Conclusions

In this chapter, an innovative process for the pre-treatment of anodes for lithium and sodium ion batteries based on silicon and hard carbon is presented in the attempt to substantially decrease the first cycle irreversible capacity. The treatment was based on the overnight washing of the electrodes with 1 M solutions of Li/Na-naphthalenide in THF. Li-naphthalenide was employed to treat silicon anodes whilst both Li and Na-naphthalenide were used to treat the hard carbon anodes since hard carbon can be employed in both Li and Na ion batteries as the anode. The treatments on the electrodes

appear to work with a sensible reduction of the first irreversible capacity in all cases although the most dramatic effect was observed for the hard carbon treated with Na-naphthalenide in which the coulombic efficiency goes from 64% before the treatment to 99% after the treatment during the first cycle.

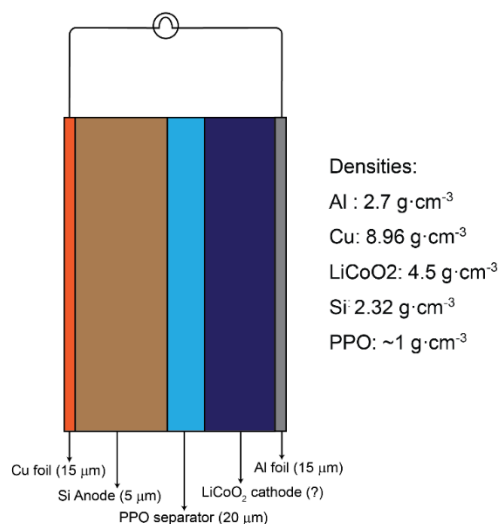


Figure 6.16 Schematic of a hypothetical full cell made up by a silicon anode casted on a copper current collector and a LiCoO₂ cathode casted on an aluminium current collector. The separator is a polypropylene oxide film. On the right-hand side the densities values for the different cell components are reported to calculate the specific energy density values with and without naphthalenide treatment.

This strong improvement could be also related to the low redox potential (0.25 V vs. Na⁺/Na) of the Na-naphthalenide solution that could sodiate the HC beside exerting its reductive action on the material surface. In all cases no anomalous behaviour was observed in the electrochemistry of the electrodes after the treatments indicating that the treatment does not affect the overall performance of the materials. To have a rough idea of the energy density gain achievable thanks to the treatment, one can estimate the weight of cathode material needed to balance the charge of the anode with and without the naphthalenide treatment for the silicon electrode.

In Figure 6.16 is reported the schematic of a full cell with a silicon anode and LiCoO₂ cathode. It is possible to calculate the quantity of LiCoO₂ required to balance the silicon

(see Appendix) using the values for the densities and thicknesses reported in the figure and making the following assumptions:

- The electrodes are assumed to be 100% active material
- The materials particles are assumed to be all equal and spherical forming perfect packing of sphere ($\sim 74\%$ of the volume is occupied).
- Is possible to extract only 0.5 moles (i.e. $\sim 137 \text{ mAhg}^{-1}$) of lithium from LiCoO_2 to avoid material degradation.
- The charge inserted at the silicon anode during the first lithiation process is as reported in Figure 6.8 (panel (a)) 2800 mAhg^{-1} for the pristine electrode and 2500 mAhg^{-1} for the naphthalenide treated one, with 500 mAhg^{-1} of FIC in the first case and 250 mAhg^{-1} in the second.
- The area of the cell is taken to be 1 cm^2
- The working potential of the cell is set to $3.3 \text{ V vs. Li}^+/\text{Li}$

From the calculation, 175 mg ($39 \text{ }\mu\text{m}$ film thickness) of LiCoO_2 are required to balance the silicon and account for the charge loss in the first cycle, corresponding to a full cell specific energy of 170 Whkg^{-1} .

In the case of the treated silicon electrode (i.e. 300 mAhg^{-1} of irreversible capacity have been eliminated), the amount of LCO required is 156 mg ($35 \text{ }\mu\text{m}$ film thickness), corresponding to a full cell specific energy of 176 Whkg^{-1} . Although many approximations have been made, the calculation yields reasonable numbers and above all it turns out that a 3.5% increase in specific energy is gained thanks to the naphthalenide treatment procedure. Since silicon-based electrodes appear to be the ones that benefit the least from the naphthalenide treatment in terms of FIC reduction and since the hard carbon density is comparable to the silicon one, it is evident that an even higher increase in energy density after the treatment is expected in the case of the hard carbon.

The X-ray photoelectron spectroscopy performed on the electrode components before and after the treatments showed the formation of a surface layer rich in polycarbonates and oxygenated species. This passivating layer could be crucial in limiting the formation of the SEI layer during the first lithiation, which is a major source of coulombic inefficiency in the electrodes' first cycle.

Despite the interesting results attained, the scale-up and commercial viability of the naphthalenide treatment would imply a large economic effort due to the necessity of keeping the whole process under inert atmosphere of argon given the extreme reactivity of the naphthalenide solutions and to avoid any side reactions during the treating process.

6.5 Appendix

6.5.1 Energy Density Calculation

Full cell without naphthalenide treatment:

Charge required to balance the silicon electrode

$$2800 \text{ mAhg}^{-1} \times 0.005 \text{ cm}^{-3} \times 2.32 \text{ gcm}^{-3} \times 0.74 = 24.03 \text{ mAh} \equiv 86.4 \text{ C}$$

Corresponding to a weight of LiCoO_2 given by

$$24.03 \text{ mAh} \div 137 \text{ mAhg}^{-1} = 0.175 \text{ g}$$

That assuming a density of 4.5 gcm^{-3} giving a film thickness of 0.039 cm

To evaluate the specific energy it has to be considered that the total cell weight is 0.381 g (from the density values shown in Figure 6.16) and that of the 2800 mAhg^{-1} of the first lithiation about 500 mAhg^{-1} are lost due to the FIC:

$$86.4 \text{ C} \times \left(\frac{2300 \text{ mAhg}^{-1}}{2800 \text{ mAhg}^{-1}} \right) = 70.97 \text{ C}$$

$$\frac{70.97 \text{ C}}{0.381 \text{ g}} = 186.2 \text{ Cg}^{-1}$$

$$186.2 \text{ Cg}^{-1} \times 3.3 \text{ V} = 614.4 \text{ Jg}^{-1} = 0.170 \text{ Whg}^{-1} = 170 \text{ Whkg}^{-1}$$

Full cell with naphthalenide treatment

Charge required to balance the silicon electrode

$$2500 \text{ mAhg}^{-1} \times 0.005 \text{ cm}^{-3} \times 2.32 \text{ gcm}^{-3} \times 0.74 = 21.46 \text{ mAh} \equiv 77.25 \text{ C}$$

Corresponding to a weight of LiCoO_2 given by

$$21.46 \text{ mAh} \div 137 \text{ mAhg}^{-1} = 0.156 \text{ g}$$

That assuming a density of 4.5 gcm^{-3} gives a film thickness of 0.035 cm

To evaluate the specific energy it has to be considered that the total cell weight is 0.362 g (from the density values shown in Figure 6.16) and that of the 2500 mAhg⁻¹ of the first lithiation about 250 mAhg⁻¹ are lost due to the FIC:

$$77.25 \text{ C} \times \left(\frac{2250 \text{ mAhg}^{-1}}{2500 \text{ mAhg}^{-1}} \right) = 69.52 \text{ C}$$

$$\frac{69.52 \text{ C}}{0.362 \text{ g}} = 192.04 \text{ Cg}^{-1}$$

$$192.04 \text{ Cg}^{-1} \times 3.3 \text{ V} = 633.7 \text{ Jg}^{-1} = 0.176 \text{ Whg}^{-1} = \mathbf{176 \text{ Whkg}^{-1}}$$

6.6 References

- 1 C. K. Chan, H. Peng, G. Liu, K. Mcllwath, X. F. Zhang, R. a Huggins and Y. Cui, *Nat. Nanotechnol.*, 2008, **3**, 31–5.
- 2 M. T. McDowell, S. W. Lee, W. D. Nix and Y. Cui, *Adv. Mater.*, 2013, **25**, 4966–4985.
- 3 S. Bourderau, T. Brousse and D. . Schleich, *J. Power Sources*, 1999, **81–82**, 233–236.
- 4 K. Hong, L. Qie, R. Zeng, Z. Yi, W. Zhang, D. Wang, W. Yin, C. Wu, Q. Fan, W. Zhang and Y. Huang, *J. Mater. Chem. A*, 2014, **2**, 12733.
- 5 E. Buie and J. R. Dahn, *J. Electrochem. Soc.*, 1998, **145**, 1977–1981.
- 6 E. Irisarri, A. Ponrouch and M. R. Palacin, 2015, **162**, 2476–2482.
- 7 E. Buie, *J. Electrochem. Soc.*, 1998, **145**, 2252.
- 8 Y. Bai, Z. Wang, C. Wu, R. Xu, F. Wu, Y. Liu, H. Li, Y. Li, J. Lu and K. Amine, *ACS Appl. Mater. Interfaces*, 2015, **7**, 5598–5604.
- 9 Z. Yan, L. Liu, J. Tan, Q. Zhou, Z. Huang, D. Xia, H. Shu, X. Yang and X. Wang, *J. Power Sources*, 2014, **269**, 37–45.
- 10 J. Graetz, C. C. Ahn, R. Yazami and B. Fultz, *Electrochem. Solid-State Lett.*, 2003, **6**, A194.
- 11 S.-H. Ng, J. Wang, D. Wexler, K. Konstantinov, Z.-P. Guo and H.-K. Liu, *Angew. Chemie Int. Ed.*, 2006, **45**, 6896–6899.
- 12 D. W. Murphy and P. A. Christian, *Science (80-.)*, 1979, **205**, 651–656.
- 13 K. Zaghib, R. Yazami and M. Broussely, *Scan. Electron Microsc.*, 1997, **68**, 239–241.
- 14 E. Buie and J. . Dahn, *Electrochim. Acta*, 1999, **45**, 121–130.
- 15 H. J. Liu, J. Yip and K. S. Shia, *Tetrahedron Lett.*, 1997, **38**, 2253–2256.

7 General Conclusions and Future Work

In this work have been investigated promising materials for the cathode (lithium-rich nickel substituted TM-oxides) and the anode (silicon and hard carbon) of an hypothetical new generation lithium-ion battery that would feature higher energy densities with respect to the commercial batteries currently available on the market.

The main reason behind the choice of these materials was the high capacity that they can display over cycling that would lead to longer lasting batteries. Additionally, the average working potentials of silicon (0.3 V vs. Li^+/Li) and lithium-rich oxides (3.5 V vs. Li^+/Li) would yield a cell that operates at 3.2 V, a value that is comparable to the lower capacity $\text{LiFePO}_4//\text{Graphite}$ commercial cells, providing high quality energy during its discharge.

Despite their appealing characteristics both the anodes and cathodes materials herein investigated are affected by major issues that have prevented, so far, a full development of commercial cells based on these materials. The aim of this work was mainly to deepen the understanding of the working mechanisms governing the performance of these materials:

Lithium rich cathodes:

The family of $\text{Li}_{(4/3-2/3x)}\text{Ni}_x\text{Mn}_{(2/3-1/3x)}\text{O}_2$ layered oxides was synthesized through a one-pot synthetic route and thoroughly investigated to understand the origins of the oxygen redox phenomenon responsible for the excess capacity with respect the transition metal redox activity.

It was demonstrated, first for the well renown $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$, that the charge associated with gas loss together with the charge accounted for by the nickel redox activity, over the first de-lithiation, does not account for the whole charge extracted from the material indicating the possible presence of anion redox. Employing advanced spectroscopic techniques such as SXAS, RIXS and XANES was possible to show the formation of

localised and reversible holes states on the oxygens during the de-lithiation of the material and a model in which the oxygen redox process is promoted by a more ionic environment for the coordination of the oxygen was proposed.

Subsequently several other members of the same family of compounds with different degrees of nickel substitution, including the parent compound Li_2MnO_3 , were synthesised and investigated trying to understand the role of nickel in the suppression of the oxygen loss phenomenon. It was demonstrated that a nickel content of 0.3 moles per formula unit suppresses almost completely the oxygen loss whilst maintains the reversible oxygen redox process. A preliminary model has also been proposed in the attempt to rationalize the different working mechanisms behind the parent compound Li_2MnO_3 and the nickel doped layered oxides although the reason why nickel would suppress the oxygen loss is not fully understood yet.

Future work:

A deeper investigation of the structural changes occurring during the cycling of the nickel substituted materials is necessary to understand the origin of the large hysteresis present in the electrochemistry of these materials. Operando X-ray diffraction together with ex-situ neutron diffraction analysis at different states of charge would provide a great deal of information relative to the evolution of the oxides structure during the extraction/insertion of lithium ions. As well, DFT calculations simulating what observed experimentally would help to unravel the changes in the electronic structure and clarify the role of nickel in the suppression of the oxygen loss.

Silicon and hard carbon anodes:

An optimisation of the electrochemical performance for silicon-based anodes has been proposed, employing new binders. It was shown that the use of PSSA binder provides

superior and more stable performance with respect to the traditional Na-CMC despite the poor coulombic efficiencies in the first cycles. To address the latter issue and try to reduce the important charge loss during the first cycle (First cycle Irreversible Capacity) a highly reducing pre-treatment was performed on the silicon electrodes employing a lithium naphthalenide concentrated solution. The low redox potential of the naphthalene/naphthalenide couple chemically reduced the electrodes surface reducing the FIC and improving the coulombic efficiencies at the beginning of cycling. The same kind of treatment was also employed on hard carbon, a material that is able to intercalate both lithium and sodium ions. Particularly in the case of sodium the hard carbon is regarded as one of the most promising anode materials although plagued by poor coulombic efficiencies. For that reason a treatment with sodium naphthalenide was performed on the hard carbon anodes reproducing the lithium naphthalenide experiment on silicon and it was shown the important improvement in the reversibility of the first cycles with no side effects on the electrochemistry.

With the help of XPS analysis the pristine and naphthalenide treated components of the anodes were investigated to understand the effect of the highly reducing treatments, leading to the formulation of a model in which the pre-treatment would have a fundamental role in reducing the surface adsorbed species on the anodes that would usually be reduced electrochemically.

Future work:

Regarding the binders for silicon anodes, consequently to the interesting results obtained from the use of PSS, it would be worth investigating how the conductivity across the electrodes' bulk evolves with cycling by means of the Impedance Spectroscopy and compare the results with the ones obtained from the electrodes having Na-CMC as binder. This may give further clues about the origin of the superior electrochemistry displayed by the electrodes with PSS binder. As well, a careful characterisation of the SEI

layer employing XPS and TOF-SIMS analyses would contribute to unravel the reasons behind the high electrochemical stability observed for PSS. As well, the work on the pre-treatment of the electrodes with the Li or Na naphthalenide solutions is close to completion although the optimisation of the treatment time and the concentration of the solutions are required to achieve a viable scale-up in which the use of a roll to roll set up would provide a fast and reproducible way to pre-treat large amount of cast material despite the high costs due to the inert atmosphere of argon required to avoid side reactions.

To conclude, it is interesting to notice that a non-optimized full cell that would employ a high nickel substituted (i.e. $\text{Li}_{1.133}\text{Ni}_{0.3}\text{Mn}_{0.566}\text{O}_2$) lithium rich layered oxide as cathode and a silicon anode treated with lithium naphthalenide would provide a specific energy density in excess of 200 Whkg^{-1} (a value that is competitive with the best cells currently on the market), assuming the same conditions used in the Appendix of chapter 6 for the silicon anode and a reversible capacity of 200 mAhg^{-1} for the cathode at an average lithiation potential of 3.2 V vs. Li^+/Li .