ELUCIDATING THE REACTION MECHANISM OF ELECTRODE MATERIALS FOR Li-ION BATTERIES USING IN SITU STRUCTURAL CHARACTERIZATION

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"You certainly have the right for prescribed activities, but never at anytime in their results. Your actions (Karma) should be directed towards the desired results, however you should never be motivated or attached to the results of the action; nor should there be any attachment in not doing your prescribed work."

-Bhagvat Gita, Chapter 2 Shloka 47
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Abbreviations

\(^{7}\text{Li MAS NMR}\) \(^{7}\text{Lithium Magic Angle Spinning Nuclear Magnetic Resonance}\)

\(\chi^2\) \(\text{Reduced chi-square}\)

\(a, b, c, \alpha, \beta, \gamma\) \(\text{Unit cell parameters}\)

\(B_{iso}\) \(\text{Thermal isotropic displacement parameter}\)

Celgard\(^{\text{®}}\) 2400 \(25 \mu\text{m monolayer polypropylene separator}\)

CuTOP \(\text{Cu}_{0.5}\text{TiOPO}_4\)

CV \(\text{Cyclic voltammetry}\)

D20 beamline \(\text{High intensity 2-axis diffractometer with variable resolution at ILL, Grenoble}\)

DEMS \(\text{Differential Electrochemical Mass Spectrometry}\)

DMC \(\text{Dimethyl carbonate}\)

DME \(\text{Dimethoxyethane}\)

ED \(\text{Electron Diffraction}\)

EDX \(\text{Energy Dispersive X-ray Spectroscopy}\)

EV \(\text{Electric Vehicle}\)

FC \(\text{Field cooled}\)

FEG \(\text{Field Emission Gun}\)

GITT \(\text{Galvanostatic Intermittent Titration Technique}\)

Goodness of fit \(S = R_{wp}/R_{exp}\)

H1-3 phase \(\text{Intermediate phase between O3 and O1 phase with periodic O3 and O1 type stacking of } O^2^-\text{ ions}\)

H1, H2, H3 phases \(R-3m\text{ phases of layered oxides with different unit cell parameters than the O3 phase}\)

HEV \(\text{Hybrid Electric Vehicle}\)

HRPT \(\text{High Resolution Powder Diffractometer for Thermal Neutrons}\)

HRTEM \(\text{High Resolution Transmission Electron Microscopy}\)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ILL</td>
<td>Institut Laue-Langevin, Grenoble, France</td>
</tr>
<tr>
<td>Kapton®</td>
<td>Polyimide</td>
</tr>
<tr>
<td>Kynar FLEX® 2801</td>
<td>Poly(vinylidene fluoride)-co-hexafluoropropylene</td>
</tr>
<tr>
<td>Li-ion batteries</td>
<td>Lithium ion batteries</td>
</tr>
<tr>
<td>MgTOP</td>
<td>Mg$_{0.5}$TiOPO$_4$</td>
</tr>
<tr>
<td>M phase</td>
<td>Monoclinic phase of the layered oxides</td>
</tr>
<tr>
<td>MS-powder beamline</td>
<td>Materials Science X04SA beamline, SLS, PSI Villigen</td>
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<tr>
<td>MTOP-AS</td>
<td>As synthesized M$_{0.5}$TiOPO$_4$ (M = Ni, Cu, Mg) samples</td>
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<td>MTOP-BM8h</td>
<td>M$_{0.5}$TiOPO$_4$ (M = Ni, Cu, Mg) samples after 8h of ball milling</td>
</tr>
<tr>
<td>MTOP-SPC</td>
<td>M$_{0.5}$TiOPO$_4$ (M = Ni, Cu, Mg) ball milled 8h and then ball milled again for 2h with Super-P carbon</td>
</tr>
<tr>
<td>NASICON</td>
<td>Sodium super ionic conductor</td>
</tr>
<tr>
<td>Ni-MH</td>
<td>Nickel Metal Hydride batteries</td>
</tr>
<tr>
<td>NiTOP</td>
<td>Ni$_{0.5}$TiOPO$_4$</td>
</tr>
<tr>
<td>NMC</td>
<td>Li$<em>{1+x}$$(\text{Ni}</em>{1/3}\text{Mn}<em>{1/3}\text{Co}</em>{1/3})_{1-x}\text{O}_2$ (0 ≤ x ≤ 0.13)</td>
</tr>
<tr>
<td>NPD</td>
<td>Neutron powder diffraction</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl pyrrolidone</td>
</tr>
<tr>
<td>O1 phase</td>
<td>P-3m1 phase of layered oxides with ABAB packing of O$^{2-}$ ions</td>
</tr>
<tr>
<td>O3 phase</td>
<td>R-3m phase of layered oxides with ABCABC packing of O$^{2-}$ ions</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>OPA</td>
<td>Oriented polyamide</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyetheretherketone</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cells</td>
</tr>
<tr>
<td>PHEV</td>
<td>Plug-in Hybrid Electric Vehicle</td>
</tr>
<tr>
<td>PSI</td>
<td>Paul Scherrer Institut, Villigen</td>
</tr>
</tbody>
</table>
PVdF Poly(vinylidene fluoride) binder
PVdF-HFP Poly(vinylidene fluoride)-co-hexafluoropropylene
\( R_B \) Bragg factor
\( R_{\text{exp}} \) Expected weighted profile factor
RFID Radio frequency identification tags
\( R_p \) Profile factor
\( R_{wp} \) Weighted profile factor
SEI Solid Electrolyte Interphase
SEM Scanning Electron Microscopy
SHE Standard Hydrogen Electrode
SINQ Swiss Spallation Neutron Source, PSI Villigen
SLS Swiss Light Source
SLS-XX \( \text{Li}_{1+x} (\text{Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3})_{1-x} \text{O}_2 \ (x \geq 0) \), where XX denotes the percentage of overlithiation i.e. \( x \times 100 \)
SQUID Superconducting Quantum Interference Device
TEM Transmission Electron Microscopy
THF Tertrahydrofuran
\( u, v, w, x, y \) Peak width parameters
\( U_{\text{iso}} \) Root mean square displacement of an atom from its average position
US-D.O.E. United States Department of Energy
\( x, y, z \) Atomic position in fractional coordinates
XPS X-ray Photoelectron Spectroscopy
XRD X-ray diffraction
ZFC Zero Field Cooled
Abstract

Li-ion batteries are widely used in cellphones, laptops, and are gaining attention for use in the electromobility sector. For use of Li-ion batteries in the automotive applications, the specific energy and specific power of the battery system has to be improved while maintaining the safety standards. Possible routes towards achieving these goals involve further development of existing electrode materials or use of novel electrode materials in the battery. In both the cases a thorough knowledge of the reaction mechanism is warranted, which can shed light on the involved safety issues and ways to overcome them.

Thus this thesis deals with the study of reaction mechanism of Li$_{1+x}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{1-x}$O$_2$ (0 ≤ x ≤ 0.13), NMC compounds, when charged till very positive potentials (5.0 V vs. Li/Li$^+$). These positive electrode materials show very interesting electrochemical behavior when charged positive to 4.4 V vs. Li/Li$^+$, where the overlithiated NMC (x = 0.1) shows better charge retention as opposed to stoichiometric NMC (x = 0) after few cycles. This electrochemical behavior is supposed to be an effect of the structural changes occurring during the positive potential charging of the material. Thus the reaction mechanism of a range of NMC materials has been studied by using in situ and ex situ synchrotron X-ray diffraction and ex situ neutron powder diffraction. Several structural changes occurring in the materials were identified viz. formation of O1 phase, loss of Li$_2$MnO$_3$ ordering and O$_2$ evolution, and a reaction mechanism has been proposed based on the available information.

In this work M$_{0.5}$TiOPO$_4$ (M = Ni, Cu, Mg), metal titanium oxyphosphates, were also investigated. This family of novel negative electrode material was shown to react with 3 Li$^+$ as opposed to 1 Li$^+$ expected from the structure. Thus the electrochemical performance of M$_{0.5}$TiOPO$_4$ (M = Ni, Cu, Mg) was studied in relationship to the metal (M) in the structure and the particle size. Cu$_{0.5}$TiOPO$_4$ and in general materials with larger particle size were seen to have better electrochemical performances. These studies also gave clues to the possible reaction occurring in the materials. Of the three studied oxyphosphates, Ni$_{0.5}$TiOPO$_4$ was chosen for the study of reaction mechanism using in situ and ex situ synchrotron XRD, $^7$Li MAS NMR, XPS measurement, Raman spectroscopy, etc. Vital information could be obtained using different analytical techniques, combining which a plausible reaction mechanism has been proposed.
The study of reaction mechanism in materials for Li-ion batteries mainly involves localization of lighter elements like Li or even O in the structure. Thus in order to facilitate \textit{in situ} localization of lighter elements and \textit{in situ} study of structural evolution in the electrode materials; a circular \textit{in situ} neutron diffraction cell capable of cycling small amounts of electrode materials (0.2-0.3 g) was developed for use at the D20 beamline at ILL, Grenoble, France. The circular cell design was tested using LiFePO$_4$ as the model electrode material. The effect of using deuterated electrolyte versus hydrogenated electrolyte on the quality of the \textit{in situ} neutron diffraction data was also investigated. The first \textit{in situ} neutron diffraction measurements at ILL, Grenoble were successfully conducted where each neutron diffraction pattern was recorded only in 24 min, delivering very good time resolution. It was also found that using the circular cell design holding small amount of material soaked in deuterated electrolyte, Rietveld refinement could be performed over the complete 2Theta range, while showing no apparent anisotropic absorption of the diffracted neutron beams.

This thesis presents and discusses the results obtained on the three interrelated parts and provides an outlook for further investigation of these materials and for further development of the circular \textit{in situ} neutron diffraction cell.
Zusammenfassung


Diese Arbeit befasst sich also mit der Untersuchung des Reaktionsmechanismus von \( \text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2 \) \((0 \leq x \leq 0.13)\), NMC-Materialien, wenn diese auf sehr positive Potentiale (5.0 V vs. Li/Li\(^+\)) geladen werden. Diese positiven Elektrodenmaterialien zeigen ein sehr interessantes elektrochemisches Verhalten, wenn sie auf ein Potential positiv zu 4.4 V vs. Li/Li\(^+\) geladen werden, welches das überlithiierte NMC \((x = 0.1)\) nach wenigen Zyklen eine bessere Zyklenfestigkeit zeigt als stöchiometrisches NMC \((x = 0)\). Es wird angenommen, dass dieses elektrochemische Verhalten ein Effekt der Strukturveränderungen des Materials, welche während dem Ladungsprozess bei positiven Potentialen geschehen, ist. Daher wurde der Reaktionsmechanismus einer Reihe von NMC-Materialien mittels \textit{in situ} und \textit{ex situ} Synchrotron-Röntgen-Diffraktion und \textit{ex situ} Neutronenpulverdiffraktion untersucht. Mehrere im Material stattfindende Strukturveränderungen, das heisst Formierung der O1-Phase, Verlust von Li\(_2\)MnO\(_3\)-Ordnung und Sauerstofffreisetzung, wurden identifiziert und ein auf den verfügbaren Informationen basierender Reaktionsmechanismus wurde vorgeschlagen.

In dieser Arbeit wurde auch M\(_{0.5}\text{TiOPO}_4\) \((M = \text{Ni}, \text{Cu}, \text{Mg})\), Metall-Titan-Oxyphosphat, untersucht. Es wurde gezeigt, dass diese Familie von neuartigen, negativen Elektrodenmaterialien mit 3 Li\(^+\) statt nur 1 Li\(^+\), wie von der Struktur erwartet wird reagiert. Daher wurden die elektrochemischen Eigenschaften von M\(_{0.5}\text{TiOPO}_4\) \((M = \text{Ni}, \text{Cu}, \text{Mg})\) in Abhängigkeit des Metalls \((M)\) in der Struktur und der Partikelgrösse untersucht. Cu\(_{0.5}\text{TiOPO}_4\) und Materialien mit grösseren Partikeln generell haben sich als elektrochemisch besser erwiesen. Diese Untersuchungen haben auch Hinweise auf mögliche Reaktionen, die in den Materialien stattfinden, geliefert. Von den drei Oxyphosphaten, die untersucht wurden, wurde Ni\(_{0.5}\text{TiOPO}_4\) ausgewählt, um den

Die Untersuchung der Reaktionsmechanismen in Materialien für Lithium-Ionen-Batterien beinhaltet vor allem die Lokalisierung von leichten Elementen, wie Li oder sogar O, in der Struktur. Daher wurde, um die *in situ* Lokalisierung der leichten Elemente und die *in situ* Untersuchung der strukturellen Entwicklung der Elektrodenmaterialien zu untersuchen, eine zylindrische *in situ* Neutronendiffractionzelle, welche in der Lage ist, kleine Mengen an Elektrodenmaterialien (0.2-0.3 g) zu zykeln, für den Einsatz in der D20 Beamline am ILL, Grenoble, Frankreich entwickelt. Das zylindrische Zellendesign wurde mit LiFePO$_4$ als Modellelektrodenmaterial getestet. Der Effekt bei Benutzung von deuteriertem Elektrolyt im Vergleich zu wasserstoffhaltigem Elektrolyten auf die Qualität der *in situ* Neutronendiffraktionsdaten wurde ebenfalls untersucht. Die ersten *in situ* Neutronendiffraktionsmessungen am ILL, Grenoble wurden erfolgreich durchgeführt, wobei jedes Neutronendiffraktogramm nur während 24 min aufgenommen wurde, was zu einer sehr guten Zeitauflösung führte. Es zeigte sich, dass bei Verwendung des zylindrischen Zellendesigns, welches eine kleine Menge an in deuteriertem Elektrolyten getränktem Material beinhaltete, Rietveldverfeinerung über den gesamten Bereich von 2Theta durchgeführt werden konnte, wobei keine offensichtliche anisotrope Absorption des gestreuten Neutonenstrahls beobachtet wurde.

In dieser Arbeit wurden die Resultate der drei von einander abhängigen Teile vorgestellt und diskutiert. Ausserdem wird ein Ausblick auf weitere Untersuchungen mit diesen Materialien und der Weiterentwicklung der zylindrische *in situ* Neutronendiffraktionszelle gegeben.
Chapter 1
Introduction
1.1 General introduction and motivation

With the booming world population, the mobility sector too is growing rapidly. According to one prediction, in 2050 the number of cars sold in the world is expected to be over 170 million as opposed to 62 million vehicles sold in 2010\(^1\); thus also increasing the demand for gasoline. In the last decade the price of crude oil has soared significantly. Coupling this with the fact that the oil reserves are expected to be depleted by around 2075-2150\(^2\), it is quite clear that to sustain the mobility at required pace an alternative source of energy is needed to power the vehicles.

Renewable sources of energy especially wind and solar energy are seen as the viable solutions, mostly due to the fact that these energy sources are not concentrated in specific areas of the world and are freely available to everyone. Thus more and more investment is being made in the future energy technologies. However these renewable sources of energy are intermittent and hence energy storage devices are needed, which store the produced energy and convert it back into usable form on demand. United States Department of Energy (US-D.O.E.) has set different goals which the energy storage or conversion system has to meet in order to be successfully incorporated into Hybrid Electric Vehicles (HEV), Plug-in Hybrid Electric Vehicles (PHEV), and Electric Vehicles (EV). The Ragone plot in Figure 1.1 marks the US-D.O.E. goals for HEV, PHEV and EV in terms of their specific energy (Wh/kg) and specific power (W/kg) and compares them with the values delivered by the three electrochemical systems viz. capacitors, batteries and fuel cells. The capacitors usually utilize high specific area carbon, and operate on the principle of double layer charging. These are high power systems with low specific energy and hence are on the upper left hand corner of the Ragone plot. These systems are capable of delivering their complete energy in few milliseconds to few seconds. Fuel cells, on the other hand, have high specific energy but lower power. Most common fuel cells, Proton Exchange Membrane Fuel Cells (PEMFC), work on the electrochemical combination of H\(_2\) and O\(_2\) to form H\(_2\)O and electricity. Fuel cells can run for hundreds of hours, until there is a continuous supply of the fuel, where the H\(_2\) is usually stored in tanks while O\(_2\) can be stored in tanks or consumed directly from the air. Both the supercapacitors and fuel cells lie far away from the goals set by the US-D.O.E.

Conveniently the batteries sit between fuel cells and supercapacitors, with intermediate specific energy and specific power values. Batteries store the electrical energy as chemical energy and convert it back when needed. Depending on the chemistry
used, battery systems are capable of discharging anywhere between few minutes to several hours. From the Ragone plot (Figure 1.1) it is clear that the goals for HEV are exceeded by the Nickel Metal Hydride (Ni-MH) batteries, while that of PHEV are met by the current Lithium ion batteries (Li-ion). However for the goals of the EV to be met, advances are needed in the field of Li-ion batteries especially in terms of the specific energy (Wh/kg), which at least needs to be doubled.

![Figure 1.1: Ragone plot showing the fuel cells, various types of capacitors and common battery systems. Stars mark the goals of US-D.O.E. set for the HEV, PHEV and EV’s.](image)

To improve the specific energy of the batteries, research is focused on the electroactive materials. Over the years many novel electroactive materials have been studied while many known materials have been reinvestigated to achieve this goal. The race is on, to find better, cheaper and safer electroactive material with good electrochemical performance. The most important criteria that any material has to fulfill before being used in a Li-ion battery is its safety. Vehicles which use tens of kilo-Watt hour (kWh) batteries need to be absolutely safe, even under the adverse conditions. Thus before using a modified or novel electroactive material in a battery, comprehensive understanding of the reaction mechanism of these materials is required.
This thesis thus deals with the electrochemical and structural investigation of positive and negative electroactive materials, with focus on:

- Study of overcharge behavior of Li$_{1+x}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{1-x}$O$_2$ (0 ≤ x ≤ 0.13), which is seen as the next generation positive electrode material, using *in situ* synchrotron X-ray diffraction and *ex situ* neutron powder diffraction.

- Electrochemical and structural investigation of novel model negative electrode material M$_{0.5}$TiOPO$_4$ (M = Ni, Cu, Mg), delivering high specific charge, using various techniques like synchrotron X-ray diffraction, High Resolution Transmission Electron Microscopy, Lithium Magic Angle Spinning Nuclear Magnetic Resonance and other analytical techniques, to gain understanding of the reaction mechanism of these compounds for Li$^+$ insertion/deinsertion.

- Designing and testing a small circular *in situ* neutron powder diffraction cell facilitating the study of reaction mechanism, and performing first *in situ* measurements showing the proof of concept.

This thesis presents and discusses the results obtained on the three interrelated parts and provides an outlook for further investigation of the materials and for further development of the new *in situ* neutron diffraction cell.

1.2. Batteries

Batteries store the electrical energy in the form of chemical energy and transform it back on demand. The battery systems can be of several different types depending of their underlying chemistry. They can also be further classified into primary and secondary batteries, depending on whether they are intended for single use or are rechargeable respectively. However the principle of a battery system is essentially the same. When an external load is attached to the battery i.e. on discharge of the battery, the negative electrode material is oxidized sending the electron through the external circuit. At the positive electrode, the electroactive material reacts with the electron and is reduced. The circuit is completed in this manner resulting in flow of electricity through the external circuit. In case of a rechargeable battery, a reverse process occurs when a current is applied to the battery. Thus during charging of the battery, positive electrode material is oxidized while the negative electrode material is reduced. Depending on the redox couple used, the
different battery systems have different specific energy (Wh/kg) and specific power (W/kg). It is unambiguous from the values in Figure 1.1 that Li-ion battery is the best system of choice for use in the automotive applications.

1.2.1. Lithium battery and Li-ion battery

Lithium metal has very interesting properties in terms of electrochemistry. It has a reduction potential at -3.04 V vs. Standard Hydrogen Electrode (SHE) and with a molecular weight of only 6.941 g/mol; its theoretical specific charge is 3861 mAh/g. This value is much higher than many other electroactive materials. It is the ideal negative electrode material for batteries, where its reduction reaction can be represented as follows:

\[ \text{Li}^+ + \text{e}^- \rightarrow \text{Li} \ (\text{-3.04 V vs. SHE}) \]

However one of the main drawbacks of lithium is its reactivity versus air and moisture. Due to this reason non-aqueous organic carbonate based electrolytes are used in the batteries. Secondly, bare lithium cannot be used in commercial rechargeable batteries, due to the safety issues related with it. Bare lithium has very low columbic efficiency and results in formation of lithium moss at the solid/electrolyte interface. During long term and/or high rate cycling lithium dendrites are formed, which eventually result in short-circuit in the battery. Thus use of lithium as negative electrode material is mostly limited to non-rechargeable primary lithium batteries. If one replaces the bare lithium by a host matrix, intercalating or alloying with the lithium, much safer negative electrode materials can be designed and are described in detail in section 1.2.3.

1.2.1.1. Primary lithium batteries

Primary lithium batteries are non-rechargeable batteries, which have higher voltage and specific energy than other primary battery systems commercially available. Despite the higher initial costs, lithium batteries have longer shelf as well as cycle life. The most common chemistries used in the primary lithium batteries are the Li/MnO$_2$, Li/SOCl$_2$, Li/FeS$_2$ and Li/AgV$_2$O$_{5.5}$\textsuperscript{4}. These batteries are used in cameras, watches and also in medical and military applications. A summary of different primary lithium batteries is given in Table 1.1.
<table>
<thead>
<tr>
<th>Battery System</th>
<th>Electrolyte</th>
<th>Cell voltage (V)</th>
<th>Specific energy (Wh/kg)</th>
<th>Energy density (Wh/L)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/MnO₂</td>
<td>LiClO₄ in propylene carbonate (PC)</td>
<td>3.0</td>
<td>230</td>
<td>535</td>
<td>cameras, watches, motor drives, radio frequency identification tags (RFID)</td>
</tr>
<tr>
<td>Li/SOCl₂</td>
<td>LiAlCl₄ in SOCl₂</td>
<td>3.6</td>
<td>590</td>
<td>1100</td>
<td>wireless security systems, RFID,</td>
</tr>
<tr>
<td>Li/FeS₂</td>
<td>LiI in PC, dioxolane, and dimethoxyethane (DME)</td>
<td>1.5</td>
<td>310</td>
<td>562</td>
<td>cameras, radio, portable lights, toys, digital audio systems</td>
</tr>
<tr>
<td>Li/Ag₅V₂O₅.₅</td>
<td>LiPF₆ in PC or LiAsF₆ in PC/DME</td>
<td>3.2-2.0</td>
<td>270</td>
<td>780</td>
<td>cardiac defibrillators, implantable neurosimulators, drug infusion devices</td>
</tr>
</tbody>
</table>

Table 1.1: Summary of different primary lithium battery systems⁴.

### 1.2.1.2. Secondary Li-ion batteries

Rechargeable Li-ion batteries were first commercialized in 1991 by Sony. This battery used a layered LiCoO₂ as the positive electrode material and graphite as the negative electrode material. Like any other battery, the principle of functioning of a Li-ion battery is based on presence of two redox couples as shown in the Schematic in Figure 1.2.
Figure 1.2: Schematic showing principle of functioning of Li-ion battery.

During charging of the battery the Li$^+$ are removed from the positive electrode material resulting in its oxidation, while simultaneously sending e$^-$ through the external circuit. The Li$^+$ pass through the separator soaked with electrolyte, usually a lithium salt in carbonate based solvent, and react with the negative electrode material, which combines with the e$^-$ resulting in reduction of the negative electrode material. During the discharge a reverse process occurs where the Li$^+$ go from the negative to the positive electrode. In the Li-ion batteries only the Li$^+$ are moving back and forth in the system and hence the reaction mechanism is also known as the “rocking chair” mechanism. Because both the electroactive materials use a host matrix capable of intercalating the Li$^+$, no metallic lithium is present in the system and hence the name “Li-ion” battery.

Today the Li-ion batteries are used in all aspects of life, from camera, mobile phones, laptops to electric bikes. The Li-ion batteries are also seen as the future of the electromobility, but still need further improvements. However before exploring for new solutions, one needs to have a thorough knowledge of the state-of-art battery materials. On the positive side the main categories of the materials are the layered oxides $\text{Li}_x\text{M}_y\text{O}_2$ ($\text{M} = \text{Ni, Co, Mn}$), the spinel $\text{LiMn}_2\text{O}_4$, polyanion containing $\text{LiFePO}_4$ and mixed layered oxides $\text{Li}_x(\text{Ni}_a\text{Mn}_b\text{Co}_c)_y\text{O}_2$. On the negative side, the materials can be classified into the intercalation compounds like graphite, the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the alloy electrodes Si and Sn, the conversion materials and the extrusion materials. Figure 1.3 details the redox potential and theoretical specific charge for some of the electroactive materials.
Figure 1.3: Redox potential of various materials versus lithium, along with their respective specific charge. The lower legend on the x-axis gives values of specific charge for the negative electrode materials while the upper legend on x-axis is for the positive electrode materials.

1.2.2. Positive electrode materials

1.2.2.1. Layered Li\textsubscript{x}M\textsubscript{y}O\textsubscript{2} (M = Co, Ni, Mn)

LiCoO\textsubscript{2} is the most widely used positive electrode material for Li-ion battery. This material crystallizes in $\alpha$-NaFeO\textsubscript{2} layered structure with hexagonal $R\bar{3}m$ space group and cell parameters close to $a = 2.815$ Å and $c = 14.054$ Å\textsuperscript{5}. In the structure, the Li sits in the 3a site, Co in the 3b site while O is in the 6c Wyckoff position. In 3-dimension (Figure 1.4A, page 10) the structure of LiCoO\textsubscript{2} can be described by chains of edge shared $[\text{CoO_6}]_{\text{tet}}$...
forming \((\text{CoO}_2)_n\) slabs along the c-axis, in between which are the \((\text{LiO}_2)_n\) interslabs. The transition metal slabs and lithium interslabs are stacked alternatively along the c-axis, where the octahedra in slabs and interslabs are edge connected with each other. This stacking of slabs and interslabs results from a hexagonal close-packed oxygen layers with ABCABC sequence, forming the O3 phase (Figure 1.4A). Here the O describes the octahedral sites where the metal ions are sited and should not be confused for oxygen, while the 3 indicates the presence of three slabs within one unit cell. Since there exists “sea” of \(\text{Li}^+\) in between the slabs, Li-ion diffusion is possible along a and b axes.

Theoretically 1 \(\text{Li}^+\) can be extracted from \(\text{LiCoO}_2\) delivering 274 mAh/g specific charge. However on extraction of more than a 0.5 \(\text{Li}^+\) there occurs sliding of the slabs, resulting in a phase transition of the O3 phase via the H1-3 to the O1 phase, where the O1 phase (Figure 1.4B) can be described by cubic close-packed oxygen layers having ABAB stacking sequence, where the octahedra in slabs and interslabs are face shared with each other. Here again, the `O1` describes presence of metal ions in octahedral sites with only 1 slab in the unit cell. The H1-3 phase (Figure 1.4C) is an intermediate phase between O3 and O1 phases, with both hexagonal and cubic close-packed arrangement of oxygen, leading to edge and face sharing between octahedra in slabs and interslabs. Here the H stands for the hexagonal unit cell that describes the structure. Thus practically, around 140 mAh/g specific charge can be reversibly extracted from \(\text{LiCoO}_2\). This limitation in amount of lithium extracted, also limits the potential range for the reaction, which is generally set at upper cut-off potential of 4.2 V vs. Li/Li\(^+\). This combined with the toxicity and price of cobalt warrants the need to find cheaper positive electrode materials, with higher specific charge reacting at more positive potential, thus finally resulting in increased specific energy of a battery.

\(\text{LiNiO}_2\), isostructural to \(\text{LiCoO}_2\), is cheaper, less toxic and is theoretically expected to deliver 274 mAh/g specific charge. However the synthesis of pure \(\text{LiNiO}_2\) on a large scale showing reproducible electrochemical performance is difficult. This material delivers 220 mAh/g during 1\(^{\text{st}}\) cycle; however this value drops after 100 cycles to 70 mAh/g\(^7\). When cycled between 4.4-3.0 V vs. \(\text{Li}/\text{Li}^+\), the \(\text{LiNiO}_2\) undergoes several reversible phase transformation from initial O3 phase to H3 phase via intermediate H1–M–H2 phases\(^8-9\). H1, H2 and H3 are hexagonal phases in same \(R-3m\) space group as the O3 phase, but different unit cell parameters while M describes the monoclinic space group (Figure 1.4D). These phase transformations are also reflected in large lattice parameter changes\(^9\), resulting in formation of micro-cracks in the particles during the course of cycling.
Moreover due to the similar ionic radii of Li ($r_{Li}^+ = 0.72\text{Å}$) and Ni ($r_{Ni}^{+2} = 0.69\text{Å}$), there occurs a Li-Ni exchange in the structure resulting in certain amount of Li to be in the transition metal slabs and same amount of Ni in the Li interslabs. This Ni in the Li interslabs impedes the diffusion of Li$^+$ in and out of the structure and hence also affects the electrochemistry. Thus although, the LiNiO$_2$ seems exciting from the initial higher specific charge, many issues related with it hinder its use in commercial batteries.

Another very interesting case is LiMnO$_2$, which theoretically would be expected to deliver 285.5 mAh/g specific charge. The layered LiMnO$_2$, isostructural to LiCoO$_2$, is however thermodynamically metastable and the structure crystallizes in the orthorhombic $Pmnm$ space group. A layered hexagonal structure in $R-3m$ space group can be stabilized using doping of LiMnO$_2$ with Al$^{+3}$ or Cr$^{+3}$ 12, 13. Cr$^{+3}$ doping suppresses the transformation of layered to defect spinel structure on cycling$^{12-14}$, but a phase transformation away from the original $R-3m$ space group is observed. A layered LiMnO$_2$ can be synthesized using ion-exchange, but the material crystallizes in a monoclinic symmetry with $C2/m$ space group, owing to the Jahn-Teller effect of Mn$^{+3}$ ions causing distortion of $[\text{MnO}_6]_{\text{oct}}$ 15. Both, orthorhombic and monoclinic phases can be cycled versus lithium as positive electrode materials, however during the first charge, spinel phase nucleates and growth of a disordered spinel phase is observed on cycling$^{16}$. Due to this irreversible transformation of starting material, LiMnO$_2$ can not be successfully commercialized.

1.2.2.2. Spinel LiMn$_2$O$_4$

LiMn$_2$O$_4$ crystallizes in $Fd\bar{3}m$ space group, which owing to its spinel structure results in 3-dimensional diffusion of Li$^+$ in an out of the material (Figure 1.5A, page 12). LiMn$_2$O$_4$ can undergo a phase transformation to $\lambda$-Mn$_2$O$_4$ phase on delithiation, while keeping the spinel structure intact$^{17}$ or transform on lithiation to Li$_{2.6}$Mn$_2$O$_4$ in tetragonal $I4_1/amd$ space group$^{18}$, at 4.0 V and ~3.0 V vs. Li/Li$^+$ respectively. However only the first potential plateau at 4.0 V corresponding to LiMn$_2$O$_4$↔$\lambda$-Mn$_2$O$_4$ can be used in practical batteries, as going down to Li$_2$Mn$_2$O$_4$ results in phase transformation with highly soluble Mn$^{+2}$ in the structure. Even so, the main drawback of LiMn$_2$O$_4$ is that during deep cycling Mn$^{+3}$ is formed, which disproportionates into Mn$^{+4}$ and soluble Mn$^{+2}$. Thus Mn is “lost” during the course of electrochemical cycling. This dissolution of Mn is also accelerated by the HF impurity formed as a result of reaction of LiPF$_6$ salt used in the electrolyte with the remaining traces of water$^{19}$.The structure of LiMn$_2$O$_4$ can be stabilized by doping, however it is out of the scope of current study and hence is not discussed further.
Figure 1.4: Crystal structure of layered LiMO$_2$ (M = Co, Ni, Mn). (A) O3 phase, (B) O1 phase, (C) H1-3 phase, and (D) monoclinic phase.
1.2.2.3. Olivine LiFePO$_4$

In 1997 Goodenough introduced LiFePO$_4$ as a non-toxic, inexpensive positive electrode material for the Li-ion batteries\textsuperscript{[20]}. LiFePO$_4$ is a polyanion based compound crystallizing in $Pnma$ space group with triphylite structure (Figure 1.5B) and is expected to deliver theoretically 170 mAh/g at 3.45 V vs. Li/Li$^+$. The lithium extraction from LiFePO$_4$ proceeds via a 2 phase reaction to form the FePO$_4$. The reaction mechanism for the delithiation of LiFePO$_4$ has been intensively studied. Different mechanisms have been suggested like the core-shell model\textsuperscript{[21]} or Domino cascade model\textsuperscript{[22]}. It has also been shown that depending on the particle size\textsuperscript{[23]} of LiFePO$_4$ used, the reaction can follow a solid solution path. Though this material initially seemed to be plagued with lower electronic conductivity ($\sim 10^{-9}$ S/cm)\textsuperscript{[24]}; carbon coating\textsuperscript{[25, 26]}, moving to nanoscale\textsuperscript{[27, 28]} and doping the material with supervalent cations\textsuperscript{[24, 29]} solved the problems. Today polyanion containing LiFePO$_4$ (olivine) is successfully commercialized. Practically however LiFePO$_4$ delivers only 20-25 mAh/g higher specific charge than LiCoO$_2$ at a lower potential. Many other polyanion based LiMPO$_4$ ($M = \text{Co, Mn, Ni}$) have been studied however due to many drawbacks related with them, they have not yet been commercialized.

1.2.2.4. Layered Li$_x$(Ni$_a$Mn$_b$Co$_c$)$_y$O$_2$

The layered Li$_x$(Ni$_a$Mn$_b$Co$_c$)$_y$O$_2$ are isostructural to LiCoO$_2$ and are usually seen as solid solution of LiCoO$_2$, LiNiO$_2$, LiMnO$_2$ or a substitution of Co in solid solution of LiNiO$_2$ and LiMnO$_2$. Many different compositions of layered Li$_x$(Ni$_a$Mn$_b$Co$_c$)$_y$O$_2$ have been studied\textsuperscript{[30-32]}, along with studies involving substitution of transition metals in slabs by other metals like aluminium, silicon, magnesium\textsuperscript{[33-35]} or even lithium i.e. overlithiation\textsuperscript{[11, 36]}. However, since Ohzuku et al.\textsuperscript{[37]} reported that the symmetric Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ can deliver up to 200 mAh/g over wide potential range, the stoichiometric LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC) has been viewed as the next generation of positive electrode material. Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$, utilizes just a third of the cobalt in the structure as compared to LiCoO$_2$, while keeping its concentration still high enough for good electrochemical reversibility. It also incorporates nickel for higher specific charge and manganese for structural stability and safety. As opposed to the individual starting layered compounds LiMO$_2$ ($M = \text{Co, Ni, Mn}$) where the $M$ is in $+3$ oxidation state, Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ has Ni in +2, Co in +3 and Mn in +4 oxidation state\textsuperscript{[38]}. In other layered oxides, the presence of metals with different ionic radii and charge, is shown to result in flower like arrangement of the metal ions in the transition metal slabs, which was calculated to have least configurational energy\textsuperscript{[39]}. This arrangement of ions results in appearance of extra
superstructure peaks in XRD patterns, which can be indexed with a larger $\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$ superlattice\textsuperscript{40}. However the large amount of Co in Li(Ni\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3})O\textsubscript{2} avoids the long term ordering of the cations and hence no superlattice peaks are generally observable in the XRD\textsuperscript{41}. 

![Crystal structure of LiMn\textsubscript{2}O\textsubscript{4} and LiFePO\textsubscript{4}](image)

Figure 1.5: Crystal structure of (A) spinel LiMn\textsubscript{2}O\textsubscript{4} and (B) olivine LiFePO\textsubscript{4}.

Theoretically Li(Ni\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3})O\textsubscript{2} is expected to deliver 276 mAh/g by removal of 1 Li\textsuperscript{+}, via oxidation of Ni\textsuperscript{+2} to Ni\textsuperscript{+4} and Co\textsuperscript{+3} to Co\textsuperscript{+4}, while keeping the Mn in +4 oxidation state and was shown to be true\textsuperscript{38}. Unlike the layered LiMO\textsubscript{2}, on delithiation, Li(Ni\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3})O\textsubscript{2} undergoes a direct phase transformation from hexagonal O3 phase to the O1 phase, without the formation of the intermediate H1-3 phases. For the chemically delithiated sample, O1 phase is formed after removal of 0.7 Li\textsuperscript{+4}\textsuperscript{42}. Owing to its good cyclability and higher specific charge, Li(Ni\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3})O\textsubscript{2} has been successfully commercialized.
Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2 (x > 0), overlithiated NMC, contains x Li in the transition metal slabs. This substitution of transition metals by a monovalent Li results in oxidation of the Ni^{2+} to Ni^{3+} to compensate for the charge balance. At a value of x = 0.14 all the Ni^{2+} in the structure is oxidized to Ni^{3+} state. Since the overlithiated NMC have higher amount of Li in the structure, the theoretical specific charge of these materials is higher. Experimentally it has been found that the when charged till more positive potentials, higher specific charge can be drawn from the overlithiated NMC and hence they are even more interesting than the stoichiometric NMC\textsuperscript{11}. As the overlithiated NMC contain x Li in the transition metal slabs, they should result in preferential arrangement of Ni and Mn around the Li. The arrangement of Ni and Mn around Li usually gives rise to a Li_2MnO_3 type domain in the structure, which crystallizes in the C2/m space group. This Li_2MnO_3 domain is reported to result in appearance of extra peaks in the X-ray diffraction patterns for other compositions of layered Li_{x}(Ni_{a}Mn_{b}Co_{c})_{y}O_2, however due to presence of large amount of Co, which impedes the preferential ordering, the Li_2MnO_3 type domain appears almost amorphous to normal XRD machine\textsuperscript{43} and has not been reported for overlithiated NMC.

Both stoichiometric and overlithiated NMC [Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2, x ≥ 0] are good in terms of the achievable specific charge and the cyclability and hence have great potential for use in batteries for electromobility. Usually these NMC materials are electrochemically cycled within the stability limit of the electrolyte (<4.5 V vs. Li/Li\textsuperscript{+}) in order to minimize the electrolyte decomposition. But this also limits the amount of lithium that can be extracted from the material and thus the value of specific charge from the material below 150-170 mAh/g. Hence now a days cycling behavior of these materials when charged till very positive potentials is under study\textsuperscript{44} and more and more efforts are concentrated on elucidating the reaction mechanism during charging till these very positive potentials\textsuperscript{45}. This thesis therefore deals with investigation of structural changes occurring in Li_{1+x}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}O_2 (x ≥ 0) during their very positive potential (5.0 V vs. Li/Li\textsuperscript{+}) charging using \textit{in situ} synchrotron XRD and \textit{ex situ} neutron powder diffraction.

1.2.3. Negative electrode materials

1.2.3.1. Graphite

Graphite is the classical commercial negative electrode material in Li-ion batteries. Graphite consists of sp\textsuperscript{2}-hybridized carbon atoms forming a honey-comb like structure giving rise to the graphene sheets. These graphene sheets are stacked on top of each
other either in ABAB stacking to form the hexagonal α-phase or in ABCABC stacking to form the rhombohedral β-phase. Graphite is known to accommodate 1 Li\(^+\) electrochemically and deliver 372 mAh/g to form LiC\(_6\), where the graphene sheets are now stacked in AA sequence. The process of lithium intercalation in graphite occurs via several stage formations at different potentials as shown in Figure 1.6\(^{46}\), where the stage number describes the number of graphene sheets between 2 filled Li layers.

![Figure 1.6: Electrochemical lithiation in graphite showing various intercalation stages\(^{46}\).](image)

### 1.2.3.2. Li\(_4\)Ti\(_5\)O\(_{12}\)

Li\(_4\)Ti\(_5\)O\(_{12}\) crystallizes in cubic Fd-3m space group delivering 175 mAh/g specific charge at 1.55 V vs. Li/Li\(^+\) by 3 Li insertion to form Li\(_7\)Ti\(_5\)O\(_{12}\)\(^{47}\). Only the position of Li\(^+\) changes in the structure resulting in phase transformation of the spinel to cubic rock-salt structure, showing negligible volume changes in the material. Due to this reason the Li\(_4\)Ti\(_5\)O\(_{12}\) is also known as the “no strain” material. This material suffers from its relatively positive reaction potential as opposed to other anodic materials. Thus use of spinel Li\(_4\)Ti\(_5\)O\(_{12}\) as negative electrode material results in higher safety at the expense of the cell voltage.

### 1.2.3.3. Alloy electrodes

One of most interesting class of electrode materials for Li-ion batteries are the alloy electrodes like Si, Sn, etc. These materials form an alloy with Li on cycling at low potentials. Si can deliver 4010 mAh/g at 0.4 V vs. Li/Li\(^+\), while Sn reacts at around 0.6 V
vs. Li/Li$^+$ delivering 959 mAh/g$^{48}$. Owing to such high specific charges, these materials have drawn a great amount of interest; however the main drawback in these alloying materials is the huge volume expansion on cycling. Si undergoes 297% volume expansion to form Li$_{21}$Si$_5$, while Sn expands by 257% to form Li$_{17}$Sn$_4$. This huge volume expansion drastically affects the cyclability of the material; as on cycling, the electroactive material looses contact with the current collector or neighboring electrode particles and becomes electrochemically inactive$^{49}$. Many studies have been conducted to improve the cycling performance of these materials. Coating with carbon$^{50}$, using structured pillars$^{51}$ or nanowires$^{52}$ have shown improvement in cycling. Few companies have commercialized composite Si or Sn alloy electrodes; however these materials do not cycle at their theoretical specific charge yet.

1.2.3.4. Conversion materials

Conversion materials have been recently suggested as the novel electrode materials for Li-ion batteries. CoO and Co$_2$O$_4$$^{53}$, Fe$_2$O$_3$$^{54}$, etc. react with Li$^+$ to undergo a complete conversion to form the corresponding metal and Li$_2$O. Due to the formation of an intimate nano 2-phase mixture; these materials can be reversibly cycled versus lithium at 0.8-1.0 V vs. Li/Li$^+$. Apart from oxides, sulphides$^{55}$, nitrides$^{56}$, phospides$^{57}$ and hydrides$^{58}$ have also been shown to undergo conversion reaction. However similar to the alloy electrodes the volume expansion in these materials is very high (85-100%) and the specific charge lower than their theoretical values.

1.2.3.5. Extrusion materials

Cu$_{2.33}$V$_4$O$_{11}$ was reported in 2003 as the novel extrusion material$^{59}$. It was shown that during the course of lithiation, the Li$^+$ are intercalated in the structure at the expense of Cu, which is reduced from Cu$^{+2}$ to Cu$^0$ and is extruded out of the structure. This process is reversible and Cu can be reinserted in the matrix during delithiation. This material reacts at 2.7 V vs. Li/Li$^+$ reacting with ~5.6 Li$^+$ to deliver 250-270 mAh/g specific charge and was proposed as a novel positive electrode material. Since then many other extrusion materials have been studied. CuNb$_2$O$_6$ and Ag$_2$Nb$_4$O$_{11}$ were recently reported as novel negative electrode materials also showing extrusion reaction, however in these materials the extrusion process is irreversible and a complete structural change is observed on cycling$^{60}$. Although this reaction mechanism is very interesting, the choice of materials is limited and hence these materials have not yet been commercialized.
1.2.3.6. $M_{0.5}$TiOPO$_4$ ($M$ = Ni, Co, Fe)

Recently a large amount of interest has been invoked by the metal titanium oxyphosphate family ($M_{0.5}$TiOPO$_4$, $M$ = Ni, Fe, Mn, Co), as novel electroactive materials$^{61, 62}$. $M_{0.5}$TiOPO$_4$, sometimes also referred to as metal titanyl orthophosphates, crystallizes in monoclinic $P2_1/c$ space group. In 3-D the structure can be visualized by chains of corner sharing [TiO$_6$]$_{oct}$ running along the c-axis, connected together by corner sharing [PO$_4$]$_{tet}$ and/or by face sharing [MO$_6$]$_{oct}$. A closer look at the structure (Figure 1.7) reveals that there exists vacant sites for Li$^+$ insertion. Thus theoretically these materials are expected to accommodate 1 Li$^+$ per formula unit by reduction of Ti$^{4+}$ to Ti$^{3+}$ delivering 142 mAh/g. However it was reported for Ni$_{0.5}$TiOPO$_4$ that this material reacts with 3 Li$^+$ instead delivering 426 mAh/g (Figure 1.8A)$^{61}$. Similar behavior has also been reported for the isostructural Co$_{0.5}$TiOPO$_4$, which delivers 434 mAh/g (Figure 1.8B)$^{62}$. In both the cases, on delithiation only 2 Li$^+$ are extracted reversibly, indicating that 1 Li$^+$ is irreversibly trapped during the first cycle. The reaction mechanism in this family of compounds is not yet understood. Also it is unknown if the reaction is possible if one changes the metal ($M$) in $M_{0.5}$TiOPO$_4$ to copper or a non-transition metal like magnesium. These materials are ideal model compounds delivering 200% excess specific charge and hence their reaction mechanism for Li insertion/deinsertion is extensively under investigation.

Thus this thesis also deals with elucidating the reaction mechanism of Ni$_{0.5}$TiOPO$_4$, using several analytical techniques. The thesis also looks into the effect of changing the metal in $M_{0.5}$TiOPO$_4$ ($M$ = Ni, Cu, Mg) and particle size on the electrochemistry of these materials.
Figure 1.7: 3-D structure of M$_{0.5}$TiOPO$_4$ (M = Ni, Co, Fe, Cu, Mg) showing vacant sites for Li$^+$. The [TiO$_6$]$_{otd}$ are corner connected along c axis.

Figure 1.8: Electrochemical cycling curves for (A) Ni$_{0.5}$TiOPO$_4$ and (B) Co$_{0.5}$TiOPO$_4$.

(A) 

(B)
1.3. Goal of this work

Several different electrode materials are available for use in the Li-ion batteries showing various structures, different reaction mechanisms, several phase transformations and different issues related with them. To obtain or design a high specific energy electroactive material one needs to explore beyond the realm of conventional systems, while still maintaining the same safety standards. The study of reaction mechanism of a material is of utmost importance to achieve this goal. This thesis has thus three main objectives:

- Structural study of Li$_{1+x}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{1-x}$O$_2$ \(0 \leq x \leq 0.13\) NMC materials when charged till very positive potentials (5 V vs. Li/Li$^+$).

- Electrochemical and structural study of the model M$_{0.5}$TiOPO$_4$ \(M = \text{Ni, Cu, Mg}\) materials.

- Designing a new \textit{in situ} neutron diffraction cell to facilitate the study of reaction mechanism and \textit{in situ} localization of lighter elements like Li and O.
Chapter 2

*In situ* synchrotron and neutron diffraction cells
2.1. Diffraction

Diffraction is widely used analytical technique to study the structural changes occurring in the electroactive materials during or after their lithiation/delithiation process. Diffraction can be performed on single crystals and powder samples, where a Bragg reflection is observed for a particular wavelength and distance between interatomic planes, if it satisfies the Bragg’s law:

\[ n \lambda = 2d \sin \theta \]

where \( \lambda \) is the wavelength (Å), \( d \) is distance between interatomic planes (Å), \( \theta \) is angle of incident radiation beam (°) and \( n \) is integer number of the wavelength. The Bragg’s law can be derived as follows:

Figure 2.1: Schematic representation of Bragg’s law.

for incident beams 1 and 2 to be diffracted in a constructive interference by the planes of atoms separated by distance \( d \), the wave 2 needs to travel an additional path, which must be an integer value of the wavelength \( \lambda \) of the incident beam. Thus one can write that \( n \lambda = BC + BD \). As \( BC = BD = d \sin \theta \), from trigonometry, one obtains the Bragg’s law.

Although X-ray diffraction was the first technique to be implemented for crystallography, many other radiation sources with wavelength similar to interatomic distances can be used for diffraction studies viz. neutrons, electrons and muons. In this thesis X-ray and neutron diffraction have been used for the study of reaction mechanism and thus they are being discussed here.
X-rays and neutrons are known to have different interaction with matter. The X-rays interact with the electron cloud of an atom and are scattered heavily for heavier elements with higher number of electrons. Neutrons on the other hand are scattered by the nuclei, and hence show no general trend with respect to the number of electrons in the atom. These differences in scattering are schematically represented in Figure 2.2.

![Figure 2.2: Schematic representation of neutron and X-ray scattering for various nuclei. Larger the representation area, larger the scattering.](image)

The differences in the scattering of X-rays and neutrons by atom/nuclei are of great interest for electrode materials. Most of the study of reaction mechanism involves localizing lighter elements like Li or H in the structure. These elements are essentially non-scattering in X-rays, however show higher scattering in neutrons and hence can be easily localized in the structure using neutrons. Neutrons can also help in detection of different isotopes e.g. H and D which have different scattering. Another interesting aspect of neutron diffraction is that it can differentiate between neighboring elements like Mn, Co and Ni, which have essentially similar scattering in X-rays. One of the major differences between these two radiation sources is their interaction with matter. X-rays interact strongly with matter, resulting in strong diffracted beam. Thus small quantities of material can be used for the X-ray diffraction measurements. The neutrons on the other hand have very weak interaction with matter and hence large amount of material is warranted, along with longer data acquisition time.

X-ray and neutron diffraction deliver complementary information and usually a combination of both is used to study the structure of the material or the reaction mechanism. For the study of reaction mechanism, *ex situ* or *in situ* electrochemical
diffraction measurements can be performed. *Ex situ* powder diffraction involves electrochemically lithiating/delithiating the electroactive material and then using the washed, dry electrode mass for diffraction measurements. In some cases chemically lithiated/delithiated materials are also used. However, *ex situ* measurements can pose a threat of relaxation in the material and exposure to air and moisture between the sample preparation and the actual diffraction measurements. For this purpose *in situ* diffraction is preferred. In case of the X-rays, the *in situ* electrochemical diffraction cell has been well established, however due to contradictory needs of electrochemistry and neutron diffraction, in terms of the amount of material needed; *in situ* neutron diffraction cell has not been successfully developed.

### 2.2. *In situ* synchrotron X-ray diffraction (XRD) cell

The “coffee bag” or “pouch” cells have been widely used for the *in situ* XRD studies\(^{64-69}\). The “coffee bag” cells typically consist of a 10 cm*10 cm aluminium bag coated with polymers on both sides. In case of the PSI cell, this “coffee bag” has holes punched out on the sides to avoid diffraction from the aluminium itself, which are covered with adhesive Kapton\(^\circledR\) tapes (Figure 2.3). A working electrode pressed on a current collector mesh is placed on top of this Kapton\(^\circledR\) taped hole, followed by a Celgard\(^\circledR\) 2400 and thin glass fiber separators soaked with propylene carbonate (PC)/ dimethyl carbonate (DMC) 1M LiPF\(_6\) electrolyte. A lithium counter electrode pressed on a Cu current collector mesh is placed on the top and the whole assembly is sealed under vacuum. One of the major drawbacks of the “coffee bag” cell is the adhesion and brittleness of the working electrode pressed on the current collector. In previous report studying graphite\(^{69}\), slurry of graphite and poly(vinylidene fluoride) (PVdF) binder was made in N-methyl pyrrolidone (NMP) and casted onto a non-adhesive sheet. This cast was allowed to dry, a 2 cm*2 cm piece cut out of this cast and the electrode material transferred onto a Cu current collector by simple roll-pressing to make the working electrodes. Although this method works well for graphites, it results in brittle and poor electrode when an oxide is used. Thus for the study of different electrode materials using *in situ* synchrotron XRD, self standing films of active material/ Super-P carbon (TIMCAL, Switzerland)/ Kynar FLEX\(^\circledR\) 2801 (Arkema, USA) binder [poly(vinylidene fluoride)-cohexafluoropropylene] (70/10/20 by weight) were casted using the phase inversion route\(^{70}\), without using the silica for mechanical reinforcement\(^{70}\), to avoid extra diffraction peaks from it. These self standing films were
pressed from both sides on an aluminium current collector mesh of 2 cm*2 cm at 80°C in order to have better adhesion. The self standing film electrodes were found to be more flexible and hence such electrodes were used for the various in situ synchrotron XRD studies in this thesis. For the in situ measurements an automatic sample changer was used\textsuperscript{68}; capable of cycling 15 cells sequentially, giving a very good time resolution for each cell.

![Schematic of a “coffee bag” cell](image)

Figure 2.3: Schematic of a “coffee bag” cell\textsuperscript{63}, where PE, Al and OPA stand for polyethylene, aluminium, and oriented polyamide respectively.

### 2.3. In situ neutron powder diffraction (NPD) cell

Several attempts have been made to design a good in situ NPD cell for battery materials, whether for Li-ion batteries\textsuperscript{71-73} or other battery systems\textsuperscript{74-76}. However in all the published cell designs several drawbacks are clear. Most of the cell designs result in presence of many cell parts in beam viz. counter electrode, separator, both current collectors, cell body, etc. This results in appearance of extra, unwanted peaks in the diffraction pattern. Moreover, few cell designs use large quantities of electrolyte, which in turn results in higher background intensity. Thus, recently a rectangular in situ NPD cell was designed for the High Resolution Powder Diffractometer for Thermal Neutrons (HRPT) beamline at Swiss Spallation Neutron Source (SINQ), PSI Villigen\textsuperscript{77}. This cell has
an advantage over the previous designs, in that, only the electrode material soaked with electrolyte and the Al current collector is in the neutron beam. Nonetheless this cell design suffered from the large amount of electrode material (~3 g) needed for a good NPD pattern, which drastically affects the electrochemistry of the material. Previous preliminary experiments with the rectangular in situ NPD cell showed the importance of the active material to carbon ratio as only few intense peaks of the studied Li$_{1.1}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{1.9}$O$_2$ were detectable. Two issues were identified as critical for proper functioning of the cell containing large amount of electrode mass. Firstly, the current path to the current collector, and consequently the ohmic resistance, increases with the increasing distance away from the current collector. Thus to ensure good electrochemical cycling of the cell, the content of conductive additives should be optimized along the current paths to ensure homogeneous bulk current density distribution. Secondly, to get a better diffraction signal one needs to minimize the content of Super-P carbon in the electrode mixture. The role of Super-P carbon in the electrode mass, along with providing conductive pathway for the electrons, is to bring porosity in the electrode to get a good wetting of all particles independently of their location. Thus to reduce the amount of Super-P carbon, the porosity in the electrode needs to be controlled.

In this thesis an in situ NPD study of spinel Li$_4$Ti$_5$O$_{12}$ material was conducted in order to improve the cycling performance of electroactive material in the existing rectangular cell design, by optimizing the electrode composition and engineering. On 3 Li$^+$ insertion in Li$_4$Ti$_5$O$_{12}$, the spinel phase simply shifts to rock-salt type structure showing no volumic changes. Thus only the position of Li$^+$ in the structure is changing and hence Li$_4$Ti$_5$O$_{12}$ is an ideal model material for the study.

2.3.1. Experimental

2.2 g of commercial Li$_4$Ti$_5$O$_{12}$ powder obtained from Süd Chemie AG (Germany) was mixed with appropriate amount of graphite KS6 and Super-P carbon (both from TIMCAL SA, Switzerland) resulting in total ~3 g of electrode mass. The Super-P carbon provides conductivity as well as better uptake of electrolyte, while KS6 graphite provides enhanced electronic conductivity. Celgard® 2400 (Celgard, USA) and glass fiber were used as separators and lithium metal (Aldrich, 99.9%) was used as counter electrode. The electrolyte used was 1M LiPF$_6$ in ethylene carbonate (EC)/ dimethyl carbonate (DMC) (Ferro, USA). The use of deuterated electrolyte was planned but due to very high water content (~1500 ppm) in the solution (delivered shortly before the beamtime), the
The electrochemistry of Li$_4$Ti$_5$O$_{12}$ electrode in a test cell failed. Thus a standard (protonated) electrolyte was used.

Firstly to ensure good current density distribution in the entire volume of the electrode material, the electrode was divided into three layers, called bottom, middle and top layer going from the current collector to the separator. The content of graphite was set to be maximum in the top layer, which is far from the current collector, and then decreased through the middle and bottom layer. In order to tune the porosity, NH$_4$HCO$_3$ was mixed with other components of the electrode mass, and the mixtures were pressed into the Al current collector. (For more information on the rectangular cell design, see Ref.77). The electrode was then heated at 150°C under vacuum, which provoked the complete decomposition of NH$_4$HCO$_3$, resulting in release of gases that leave behind a porous network running through the electrode. Using this technique the average active material to carbon ratio was increased to 6:1, compared to the 1:1 used earlier, without compromising the electrochemical properties of the cell.

The electrochemical cycling used during the in situ NPD experiment was similar to a GITT protocol; a step consisting of a 80 min galvanostatic lithiation (or delithiation) at C/25 rate with respect to 175 mAh/g, followed by a 100 min at open circuit potential (OCP) was repeated 3 times, and then was followed by a 9 h OCP step during which the NPD pattern was acquired (Figure 2.4). This protocol was chosen to ensure equilibrium during the pattern acquisition and to reduce the polarization effects in the extremely thick electrode. During the three steps of active cycling, a second, identical cell running simultaneously allowed the recording of additional patterns, thus using the beam time more effectively. One cell was devoted to the pattern collection during the first lithiation step. The other one was lithiated before the neutron experiment and was devoted to the acquisition of patterns during the first delithiation step. Only 8 NPD patterns could be measured during the course of 1$^{st}$ cycle owing to the long data acquisition time. The patterns were acquired at the HRPT beamline at SINQ, PSI Villigen at 1.494 Å. The Rietveld refinement were carried out using Fullprof software, which was also used to analyze other diffraction patterns reported in this thesis.
2.3.2. Results

The precise structure of the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material was first determined ex situ by neutron diffraction using a vanadium tube as a sample container. As expected, the compound crystallized in the $Fd-3m$ space group with cell parameter $a = 8.3636 \, \text{Å}$, which is in accordance with the literature\textsuperscript{47, 80}. Refinement of occupancies did not bring any improvement in the fitting of data so they were fixed to their theoretical value. The results of the refinement are given in Table 2.1.

| Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} | | | | | |
|---|---|---|---|---|
| Space group: $Fd-3m$ | Cell parameter $a = 8.3636 (1) \, \text{Å}$ | $\chi^2 = 2.6$ |
| Atom | Wyckoff site | $x$ | $y$ | $z$ | Occupancy |
| Li1 | 8a | 0.125 | 0.125 | 0.125 | 1.0 |
| Li2 | 16d | 0.5 | 0.5 | 0.5 | 0.1667 |
| Ti | 16d | 0.5 | 0.5 | 0.5 | 0.8333 |
| O | 32e | 0.2625(1) | 0.2625(1) | 0.2625(1) | 1.0 |

| Li\textsubscript{7}Ti\textsubscript{5}O\textsubscript{12} | | | | | |
|---|---|---|---|---|
| Space group: $Fd-3m$ | Cell parameter $a = 8.3581 (1) \, \text{Å}$ | $\chi^2 = 1.7$ |
| Atom | Wyckoff site | $x$ | $y$ | $z$ | Occupancy |
| Li1 | 16c | 0 | 0 | 0 | 1.0 |
| Li2 | 16d | 0.5 | 0.5 | 0.5 | 0.1667 |
| Ti | 16d | 0.5 | 0.5 | 0.5 | 0.8333 |
| O | 32e | 0.2576(3) | 0.2576(3) | 0.2576(3) | 1.0 |

Table 2.1: Crystallographic data obtained from Rietveld refinement of starting Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and after end of first lithiation step (Li\textsubscript{6.78}Ti\textsubscript{5}O\textsubscript{12}). Refined parameters are in italics.

The electrochemical data for cycling of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} in the rectangular cell is shown in Figure 2.4. It is seen that during the galvanostatic part of the cycling, the polarization reaches high values which were expected due to the extreme thickness of the working electrode (around 4 mm) and the high current used (15 mA for 2.2 g of electroactive...
material). But when the current flow was stopped, the system relaxation was sufficiently fast and a potential close to the expected equilibrium (1.57 V vs. Li⁺/Li) was reached at the end of the OCP step. This was obviously due to the good repartition of the electrolyte through the electrode. The acquisition of diffraction pattern then took place when the system was in a quasi-equilibrium state. A specific charge of 163 mAh/g was achieved at the end of the first lithiation step out of the theoretically expected 175 mAh/g, which means that 93% of the material reacted. During the successive delithiation, only a small irreversible charge “loss” of 5% was noticed. These results prove that using a proper composition and design of the electrode allows overcoming challenges raised by the high amount of material required for neutron diffraction.

![Electrochemical cycling curves for Li₄Ti₅O₁₂ during first lithiation and delithiation step](image)

Figure 2.4: Electrochemical cycling curves for Li₄Ti₅O₁₂ during first lithiation and delithiation step. Arrows mark the point at which the NPD patterns were recorded.

The diffraction patterns obtained during the cycling are shown in Figure 2.5. The background shows a characteristic bend shape due to the protonated electrolyte, but still peaks due to the active material are clearly visible. The structural model obtained during the ex situ experiment was used to refine the in situ pattern obtained before cycling (pattern b). As no reaction has occurred until then, the structural model obtained from the ex situ experiment was fixed and only the zero and the scale factor were refined. The zero was then fixed for the following patterns, as the position of the material in the beam did not change during the experiment. Especially interesting is the doublet (773)/(666) at 2Theta between 135-136°, whose ratio reflects the ratio between Li₄Ti₅O₁₂ and Li₇Ti₅O₁₂. As
observed from the enlargement shown in Figure 2.5, when lithium is inserted into the structure the intensity of the (773) peak decreases as the intensity of (666) increases. This was expected from the simulation of the patterns obtained with the structural models proposed by Ozhuku \(^47\) (Figure 2.5, patterns a and g). The reversibility of this process is clearly visible on the patterns obtained during the following delithiation step.

Figure 2.5: In situ NPD patterns (\(\lambda = 1.494\ \text{Å}\)) recorded during cycling of \(\text{Li}_4\text{Ti}_5\text{O}_{12}\). a and g are simulated patterns for \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) and \(\text{Li}_7\text{Ti}_5\text{O}_{12}\) respectively. b to f and h to k are in situ NPD patterns recorded during the 1\(^{st}\) lithiation and 1\(^{st}\) delithiation respectively and correspond to the nominal composition (\(\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}\)) reported on the right-hand side.

At the end of the first lithiation, the calculated mean composition was \(\text{Li}_{6.78}\text{Ti}_5\text{O}_{12}\), which means 93% of the powder was \(\text{Li}_7\text{Ti}_5\text{O}_{12}\). Therefore this pattern was used to refine the structural model of \(\text{Li}_7\text{Ti}_5\text{O}_{12}\) proposed by Ozhuku et al.\(^81\). Only the cell parameter and the oxygen atomic position were refined using the doublet, leading to the results given in Table 2.1. A small decrease of the cell parameter from 8.3636 Å to 8.3581 Å was observed. The refinement of the oxygen position leads to longer Ti-O length (2.03 Å instead of 1.99 Å) which is consistent with the presence of Ti\(^{3+}\) that has a higher ionic radius than Ti\(^{4+}\).
The (773)/(666) doublet of all the patterns (including the one taken at OCP and the one at the end of lithiation step) were then used in a 2-phase Rietveld refinement to determine the proportion of each phase in the mixture. The structural models obtained previously were fixed and only scale factors were allowed to be refined. The results are given in Table 2.2. As expected, the amount of Li$_7$Ti$_5$O$_{12}$ increases during lithiation and decreases during the delithiation step. But an important deviation of the calculated values from the expected value (obtained using electrochemical data) is observed, especially when the two phases are present in significant amount. This is due to the strong overlapping of the peaks that hinders the good retrieval of integrated intensity. When one phase is strongly dominant this problem is not significant anymore.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Li$_4$Ti$<em>5$O$</em>{12}$ (%wt) calculated$^a$</th>
<th>Li$_7$Ti$<em>5$O$</em>{12}$ (%wt) calculated$^a$</th>
<th>Li$_4$Ti$<em>5$O$</em>{12}$ (%wt) expected$^b$</th>
<th>Li$_7$Ti$<em>5$O$</em>{12}$ (%wt) expected$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>b - Li$_4$Ti$<em>5$O$</em>{12}$</td>
<td>100.0 (±2.4)</td>
<td>-</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>c - Li$_{4.7}$Ti$<em>5$O$</em>{12}$</td>
<td>87.7 (±4.3)</td>
<td>12.3 (±2.0)</td>
<td>76.7</td>
<td>23.3</td>
</tr>
<tr>
<td>d - Li$_{5.4}$Ti$<em>5$O$</em>{12}$</td>
<td>68.8 (±3.8)</td>
<td>31.2 (±2.2)</td>
<td>53.3</td>
<td>46.7</td>
</tr>
<tr>
<td>e - Li$_{6.1}$Ti$<em>5$O$</em>{12}$</td>
<td>42.4 (±3.4)</td>
<td>57.6 (±2.9)</td>
<td>30.3</td>
<td>69.7</td>
</tr>
<tr>
<td>f - Li$_{6.8}$Ti$<em>5$O$</em>{12}$</td>
<td>2.9 (±3.2)</td>
<td>97.1 (±4.3)</td>
<td>6.7</td>
<td>93.3</td>
</tr>
<tr>
<td>h - Li$_{5.9}$Ti$<em>5$O$</em>{12}$</td>
<td>37.8 (±2.9)</td>
<td>62.2 (±2.7)</td>
<td>36.7</td>
<td>63.3</td>
</tr>
<tr>
<td>i - Li$_{5.2}$Ti$<em>5$O$</em>{12}$</td>
<td>64.6 (±3.6)</td>
<td>35.4 (±2.3)</td>
<td>58.7</td>
<td>41.3</td>
</tr>
<tr>
<td>j - Li$_{4.6}$Ti$<em>5$O$</em>{12}$</td>
<td>92.8 (±4.0)</td>
<td>7.2 (±1.7)</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>k - Li$_{4.1}$Ti$<em>5$O$</em>{12}$</td>
<td>91.2 (±4.5)</td>
<td>8.8 (±2.0)</td>
<td>96.7</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table 2.2: Results of the quantitative analysis carried through Rietveld refinement of in situ NPD patterns. The nominal composition is based on electrochemical data. $^a$ values obtained from diffraction data and $^b$ from the nominal composition.

2.3.3. Discussion

This study demonstrates the feasibility of the in situ NPD for investigation of active materials for Li-ion batteries. The rectangular cell design allows only the electrode material soaked in the electrolyte and the Al container to be in the neutron beam and has a definite advantage over the previously reported designs. However several issues were identified from this study. Firstly the study indicates that improving the electrode composition and the
engineering alone does not lead to a huge improvement in the electrochemistry. Since the cell uses 3 g of electrode mass cycled at C/25 rate, the polarization in the cell is huge. Thus to have better electrochemical performance the electrode mass has to be reduced drastically. Secondly, the rectangular cell containing electrode mass is placed vertically in the beam to facilitate maximum amount of the material to be in the beam (Figure 2.6A). This results in different path lengths travelled by the diffracted beam through the electrode mass and the Al container, which in turn leads to uneven absorption of the diffracted beam and prevents Rietveld refinement of the data over the complete 2Theta range. Figure 2.7 shows the Rietveld refinement for Li$_4$Ti$_5$O$_{12}$ soaked in deuterated EC/DMC 1M LiClO$_4$ electrolyte in a completely assembled in situ cell at open circuit potential. Structural model reported for Li$_4$Ti$_5$O$_{12}$ in Table 2.1 was used for the Rietveld refinement of this phase. Only the values of zero, scale factor, $B_{iso}$ and peak width parameters (u, v, w, x, y) were refined. Aluminium from the sample holder was refined using pattern matching. It is clear that the uneven absorption of the diffracted beam leads to a poor fitting of the data ($\chi^2 = 34$) over the complete 2Theta range. Thus for analysis of the available data, 2-phase refinement had to be performed using only the (773)/(666) doublet.

![Diagram of neutron diffraction](image.png)

Figure 2.6: Top schematic view of the Al container holding the electrode mass, for the in situ neutron diffraction cell with (A) rectangular design and (B) circular design.
To overcome this issue, a circular design is needed as illustrated in Figure 2.6B. This cell must be placed horizontally in the neutron beam to avoid uneven absorption, which would require the use of higher intensity beamline than the one at SINQ, PSI Villigen. Thus this study clearly indicates that further development in the cell design is required.

Figure 2.7: Rietveld refinement of NPD pattern ($\lambda = 1.494 \, \text{Å}$) recorded for completely assembled in situ NPD cell containing Li$_4$Ti$_5$O$_{12}$ soaked with deuterated EC/DMC 1M LiClO$_4$ electrolyte.

2.3.4. Conclusion

Thanks to improved electrode formulation, evolution of the structural parameters of Li$_4$Ti$_5$O$_{12}$ during the entire cycle could be followed using the rectangular in situ NPD cell. A small decrease of the cell parameter from 8.3636 Å to 8.3581 Å accompanied by an increase of the Ti-O bond length was observed. Quantitative analysis was carried on the obtained diffraction patterns. Although the overlapping of the peaks hindered a precise determination of weight percentage, the observation of the composition evolution is still possible using the rectangular in situ NPD cell. Nevertheless, this study identified the chance for significant improvement when changing the cell design to a circular one, which is discussed in chapter 3.
Chapter 3
Circular *in situ* neutron powder diffraction cell
3.1. Introduction

From the previous study on Li$_4$Ti$_5$O$_{12}$ exploring the rectangular cell design, it can be concluded that 3 major issues have to be solved in order to improve the performance of the in situ neutron cell:

- The electrode mass in the cell has to be minimized to reduce the electrochemical polarization in the cell.

- A circular cell design is needed in order to avoid the uneven absorption of the diffracted neutron beam.

- A high intensity neutron source is required to obtain meaningful results using small circular cell to avoid unrealistically high data acquisition time.

Thus a new in situ NPD cell based on circular design was developed for use at the D20 beamline at Institut Laue-Langevin (ILL), Grenoble. ILL uses nuclear reactor as a neutron source, which results in a neutron flux of $10^7$-$10^8$ ns$^{-1}$cm$^{-2}$ at the sample, as compared to $1.7*10^5$ ns$^{-1}$cm$^{-2}$ for HRPT beamline at SINQ, PSI Villigen, which is a spallation source. Hence it allows for design of smaller dimension cell.

3.2. Cell design

Figure 3.1 shows the cross section view of the new circular in situ NPD cell. This cell consists of several parts. The outer cell body (E) is made up of aluminium and is separated from the inner cell body by (F) polyetheretherketone (PEEK). The inner cell body consists of a titanium plunger (B) pushed down from the titanium current collector (D) by a spring (C). The titanium plunger acts as the support for the counter electrode, a disk of lithium. The sample holder (A) is a thin walled (0.5 mm) aluminium cylinder and is the only part of the cell which is in the neutron beam during diffraction measurement. This part is 15 mm in diameter and has a height of 3.5 mm. It holds the electroactive material and simultaneously acts as the current collector. Aluminium was chosen because of its low neutron absorption coefficient and small scattering cross section. To facilitate cycling of negative electrode materials, a titanium sample holder (A) was also designed. O-rings are used between different parts to seal the cell hermetically. The dimensions of the sample holder for the circular in situ NPD cell have been drastically reduced from its rectangular
predecessor [53 mm (l)*19 mm (w)*5.8 mm (h)]\textsuperscript{77}, resulting in reduction of the sample holder volume down from 5.84 cm\textsuperscript{3} to 0.62 cm\textsuperscript{3}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.1.png}
\caption{Cross section of the new circular \textit{in situ} NPD cell: (A) Al/Ti container for the electrode material (only part in neutron beam) (B) Ti plunger for Li counter electrode (C) spring (D) Ti current collector (E) Al cell body part (F) PEEK cell (G) polymeric attachment for D20 beamline.}
\end{figure}

\subsection*{3.3. Experimental validation of the circular \textit{in situ} NPD cell}

In order to test the performance of the circular \textit{in situ} NPD cell and give a fair comparison with the rectangular cell, Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} was first used as the electroactive material. The working electrode for this circular cell was made by mixing appropriate amounts of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} with Super-P carbon and NH\textsubscript{4}HCO\textsubscript{3} in mortar. No graphite was used. The mixture was then packed into the cavity of the circular aluminium current collector, followed by a heat treatment step at 150°C. Although same 6:1 ratio of active material to carbon was
used as for the rectangular cell, the total amount of electrode material was reduced by 10x down to 0.3 g. In order to assemble the cell, EC/DMC 1M LiClO₄ electrolyte was added to the aluminium container holding the electrode material. A Celgard® 2400 separator was placed on top of this electrode followed by a glass fiber separator. The whole assembly was soaked with the electrolyte. A disk of lithium pressed on the titanium plunger acts as the counter electrode. A hollow polymeric cylinder avoids short-circuit in the cell. After assembling the cell, the aluminium cell body is screwed onto the PEEK body part, which hermetically seals the complete cell. In order to test the electrochemistry of Li₄Ti₅O₁₂ in the circular cell design, the cell was cycled galvanostatically at C/25 and C/12 rate with respect to its theoretical specific charge of 175 mAh/g. Li₄Ti₅O₁₂ was also cycled at C/25 rate in the rectangular cell under similar conditions and their electrochemical performance is compared with that of Li₄Ti₅O₁₂ in a standard coin-like cell (Figure 3.2).

![Figure 3.2: Electrochemical cycling of Li₄Ti₅O₁₂ in rectangular and circular in situ NPD cells and a standard coin-like cell, between 1.0-2.5 V vs. Li/Li⁺ in EC/DMC 1M LiClO₄.](image)

As expected, the circular cell design shows lower polarization for cycling of Li₄Ti₅O₁₂ than in the rectangular cell owing to smaller amount of electrode mass used. For this reason Li₄Ti₅O₁₂ can also be cycled at faster C/12 rate in the circular cell. To test if the reduced amount of electrode material affects the quality of the neutron diffraction data, ex situ NPD pattern was recorded for a completely assembled circular cell containing Li₄Ti₅O₁₂ soaked with deuterated-EC/DMC 1M LiClO₄ electrolyte. The measurement was
performed at the D20 beamline (ILL, Grenoble) for 10 min at 1.36 Å. The data is compared with the one for Li$_4$Ti$_5$O$_{12}$ in completely assembled rectangular cell design, also using deuterated electrolyte, measured at the HRPT beamline (SINQ, PSI Villigen) over 9 h at 1.494 Å. It is clearly visible from Figure 3.3 that reducing the electrode material mass does not affect NPD data quality. All the peaks for Li$_4$Ti$_5$O$_{12}$ visible using the rectangular cell are also present using the circular cell. Moreover thanks to the use of high intensity neutron source at ILL, Grenoble, the data acquisition time was reduced by more than 50x. The intensity of Al peaks is different in both cells owing to the fact that the Al sample holders were machined in different manner, resulting in preferential orientation of the Al along different crystallographic planes.

Figure 3.3: *Ex situ* neutron diffraction patterns collected for Li$_4$Ti$_5$O$_{12}$ soaked with deuterated-EC/DMC 1M LiClO$_4$, in completely assembled (A) rectangular cell for 9 h at HRPT, PSI Villigen and (B) circular cell for 10 min at ILL, Grenoble. HRPT data measured at 1.494 Å has been converted to 1.36 Å for comparison.

Moreover thanks to the circular design, Rietveld analysis of the pattern over the complete 2Theta range is possible (Figure 3.4). For the Rietveld refinement structural
model of Li₄Ti₅O₁₂ reported in Table 2.1 was used and only the zero, scale factor, B_{iso} and peak width parameters (u, v, w, x, y) were refined for this phase. Al was refined using profile matching. Owing to the circular design no uneven absorption of the diffracted beam was evident and a good agreement between the observed and calculated intensities (χ² = 2.33) could be obtained.

Figure 3.4: Rietveld refinement of NPD pattern (λ = 1.36 Å) recorded for 20 min at ILL, Grenoble for a completely assembled circular in situ NPD cell containing Li₄Ti₅O₁₂ soaked with deuterated EC/DMC 1M LiClO₄ electrolyte.

In order to test the feasibility of the circular cell design to cycle various electroactive materials, LiFePO₄ and Li₁.1(Ni₁/₃Mn₁/₃Co₁/₃)₀.₉O₂ were cycled in an Al container, while a Ti container allowed cycling of Ni₀.₅TiOPO₄ till lower potentials. As seen from Figure 3.5 the circular cell can be used over the complete range of interest for the battery materials without having to modify the cell design. The composition for Li₁.₁(Ni₁/₃Mn₁/₃Co₁/₃)₀.₉O₂ and Ni₀.₅TiOPO₄ electrodes was not optimized and hence only their first delithiation and lithiation respectively are shown. From these results it can be concluded that the circular cell design shows marked improvement not only in the electrochemical performance of the used electroactive material, but also the data acquisition time, which allows for a higher time resolution between the diffraction patterns.
3.4. In situ neutron diffraction of LiFePO$_4$

Having experimentally validated the circular in situ NPD cell, actual in situ NPD measurements were performed using LiFePO$_4$ as the electroactive material. LiFePO$_4$ crystallizing in orthorhombic $Pnma$ space group undergoes a 2-phase reaction on 1 Li$^{+}$ deinsertion to form FePO$_4$, also crystallizing in $Pnma$ space group with slightly different unit cell parameters and atomic positions. The aim of this study was to follow the evolution of the FePO$_4$ phase in situ during the electrochemical cycling of the cell.

### 3.4.1. Experimental

**In situ measurements:** For the in situ NPD measurements, 0.28 g mixture of LiFePO$_4$ (85% wt) and Super-P carbon (15% wt) was taken as the electrode mass. No binder was used. Preliminary results showed that no NH$_4$HCO$_3$ step was needed to achieve good electrochemical cycling of LiFePO$_4$. The electrode mass was pressed into an Al container and filled with EC/DMC 1M LiPF$_6$ electrolyte. For the in situ measurements, the cell was charged versus Li counter electrode at C/24 rate with respect to 170 mAh/g till 4.5 V vs. Li/Li$^+$ and then held at open circuit potential (OCP) for 2 h. Use of deuterated electrolyte was planned for the in situ measurement, however due to...
relatively high content of water (42.7 ppm, electrolyte on molecular sieves for 3 weeks) the electrochemistry of the cell failed after 5 h and hence a protonated electrolyte had to be used. The in situ NPD patterns were recorded during the first charge of LiFePO$_4$ at 1.36 Å over the period of 24 min i.e. 2.83 mAh/g or 0.01667 Li$^+$, with total of 54 patterns recorded during the course of the first charge. Patterns could not be recorded during the first discharge, owing to lack of allocated beamtime.

Ex situ measurements: In order to have starting models for Rietveld refinement, ex situ neutron diffraction measurements were performed in a vanadium tube on the dry starting LiFePO$_4$ powder (2 g) and dry LiFePO$_4$ electrode mixture (0.25 g) charged till 4.5 V vs. Li/Li$^+$ before hand. Rietveld refinement was performed on these patterns using the structural models proposed by Andersson et al.\textsuperscript{85} For the starting LiFePO$_4$ only a single phase Rietveld refinement was used where as for the electrode obtained after first charge, a 2-phase Rietveld refinement with LiFePO$_4$ and FePO$_4$ phases was performed.

Ex situ measurements were also conducted on the LiFePO$_4$ electrode in completely assembled cell, soaked with deuterated PC/DMC 1M LiClO$_4$ electrolyte. Another circular cell was pre-charged till 4.5 V vs. Li/Li$^+$ in EC/DMC 1M LiPF$_6$ electrolyte; the electrode washed with DMC, dried and then soaked with deuterated PC/DMC 1M LiClO$_4$ electrolyte. This electrode was again assembled into a complete cell and ex situ measurement was conducted on it. The structural models obtained from refinement of dry samples were used for the Rietveld refinement of the patterns from soaked electrodes. Only the zero, scale factor and the peak width parameters were refined. In both the cases an additional Al phase was introduced to refine the peaks from the Al container. This Al phase was refined using profile matching.

3.4.2. Results and discussion

Figure 3.6 shows the electrochemistry of LiFePO$_4$ in the in situ cell and marks the points at which the ex situ NPD patterns were recorded along with their recording conditions. The charge curve for LiFePO$_4$ is flat, as expected for a 2-phase reaction. Despite its low electronic conductivity ($\sim 10^{-9}$ Scm$^{-1}$), LiFePO$_4$ delivers 154 mAh/g out of the expected 170 mAh/g, which means that around 90.5 % of the starting LiFePO$_4$ is now converted to FePO$_4$. The potential difference between the starting and end points of the 2-phase plateau is only 80 mV despite using 0.246 g of LiFePO$_4$ (0.2888 g electrode mass, 2.5 mm thick electrode), which clearly indicates that the inhomogeneous reaction
along the direction of the electrode is very small. This could be attributed to good electrical contact between the LiFePO$_4$ and Super-P carbon particles.

Figure 3.6: First charge of LiFePO$_4$ in the circular *in situ* NPD cell in EC/DMC 1M LiPF$_6$ electrolyte. The circles mark the points where the *ex situ* neutron diffraction patterns were recorded and their measurement conditions.

Figure 3.7 shows the Rietveld refinement performed on the NPD patterns of the dry LiFePO$_4$ powder and LiFePO$_4$ electrode after 1$^{\text{st}}$ charge. Table 3.1 details the results of the Rietveld analysis. As expected, starting LiFePO$_4$ and FePO$_4$ present at the end of first charge crystallize in the orthorhombic *Pnma* space group. The unit cell parameters and atomic positions in both the cases are close to those reported earlier$^{85,86}$. In case of Figure 3.7B the background is higher due to the presence of 15% Super-P carbon in the electrode, due to small amount (0.25 g) of material used for the NPD measurement and the fact that it has undergone an electrochemical delithiation step. The sloped background and lower peak to noise ratio make the selection of background points difficult and hence the refinement is not as good as that for the starting LiFePO$_4$, where 2 g of sample was used for the measurement.

These starting models reported in Table 3.1 were used for the Rietveld refinement of samples in completely assembled cells, soaked with deuterated electrolyte as shown in Figure 3.8. In accordance with the previous result on Li$_4$Ti$_5$O$_{12}$, Rietveld refinement over the complete 2Theta range is possible even for the starting LiFePO$_4$ electrode in a
completely assembled circular *in situ* NPD cell. Same was observed for the LiFePO$_4$ at the end of 1$^{st}$ charge.

Figure 3.7: Rietveld refinement of NPD ($\lambda = 1.36$ Å) for (A) LiFePO$_4$ pristine powder and (B) LiFePO$_4$ electrode with Super-P carbon after 1$^{st}$ charge till 4.5 V vs. Li/Li$^+$. Both the dry samples were measured in a vanadium tube for 20 min.
## LiFePO₄

**Space group**: Pnma, \(a = 10.3279\ (1) \text{ Å}, b = 6.0063\ (1) \text{ Å}, c = 4.6933\ (1) \text{ Å}\)

\(\chi^2 = 8.79, R_{wp} = 8.39\%\)

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## FePO₄

**Space group**: Pnma, \(a = 9.8258\ (1) \text{ Å}, b = 5.7941\ (1) \text{ Å}, c = 4.7841\ (1) \text{ Å}\)

\(\chi^2 = 9.9, R_{wp} = 24.2\%\)

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Table 3.1: Crystallographic data obtained after Rietveld analysis of starting LiFePO₄ powder and LiFePO₄ electrode after 1\textsuperscript{st} charge till 4.5 V vs. Li/Li\textsuperscript+\). Refined parameters are in italics.

For the Rietveld refinement of the starting sample, only the zero and the scale factor were refined as nothing else has been changed. For the end of charge sample, a 2-phase Rietveld refinement was performed, which showed that 94 (±1)% of LiFePO₄ has reacted to form FePO₄. This value is very close to the 90.5% expected from the electrochemistry.
Thus this *ex situ* study proves without doubt that using small quantity (~0.25-0.3 g) of electroactive material, cycled in the circular *in situ* NPD cell, a qualitative as well as quantitative study is feasible, if one uses a deuterated electrolyte.

Figure 3.8: Rietveld refinement of NPD ($\lambda = 1.36$ Å) of (A) LiFePO$_4$ pristine electrode at open circuit potential and (B) LiFePO$_4$ electrode after 1$^{\text{st}}$ charge till 4.5 V vs. Li/Li$^+$. The samples were soaked in deuterated PC/DMC 1M LiClO$_4$ electrolyte and held in completely assembled circular *in situ* NPD cell in an aluminium container.
As the deuterated electrolyte used for the *ex situ* measurements contained around 43 ppm water, it lead to curvy background in the diffraction patterns. Also owing to this large amount of water, protonated EC/DMC 1M LiPF$_6$ electrolyte had to be used for the *in situ* NPD measurement. Figure 3.9 compares the NPD patterns recorded for LiFePO$_4$ at OCP in two completely assembled circular NPD cells, one with EC/DMC 1M LiPF$_6$ electrolyte and another with deuterated PC/DMC 1M LiClO$_4$ electrolyte. It is immediately evident that moving to a protonated electrolyte leads to a huge background in the pattern. Most of the peaks from LiFePO$_4$ that were clearly visible when a deuterated electrolyte was used are no longer detectable. Only the most intense peaks of the electroactive material are visible.

Figure 3.9: Comparison of NPD patterns ($\lambda = 1.36$ Å) recorded over 24 min for LiFePO$_4$ electrode in a completely assembled circular *in situ* NPD cell in an aluminium container soaked in (A) EC/DMC 1M LiClO$_4$ and (B) deuterated PC/DMC 1M LiClO$_4$ electrolyte.

Due to the limited time allocated at the beamline, longer acquisition time during the *in situ* measurements was not possible to improve the peak/noise ratio. Thus the *in situ* patterns were recorded only over 24 min or 0.01667 Li$^+$. Every 6$^{th}$ *in situ* NPD pattern, corresponding to 10% LiFePO$_4$ converted to FePO$_4$, has been plotted in Figure 3.10.
Figure 3.10: In situ NPD patterns (\( \lambda = 1.36 \text{ Å} \)) recorded during 1\textsuperscript{st} charge of LiFePO\(_4\) till 4.5 V vs. Li/Li\(^+\). The numbers on the right hand side of the patterns represent the nominal percentage of LiFePO\(_4\) in the sample as calculated from the electrochemical curve.
It is seen qualitatively from Figure 3.10 that during the course of first charge, the peaks corresponding to the LiFePO$_4$ phase disappear, while that from FePO$_4$ emerge. When 50% specific charge has been drawn from the material, both the phases are seen to coexist; proving that evolution of different phases can be followed using the circular *in situ* NPD cell.

3.5. *In situ* neutron diffraction of graphite

The *in situ* NPD study on LiFePO$_4$ showed the importance of using dry deuterated electrolyte to obtain good electrochemical cycling and well resolved NPD patterns. Thus an *in situ* NPD study was conducted on graphite in the circular cell developed here, by Mr. Michael Hess (PhD student) using deuterated electrolyte, in order to study the different stages formed in graphite when cycled at 50°C and to elucidate the space groups for these different stages. The preliminary data has been presented here with an aim of showing the performance of the circular *in situ* NPD cell developed within the framework of this thesis, when a deuterated electrolyte is used. Note that no more beam time was available at ILL, Grenoble due to failure of the nuclear reactor, resulting in a shift of the beam time scheduled for this thesis from fall 2010 to May 2011.

3.5.1. Experimental

For the *in situ* NPD measurement a 200 mg graphite pellet was placed in a titanium container. A piece of glass fiber was placed on top of it and soaked in deuterated EC/DMC 1M LiPF$_6$ (6.8 ppm water) electrolyte. A lithium disk was used as the counter electrode and the cell was assembled in an Ar-filled glovebox. The aim of this study was to investigate the structural evolution of graphite between the stage 4 and stage 2/2L at high temperature. Thus the completely assembled cell was first lithiated at 50°C until 0.22 V vs. Li/Li$^+$ at C/1200 rate to complete the Solid Electrolyte Interphase (SEI) formation. For the *in situ* NPD measurement, the cell was lithiated from 0.23 V down to 0.11 V vs. Li/Li$^+$ at C/200 rate, during which the NPD patterns were recorded over 30 min. The NPD measurements were performed at ILL, Grenoble at 1.36 Å at a temperature of 50°C ($\pm$0.3). After the *in situ* NPD measurement, the cell was completely lithiated down till 0.01 V vs. Li/Li$^+$ at C/200 rate to show the feasibility of the circular *in situ* NPD cell to cycle graphite.
3.5.2. Results and discussion

The electrochemical lithiation curve of graphite that has been subjected to a formation step prior to the in situ NPD measurement is shown in Figure 3.11. With 80 mAh/g specific charge from the formation step and 360 mAh/g obtained for lithiation between 0.23 to 0.01 V vs. Li/Li⁺, the total specific charge for 1st lithiation step of graphite is around 440 mAh/g, which is in agreement with the results for graphite electrodes cycled in a standard coin-like cell. The in situ measurements were performed only during the first 38 h of the electrochemical lithiation step (between points 1 to 5 in Figure 3.11) in the area of interest.

![Figure 3.11: First charge of graphite in the circular in situ NPD cell in deuterated EC/DMC 1M LiPF₆. The in situ measurements were performed between the points 1 and 5. Circles highlight the points of interest for the study, + indicates fluctuation due to change in applied current and x marks potential fluctuation due to rest periods.](image)

The in situ NPD recorded during lithiation of graphite are shown in Figure 3.12. The titanium container that was used in order to assist cycling of graphite at such low potentials shows large number of diffraction peaks. However the major peaks from graphite and titanium do not overlap. From the in situ NPD patterns the main (002) peak is seen to shift to lower 2Theta values i.e. higher c unit cell parameter, which is as expected. Several other peaks are seen to evolve during the course of lithiation.
Figure 3.12: *In situ* NPD patterns (λ = 1.36 Å) recorded during 1\textsuperscript{st} lithiation of graphite between 0.23-0.11 V vs. Li/Li\textsuperscript{+}. (*) and (x) mark peaks from graphite and titanium respectively.
Owing to the fact that a deuterated electrolyte was used and that graphite itself is a very good neutron scatterer, the peak/noise ratio was sufficiently high. The analysis of the in situ NPD data is still ongoing; however this example clearly illustrates the feasibility of using the circular in situ NPD cell, developed within this thesis, to follow the structural evolution in electroactive materials for Li-ion batteries in real time.

3.6. Discussion

From the ex situ measurements it can be concluded that Rietveld refinement can be performed on the electroactive material and carbon mixture, filled in a cylindrical sample holder; soaked with deuterated electrolyte. A very good and reliable fitting can be obtained if an acceptable structural model is used. However when a protonated electrolyte is used instead of a deuterated one, less number of peaks from the sample itself are visible. Moreover use of hydrogenated electrolyte leads to very high background and low peak/background ratio, making it very difficult and unreliable to perform quantitative analysis of the data. Thus if one intends to perform qualitative and quantitative analysis of the in situ NPD data, a clean and dry deuterated electrolyte must be used. In order to achieve stable electrochemical cycling of the electroactive material, the deuterated electrolyte must be of battery grade i.e. with water content lower than 5-10 ppm. Use of hydrogenated electrolyte will only allow for qualitative analysis of evolution of different phases, if the elements in the electroactive material are strong scatterers. In terms of electrochemistry the cell can achieve rates from C/40 to C/10. Cycling at higher rates could be possible but would not be advisable due to problems with increased electrochemical polarization. It was found that for different electroactive materials, different electrode composition and formulation is required, which must be tested and optimized separately before using the electroactive material for in situ measurements.

Another issue that is clearly evident when looking at the in situ NPD data is that the Al and Ti containers result in strong Bragg peaks, which are at the same position as the peaks from the electroactive material. The solution to this problem would be using a metal that is inherently non- or low- scattering in neutrons for e.g. vanadium\textsuperscript{87}, which is used as sample holder for ex situ measurements.

Vanadium however is reactive versus Li at low potentials and hence bare V cannot be used. V cylinders coated with thin layer of inert metal can be the solution, but the most common metal stable over the complete range of interest for Li-ion batteries i.e. 0-5 V vs. Li/Li\textsuperscript{+} is Ti. Ti however is neutron absorber\textsuperscript{87} and even as small layer might affect the
recorded NPD data. The answer to this problem could be the Ti-Zr null matrix alloy\textsuperscript{88}. Ti-Zr alloy in atomic ratio 62\%:38\% is essentially a non scatterer for neutrons\textsuperscript{88}. As it is made up of two elements that are non-reactive versus lithium, a Ti-Zr alloy could be stable over the complete 0-5 V vs. Li/Li\textsuperscript{+} range. Nevertheless making a pure Ti-Zr alloy that is non-scattering in neutron beam is extremely difficult. This alloy being commercially unavailable, no replacement for the Al or Ti current collector could be found as of now. Nonetheless, in the future, a possible replacement could be found in the Ti-Zr alloy or V container coated with a non-reactive, low scattering metal.

3.7. Conclusion

A new circular \textit{in situ} neutron diffraction cell based on a circular geometry, capable of cycling 0.2-0.3 g of electrode mass, was designed and successfully tested at the D20 beamline at ILL, Grenoble (FR). \textit{Ex situ} NPD measurements on Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and LiFePO\textsubscript{4} using the new circular cell proved that Rietveld refinement is possible over the complete 2Theta range when a low scattering deuterated electrolyte is used. The electrochemistry of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} in this cell was seen to be much better than in the previous rectangular design, owing to 10 times lower amount of electrode mass used. Moreover moving to a neutron source with higher neutron flux resulted in reduction of the acquisition time by a factor of more than 50. These two effects directly correlated to faster electrochemical cycling and higher time resolution of the diffraction data. First \textit{in situ} NPD runs using LiFePO\textsubscript{4} in hydrogenated EC/DMC 1M LiPF\textsubscript{6} electrolyte were successfully conducted at the D20 beamline. The LiFePO\textsubscript{4} was charged at C/24 rate, NPD measurements recorded over 24 min i.e. 0.01667 Li and the evolution of different phases followed qualitatively. The \textit{in situ} experiment performed using graphite soaked in deuterated EC/DMC 1M LiPF\textsubscript{6} electrolyte showed very good electrochemistry and high peak/noise ratio for the NPD patterns. The evolution of several peaks from graphite could be followed qualitatively and analysis is ongoing to identify and quantify the different phases. In conclusion it can be said that a reliable \textit{in situ} NPD cell cycling small amount of electroactive material at faster rates and lower data acquisition time has been successfully developed.
Chapter 4

Overcharge behavior of $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ ($x \geq 0$)
4.1. Introduction

Since the introduction of LiCoO$_2$ in Li-ion batteries by Sony, layered metal oxides have drawn a lot of attention. Li$_2$MnO$_3$ crystallizing in $C2/m$ space group$^{89}$ with a quasi-layered structure is one such example, relevant to this work. The structure of Li$_2$MnO$_3$ does not present any interstitial sites for Li$^+$ intercalation and hence it is electrochemically inactive in the lower potential region. The Mn in the structure is in +4 oxidation state and thus it cannot be oxidized further to remove Li$^+$ when charged negative to 4.4 V vs. Li/Li$^+$. However Kalyani et al.$^{90}$ showed that the electrochemically inactive Li$_2$MnO$_3$ can be activated when charged positive to 4.5 V vs. Li/Li$^+$ resulting in loss of Li$_2$O and formation of MnO$_2$.$^{91, 92}$ Li$^+$ intercalation is then possible during discharge in the MnO$_2$ that is formed, which is electrochemically active. The material however undergoes structural changes on long term cycling to form a spinel phase and shows poor cyclability$^{93}$. Due to these reasons Li$_2$MnO$_3$ itself is not a successful positive electrode material.

However inspired by the principle of stabilizing β-MnO$_2$, a 3 V positive electrode material, using ramsdellite MnO$_2$ to form γ-MnO$_2$$^{19}$ or using γ-Al$_2$O$_3$ to stabilize the structure of Na$^+$ conducting Na$_2$O to form the β$''$-Al$_2$O$_3$$^{94}$, several groups investigated stabilization of layered LiMO$_2$ oxides by Li$_2$MnO$_3$. It was found for LiMO$_2$ ($M =$ Ni, Co or Mn) that on extraction of more than 0.5 Li$^+$, the oxides undergo several phase transitions which affects their long term cyclability. For this reason Li$_2$MnO$_3$ stabilized LiMO$_2$ were extensively studied$^{36, 95-98}$, especially for their cycling within the stability region of Li$_2$MnO$_3$. Despite the different space groups for LiMO$_2$ ($R$$-$$3m$) and Li$_2$MnO$_3$ ($C2/m$), the close packing of oxygen in these compounds is essentially the same, with $d_{001}$ for Li$_2$MnO$_3$ and $d_{003}$ for the layered O3 phase being around 4.7 Å. This results in an intergrowth of Li$_2$MnO$_3$ like domains in the structure of LiMO$_2$. These Li$_2$MnO$_3$ domains, when ordered and present in adequate weight percentage result in appearance of extra peaks in the XRD patterns of the layered oxides. However owing to the intimate intergrowth of the Li$_2$MnO$_3$ in layered oxide, they are indistinguishable even using HRTEM imaging$^{41, 43}$. It is expected that along with stabilizing the LiMO$_2$ structure, if the Li$_2$MnO$_3$ domains are small and randomly distributed, they can also act as solid Li$^+$ transport electrolyte$^{41}$.

The Li$_2$MnO$_3$ stabilized layered oxides are commonly also referred to as overlithiated layered oxides and can be represented by different notations$^{41, 92}$. For example 0.215 Li$_2$MnO$_3$·0.785 Li(Ni$_{0.4232}$Mn$_{0.1493}$Co$_{0.4232}$)O$_2$, Li$_2$MnO$_3$ stabilized layered oxide, can also be represented approximately by composition Li$_{1.1}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{0.9}$O$_2$ of
overlithiated 333 NMC. Essentially both the nomenclatures are in use to represent the same nominal composition. In case of the overlithiated layered oxides $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ ($\text{M} = \text{Ni}, \text{Mn}$ and $x > 0$), the $x\text{Li}$ is in the transition metal slabs. This presence of metal ions with different radii and charge in the slabs, leads to ordering of $\text{Mn}^{4+}$ and $\text{Ni}^{2+/3}$ around $\text{Li}^+$, forming $\text{Li}_2\text{MnO}_3$ like domains (Figure 4.1A)\textsuperscript{11, 32, 41, 43}. Presence of Co in the structure however was seen to inhibit the growth of the $\text{Li}_2\text{MnO}_3$ like domain\textsuperscript{41, 43}. Thus when large amounts of Co is present in the structure, like in the case of 333 NMC, the $\text{Li}_2\text{MnO}_3$ ordering peaks are not visible in the diffractograms recorded at laboratory diffractometer (Figure 4.1B and 4.1C).

Due to demand of electroactive materials delivering higher specific energy, many different overlithiated layered oxides have been studied for their overcharge behavior positive to 4.5 V vs. Li/Li$^+$. In all the cases a long potential plateau at ~4.5 V vs. Li/Li$^+$ was found to appear during the first charge, which was associated to activation of the $\text{Li}_2\text{MnO}_3$ and hence loss of $\text{Li}_2\text{O}$ from the structure. Several attempts have been made to identify the structural changes occurring at the very positive potentials. Different mechanisms have been proposed for the oxygen loss from $\text{Li}_2\text{MnO}_3$ during overcharge\textsuperscript{102}. However due to the inherent structural complexity of the $\text{Li}_2\text{MnO}_3$ stabilized layered oxides, all the structural changes occurring during positive potential charge are not well defined.

333 NMC are one of the most interesting family of the layered oxides. These 333 NMC combine 3 different transition metals in good ratio to decrease Li-Ni exchange, avoid formation of spinel or metastable phases on delithiation\textsuperscript{103}, deliver good rate capability while keeping the volumic resistivity low\textsuperscript{104}. Recently, similar to other layered oxides, the $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ ($x = 0$ and 0.1) 333 NMC materials were also electrochemically cycled till very positive potentials viz. 5.0 V vs. Li/Li$^+$, in order to study their overcharge behavior\textsuperscript{44}. From the cyclic voltammetric study of these compounds, it was seen that there occurs an irreversible reaction for the overlithiated NMC ($x = 0.1$) at potentials positive to 4.5 V during the first delithiation step, which was absent in the stoichiometric NMC ($x = 0$). Differential Electrochemical Mass Spectrometry (DEMS) study of both NMC’s showed the appearance of $\text{O}_2$ signal positive to 4.5 V vs. Li/Li$^+$ for the overlithiated sample but not for the stoichiometric one. Moreover the cycling stability for the overlithiated sample ($x = 0.1$) was seen to be better than the stoichiometric one ($x = 0$) owing to the lower specific charge fading than the latter after 10 cycles\textsuperscript{44}. 

50
Figure 4.1: Schematic of ionic arrangement in the transition metal slabs and XRD patterns highlighting the peaks resulting from it, for (A) Li$_2$MnO$_3$ (B) Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ and (C) Li$_{1+x}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{1-x}$O$_2$.
These results suggest involvement of an irreversible structural change at positive potentials for the overlithiated sample, accompanied by $O_2$ release, which seems to be directly related to the stability of this compound, resulting in its better cycling stability. In order to understand the structural changes involved, an in situ synchrotron X-ray diffraction study was performed on overlithiated NMC ($x = 0.1$), during its first charge till 4.7 V vs. Li/Li$^+$\textsuperscript{45}. These results were complemented by ex situ X-ray diffraction patterns recorded at lab diffractometer for samples subjected to different electrochemical cycling protocols. From this study it was concluded that the overlithiated NMC ($x = 0.1$) did not undergo any phase transformation during the course of cycling, owing to 4.4% Li-Ni exchange in the structure of the sample investigated. Only a slight change in the unit cell parameters for the O3 phase was reported for the first charge\textsuperscript{45}. An in situ neutron diffraction study was also performed on the overlithiated NMC ($x = 0.1$) when charged till 5.0 V vs. Li/Li$^+$\textsuperscript{63, 77}, however owing to several factors adversely affecting the quality of the obtained data, only evolution of the (003) peak of the O3 phase could be followed. No peaks corresponding to the Li$_2$MnO$_3$ ordering in the overlithiated NMC were observed and no information on the oxygen loss mechanism could be extracted.

A detailed structural study of 333 NMC materials when charged till 5.0 V vs. Li/Li$^+$, at a high intensity synchrotron and neutron source is still missing. Hence in this work a study of range of NMC, with different Li content ($0 \leq x \leq 0.13$) and low Li-Ni exchange (3.0-3.3%), during their first electrochemical cycle between 2.5-5.0 V vs. Li/Li$^+$ was conducted using in situ synchrotron X-ray diffraction (XRD) and ex situ neutron powder diffraction (NPD). The focus of this study was to identify the irreversible reactions occurring in the overlithiated NMC ($x > 0$) samples at very positive potentials.

4.2. Experimental

Sample preparation: A range of NMC was synthesized using a citric acid route. For this purpose stoichiometric amounts of LiNO$_3$, Ni(NO$_3$)$_2$, Mn(NO$_3$)$_2$ and Co(NO$_3$)$_2$ were dissolved in an aqueous solution of citric acid (all from Sigma-Aldrich, USA). After stirring the mixture overnight and drying at 80°C, it was subjected to two heat treatment steps at 450°C for 6 h and 850°C for 12 h respectively, with a heating and cooling step of 6 h each. With this method 11 different compositions of Li$_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}O_2$ ($0 \leq x \leq 0.10$, varied by 0.01) were synthesized, along with the overlithiated sample with $x = 0.13$, where almost all the Ni in the structure is oxidized from +2 to +3 oxidation state. These NMC
compounds were labeled as SLS-XX, where XX denotes the percentage of overlithiation, e.g. stoichiometric NMC ($x = 0$) is SLS-00 and overlithiated NMC ($x = 0.10$) being SLS-10, and so on, and will be referred to by these abbreviations henceforth.

**Sample characterization:** In order to check the purity of the samples, X-ray diffraction patterns were recorded on the pristine samples at the Brucker D8 diffractometer equipped with a Cu anti-cathode (1.5406 Å). Iodometric titrations were performed on the end members SLS-00 and SLS-10, to determine the average oxidation state of the transition metals in the compound and hence the degree of overlithiation. This method has been described elsewhere in detail\textsuperscript{36, 45} and has been proven to be reliable in this context. Scanning Electron Microscopy (SEM) images were also recorded for the SLS-00 and SLS-10 samples with the Carl Zeiss Ultra\textsuperscript{TM} 55 machine using the in lens detector.

**Electrochemical measurements:** The electrochemical measurements were carried out in a standard coin-like test cells. Electrodes for these cells were made by casting a slurry of active material/ Super-P carbon (TIMCAL, Switzerland)/ Kynar Flex\textsuperscript{®} 2801 (Arkema, USA) (70/10/20 by weight) in N-Methyl Pyrrolidinone (NMP) (Sigma-Aldrich, USA) on an aluminium foil. The casted slurry was dried under vacuum at 80°C. Circular 13 mm diameter electrodes were punched out of the dried cast and then reheated overnight at 120°C under vacuum, in order to eliminate remaining NMP and adsorbed water. Cells were assembled from these electrodes in an Ar-filled glove box using Li as the counter electrode. Glass fiber was used as the separator and was soaked with ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 w/w) 1M LiPF\textsubscript{6} electrolyte (Ferro, USA). To study the electrochemical performance of SLS-00 and SLS-10, cells were cycled galvanostatically between 2.5-5.0 V vs. Li/Li$^+$ at 25 mA/g. Cyclic voltammetric studies were also performed on SLS-00 and SLS-10 at a scan rate of 0.01 mV/s between 2.5-5.0 V vs. Li/Li$^+$.

For the *ex situ* synchrotron XRD measurements, SLS-00, SLS-10 and SLS-13 were charged in a standard coin-like cell galvanostatically till 5.0 V vs. Li/Li$^+$ at C/100 rate with respect to their theoretical specific charge of 277.8 mAh/g, 322.5 mAh/g and 336.91 mAh/g respectively. The cells were then disassembled; the electrode mass washed with DMC, dried and then used for *ex situ* synchrotron XRD measurements. For the *in situ* synchrotron XRD measurements using “coffee bag” cells, electrodes were made using self standing films of NMC materials and the “coffee bag” cells were assembled as described in section 2.2. The electrolyte used was propylene carbonate (PC): dimethyl carbonate.
(DMC) (1:1 w/w) 1M LiPF₆ (all from Ferro, USA). This electrolyte was chosen because of its better wettability towards Celgard® 2400 as compared to EC:DMC 1M LiPF₆. For the in situ synchrotron XRD measurements, the “coffee bag” cells were cycled galvanostatically at C/20 rate between 2.5-5.0 V vs. Li/Li⁺.

**Ex situ** NPD measurements were only performed on the SLS-10 sample. To prepare the samples for the ex situ NPD measurements, 0.12-0.15 g of electrode materials (85% SLS-10 and 15% Super-P carbon by weight) were cycled galvanostatically in coin-like cells capable of cycling large amount (0.1-1.0 g) of electroactive material. The cells were cycled till various potentials or specific charge at C/20 rate with respect to 322.5 mAh/g; the electrode mass removed, washed with DMC, dried and then used for ex situ NPD measurements.

**In situ/ex situ synchrotron XRD:** In situ synchrotron XRD patterns were recorded at the Materials Science (MS) X04SA beamline of the Swiss Light Source, PSI Villigen. An automatic sample changer was used during the measurements that allowed sequential measurement of 15 cells, delivering very good time resolution. Around 125 high quality patterns were recorded for every cell during the first electrochemical cycle of the materials in transmission mode using a monochromatic focused beam with a spot size of 0.5 mm*0.5 mm at 0.7085 Å. The data acquisition time for the in situ synchrotron XRD measurements was 40 sec. Ex situ synchrotron XRD was performed on SLS-00, SLS-10 and SLS-13 samples at open circuit potential (OCP) and after the first charge till 5.0 V, with an acquisition time of 240 sec. For the ex situ measurements, the samples were held in between two self adhesive Kapton® tapes.

**Ex situ NPD:** Ex situ NPD measurements were performed on 0.12-0.15 g of dry SLS-10 samples cycled till various steps. The measurements were performed in 5 mm diameter vanadium tubes at 1.36 Å in transmission mode for 20 min at the D20 beamline of ILL, Grenoble, France.

### 4.3. Results and discussion

The results from the iodometric titrations on SLS-00 and SLS-10 confirmed that the experimentally observed average oxidation state of the transition metals, 3.00 ± 0.02 and 3.22 ± 0.02 respectively, are very close to the calculated values for the expected composition from synthesis, 3.00 and 3.22 respectively, and are well within the error limit.
No impurities were detected from the profile matching of X-ray diffraction patterns recorded at lab diffractometer for SLS-00 and SLS-10 (Figure 4.2). All the peaks could be indexed with the hexagonal $R-3m$ space group. SEM images recorded for the starting pristine powders of SLS-00 and SLS-10 are shown in Figure 4.3. The primary particles in both case of SLS-00 and SLS-10 show well defined edges and are in the size range of 40-200 nm and 70-300 nm respectively.

Pattern matching was performed for the *in situ* synchrotron XRD patterns recorded before cycling at open circuit potential (OCP) for all the samples. As expected all NMC samples crystallized in the $R-3m$ space group. The variation in the unit cell parameters for the starting materials with respect to the initial lithium content is shown in Figure 4.4. On overlithiation, the `$x$´ Li of $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ ($x > 0$) present in the transition metal layers, results in oxidation of part of the $\text{Ni}^{2+}$ ($r\text{Ni}^{2+} = 0.69$ Å) to $\text{Ni}^{3+}$ ($r\text{Ni}^{3+} = 0.56$ Å)$^{11, 42}$, and hence shorter Ni-O bond, which explains the decrease in the unit cell parameters with increasing initial lithium content.

Rietveld refinement was performed on the OCP synchrotron XRD patterns recorded for the SLS-00, SLS-10 and SLS-13. The Rietveld refinement of SLS-00 and SLS-13 are shown in Figure 4.5 as an example. Along with the peaks from the Celgard® 2400 separator used in the “coffee bag” cell, an amorphous bump from the glass fiber separator, used in the cell as the electrolyte reservoir, is also seen at angles below 15°. This amorphous bump at lower angles covers part of the intensity from the (003) peak of the O3 phase and is at the same position where one would expect the peaks from the $\text{Li}_2\text{MnO}_3$ ordering for the overlithiated NMC. Thus for the Rietveld refinement, model with a single O3 phase was used, where the peaks from the Celgard® 2400 separator were not refined while the amorphous bump was selected in the background. Owing to the high crystallinity of the starting materials, the Rietveld refinement of the OCP patterns was only slightly affected by the higher background below 15°. Table 4.1 details the conditions for the diffraction runs and for the Rietveld refinement on SLS-13. Table 4.2 reports the results of the Rietveld refinement for SLS-13, which shows a 3.3% Li-Ni exchange. Similar results were also obtained for SLS-00 and SLS-10, which showed Li-Ni exchange of 3.1% and 3.0% respectively.
Figure 4.2: Profile matching of XRD patterns recorded at laboratory diffractometer ($\lambda = 1.5406 \text{ Å}$) for pristine powders of (A) SLS-00 and (B) SLS-10.

Figure 4.3: SEM images recorded for (A) SLS-00 and (B) SLS-10 using in-lens detector.

Figure 4.4: Evolution of a and c parameters as a function of initial lithium content (1+x) in $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ ($0 \leq x \leq 0.13$), obtained from profile matching of synchrotron XRD patterns recorded at open circuit potential.
Figure 4.5: Rietveld refinement of the *in situ* synchrotron XRD patterns ($\lambda = 0.7085$ Å) recorded at open circuit potential for (A) SLS-00 and (B) SLS-13. 0 marks the peaks from the Celgard® 2400 separator. Amorphous bump from the glass fiber separator is also visible.

Thus using the citric acid route, pure stoichiometric NMC and range of overlithiated NMC’s were synthesized. These samples were found to be well crystalline with particle size in the range of 100-300 nm and showed low Li-Ni exchange (3.0-3.3%).
**General conditions for synchrotron XRD data acquisition**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
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<td>Beamline</td>
<td>MS-powder X04SA, PSI Villigen</td>
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<tr>
<td>Temperature</td>
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<tr>
<td>Wavelength</td>
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<tr>
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<td>Spot size</td>
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<tr>
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<td>scan step increment (2Theta)</td>
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<tr>
<td>Data collection time: <em>in situ</em></td>
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**Conditions for Rietveld refinement of SLS-13 pattern**

<table>
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<tr>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal composition</td>
<td>Li$<em>{1.13}$(Ni$</em>{1/3}$Mn$<em>{1/3}$Co$</em>{1/3}$)$_{0.87}$O$_2$</td>
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<tr>
<td>Unit cell parameters</td>
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<tr>
<td>Unit cell volume</td>
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</tr>
<tr>
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<tr>
<td>Number of reflections collected</td>
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</tr>
<tr>
<td>Method of refinement and program</td>
<td>Rietveld refinement using Fullprof suite version 2007</td>
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<tr>
<td>Number of reflections included in refinement</td>
<td>55</td>
</tr>
<tr>
<td>Zero/Number of refined parameters</td>
<td>-0.0119°(2)/23</td>
</tr>
<tr>
<td>Reliability factor</td>
<td>$R_F$= 7.83%, $R_B$= 18.3%, $R_{wp}$= 26.8%, $R_p$= 26.8%, $\chi^2$= 9.51</td>
</tr>
</tbody>
</table>

Table 4.1: Conditions for the synchrotron XRD measurements and for the Rietveld refinement of SLS-13 pattern recorded at open circuit potential.
Table 4.2: Crystallographic data obtained from Rietveld refinement of SLS-13
\[\text{[Li}_{1.13}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{0.87}\text{O}_2]\] pattern recorded at open circuit potential in a “coffee bag” cell. Refined parameters are in italics.

<table>
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<tr>
<th>Atom</th>
<th>Wycoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(B_{iso} (\text{Å}^2))</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>6c</td>
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<td>0</td>
<td>0.2412 (1)</td>
<td>0.962 (2)</td>
<td>1.00</td>
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<tr>
<td>Mn1</td>
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<td>0</td>
<td>0.5</td>
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<tr>
<td>Co1</td>
<td>3b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.314 (5)</td>
<td>0.29</td>
</tr>
<tr>
<td>Ni1</td>
<td>3b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.314 (5)</td>
<td>0.2569 (0)</td>
</tr>
<tr>
<td>Li1</td>
<td>3b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.314 (5)</td>
<td>0.1630 (0)</td>
</tr>
<tr>
<td>Ni2</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.863 (7)</td>
<td>0.0331 (0)</td>
</tr>
<tr>
<td>Li2</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.863 (7)</td>
<td>0.9668 (0)</td>
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</tbody>
</table>

Figure 4.6 reports the electrochemical cycling curves for SLS-00 and SLS-10 during 1\(^{st}\), 5\(^{th}\), 10\(^{th}\) and 20\(^{th}\) cycle. Due to higher amount of initial lithium content in SLS-10, the specific charge from SLS-10 sample is higher than that from SLS-00 during the first charge till 5.0 V vs. Li/Li\(^+\). This is directly correlated to the elongated plateau at ~4.5 V vs. Li/Li\(^+\). However on the 1\(^{st}\) discharge till 2.0 V vs. Li/Li\(^+\), less reversible specific charge is drawn from SLS-10 as compared to SLS-00. This is because during the 1\(^{st}\) charge of the overlithiated SLS-10 sample, part of the charge is expected to be consumed in the irreversible release of oxygen positive to 4.5 V, which is hence lost in the following discharge. On cycling further, SLS-00 delivers higher specific charge than SLS-10 until 10\(^{th}\) cycle after which the charge fading in SLS-00 is much higher than for SLS-10, resulting in higher specific charge drawn from SLS-10 during the 20\(^{th}\) cycle as opposed to the former. The charge retention curves for SLS-00 and SLS-10 samples cycled galvanostatically in standard coin-like test cells (Figure 4.7), confirm this observation, where the overlithiated NMC (SLS-10) shows better charge retention compared to the stoichiometric NMC (SLS-00) after few cycles.
Figure 4.6: Galvanostatic cycling of (A) SLS-00 and (B) SLS-10 at 25 mA/g between 2.0-5.0 V vs. Li/Li$^+$ in a standard coin-like cell.

Figure 4.7: Charge retention curves for SLS-00 and SLS-10 cycled between 2.0-5.0 V vs. Li/Li$^+$ in a standard coin-like cell at 25 mA/g.
Figure 4.8 shows the results of cyclic voltammetry for SLS-00 and SLS-10 samples. When cycled between 2.5-5.0 V vs. Li/Li⁺, the SLS-00 sample shows no huge difference between the 1st and the 5th cycle (Figure 4.8A). On the other hand a large irreversible oxidation current is seen during the 1st charge of the SLS-10 sample, which does not appear in the 5th cycle (Figure 4.8B). This irreversible oxidation current could be associated with loss of oxygen from overlithiated NMC. These results indicate that using a different synthesis route as opposed to the one reported earlier⁴⁴, resulting in lower Li-Ni exchange, has no drastic effect on the electrochemical performance of the 333 NMC materials.

![Cyclic voltammograms for SLS-00 and SLS-10](image)

Figure 4.8: Cyclic voltammograms for (A) SLS-00 and (B) SLS-10 at scan rate of 0.01 mV/s between 2.0-5.0 V vs. Li/Li⁺ in a standard coin-like cell.

Having confirmed the purity and electrochemical performance of the synthesized materials, in situ synchrotron XRD measurements were performed on all the samples. The electrochemical cycling curves for few of the NMC samples used for the in situ synchrotron
XRD measurements, cycled in “coffee bag” cells are shown in Figure 4.9. It has to be noted that although none of the cells delivered their theoretical specific charge, owing to the high polarization in the “coffee bag” cells as opposed to the standard coin-like cells, which in turn also results in less flat potential plateau at ca. 4.5 V vs. Li/Li⁺, most of the cells reached 5.0 V vs. Li/Li⁺ without major problems from the electrolyte decomposition. As expected from the electrochemistry, with increase in the overlithiation, the specific charge obtained from the potential plateau positive to 4.5 V vs. Li/Li⁺, associated to the oxygen release, increases.

![Figure 4.9: First electrochemical cycle of SLS-00, SLS-05, SLS-09 and SLS-13 in “coffee bag” cells used for the in situ synchrotron XRD measurements, cycled at C/20 rate between 2.5-5.0 V vs. Li/Li⁺.](image)

All the in situ synchrotron XRD patterns recorded during the first cycle of SLS-00 and SLS-13 are plotted in Figure 4.10. Only the results for the SLS-00 and SLS-13 are detailed here for clarity. As seen from Figure 4.10A, during the 1ˢᵗ charge of SLS-00, a solid solution reaction occurs where the starting O₃ phase is delithiated into O₃ phase with different cell parameters (+). No other phase formation is apparent. However on taking a closer look at the diffractograms, new peaks were seen to appear towards the end of 1ˢᵗ charge, which after careful analysis could be attributed to the O₁ phase. This O₁ phase is characterized by ABAB stacking of oxygen in the structure and results as a consequence of gliding of oxygen planes in the O₃ phase, with ABCABC stacking, on top of each other on delithiation. In case of SLS-13, similar evolution of peaks were observed, where during the beginning of the 1ˢᵗ charge a solid solution reaction occurs converting the starting O₃
phase into delithiated O3 phase with different cell parameters (+). At around 4.45 V vs. Li/Li\(^+\) new peaks corresponding to the O1 phase (*) are seen to appear in the diffraction patterns. The intensity of the peaks from the O1 phase is much larger for SLS-13 than for SLS-00, owing to the fact that more specific charge and hence more Li\(^+\) are drawn from SLS-13. From Figure 4.10B it is seen that the intensity of these new peaks corresponding to the O1 phase increases till the end of first charge till 5.0 V vs. Li/Li\(^+\). During the discharge slight shift in the cell parameter for the O1 phase was observed, however these peaks do not disappear completely, indicating that the phase transformation of the O3 phase to the O1 phase is not a completely reversible reaction. The formation of O1 phase was observed for all the studied compositions of 333 NMC.

Figure 4.11 shows the evolution of cell parameters for the O3 and O1 phase of SLS-00, SLS-05, SLS-09 and SLS-13 during the first charge till 5.0 V vs. Li/Li\(^+\). As 2-3 phases coexisted in the material, only the cell parameter for the most advanced/delithiated O3 phase has been reported. For SLS-00, the c parameter of the O3 phase increases while the a parameter drops until a certain potential, after which the cell parameter evolution is reversed. These results are in accordance with the cell parameters reported earlier for chemically delithiated samples\(^{11, 42}\). Samples SLS-05 and SLS-09 demonstrate too a comparable trend to the SLS-00 sample. The cell parameters of the O3 phase for SLS-13 on the other hand reached roughly constant value towards the end of the first charge. The percentage unit cell volume change in the O3 phase for all the samples (Figure 4.11E), shows that at any given potential the unit cell volume change is lower for samples with higher overlithiation. The SLS-13 sample shows in total only 1% volume change as opposed to 5.5% change seen for SLS-00.
Figure 4.10: *In situ* synchrotron XRD patterns ($\lambda = 0.7085$ Å) recorded during the first cycle of (A) SLS-00 and (B) SLS-13 between 2.5-5.0 V vs. Li/Li$^+$. (+) are the peaks from the delithiated O3 phase and (*) from the new O1 phase.
Figure 4.11: Evolution of unit cell parameters for O3 (black symbols) and O1 phase (orange symbols) in (A) SLS-00 (B) SLS-05 (C) SLS-09 and (D) SLS-13 samples during their first charge till 5.0 V vs. Li/Li\(^+\). The c parameter for the O1 phase has been multiplied by 3 for better comparison. (E) Unit cell volume change (%) in the O3 phase for different samples.

The \textit{in situ} detection of O1 phase for various electrochemically delithiated 333 NMC has been reported here for the first time. At first glance, the appearance of O1 phase for the overlithiated compositions seems contradictory to previous report\textsuperscript{45}. But this can be
explained by the lower Li-Ni exchange in current samples due to different synthesis route used. Phases with low Li-Ni exchange are indeed known to give O1 phase\textsuperscript{42, 105}, although higher exchange ratio can improve the structural stability thanks to the pillaring effect of Ni cation.

The potential at which the O1 phase was detected versus the initial lithium content of the samples is shown in Figure 4.12(A). More is the initial lithium content in the sample, lower is the potential for detection of the O1 phase. Figure 4.12(B) shows the patterns recorded at the end of 1\textsuperscript{st} charge for different samples. These end of charge synchrotron XRD patterns have been normalized with respect to their starting patterns using the main (003) peak. (Current collector peaks are visible for the SLS-05 sample owing to the fact that the Kapton® taped hole of the “coffee bag” cell was not properly aligned in the beam.) For samples charged till the same potential limit, the intensity of the peaks corresponding to the O1 phase is seen to increase with increasing overlithiation content. These two results suggest that the overlithiation somehow destabilizes the O3 structure resulting in formation of the O1 phase at lower potentials.

Figure 4.12: (A) Potential for detection of O1 phase for samples with different initial lithium content \((1+x)\) in \(\text{Li}_{1+x} (\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2\) \((0 \leq x \leq 0.13)\). The straight line is a guide for the eye. (B) Normalized \textit{in situ} synchrotron XRD patterns \((\lambda = 0.7085 \text{ Å})\) recorded at the end of first charge \((5.0 \text{ V vs. Li/Li}^+)\) for different NMC samples. (*) marks peaks from the O1 phase and (X) for the current collector.

To better understand this phenomenon, \textit{ex situ} synchrotron XRD measurements were performed on the SLS-00, SLS-10 and SLS-13 starting pristine powders and samples obtained after 1\textsuperscript{st} charge till 5.0 V vs. Li/Li\textsuperscript{+}. In all the cases around 95% of the
theoretical specific charge was obtained from the material during their first charge. Figure 4.13(A) shows the \textit{ex situ} synchrotron XRD patterns recorded for SLS-00, SLS-10 and SLS-13 pristine powders for 240 s. Peaks corresponding to the \( \text{Li}_2\text{MnO}_3 \) ordering in the transition metal slabs of the O3 phase\(^{106} \) are clearly visible in the SLS-10 and SLS-13 samples, while none were seen for SLS-00. The intensity of the \( \text{Li}_2\text{MnO}_3 \) ordering peaks is higher for SLS-13 sample with higher overlithiation. This intensity of the \( \text{Li}_2\text{MnO}_3 \) ordering peaks highly depends on the Co and Li content in the structure. For the studied compositions, the \( \text{Li}_2\text{MnO}_3 \) ordering peaks were not seen using laboratory diffractometer due to the high Co content and low overlithiation, owing to the structural complexity in these layered compounds\(^{44, 106} \). This inherent structural complexity of the material results in less pronounced \( \text{Li}_2\text{MnO}_3 \) ordering peaks in the \textit{ex situ} synchrotron XRD patterns. The \( \text{Li}_2\text{MnO}_3 \) ordering peaks were not visible for the overlithiated NMC in the \textit{in situ} synchrotron XRD patterns owing to comparatively low acquisition time (40 s) and the amorphous bump from the glass fiber separator below 15°. \textit{Ex situ} patterns recorded at the end of 1\(^{st} \) charge, reveal loss of \( \text{Li}_2\text{MnO}_3 \) ordering for the SLS-10 and SLS-13 samples (Figure 4.13(B)). The extraction of Li from the \( \text{Li}_2\text{MnO}_3 \) ordering is suggested to proceed via simultaneous removal of oxygen from the structure to compensate for the charge balance\(^{32, 107, 108} \), which helps explain the previously reported oxygen loss in overlithiated NMC \((x = 0.1)^{44} \). In agreement to the \textit{in situ} XRD data, in all the cases peaks corresponding to the O1 phase are also clearly visible for the end of charge samples.

Two mechanisms have been proposed for the removal of \( \text{Li}^+ \) and oxygen\(^{102} \) from the structure of overlithiated layered oxide materials (Figure 4.14). The first mechanism (Figure 4.14A) proposes that there occurs a simultaneous extraction of \( \text{Li}^+ \) and \( \text{O}^{2-} \) from the structure, where the \( \text{O}^{2-} \) are removed from the bulk, resulting in creation of oxygen vacancies in the bulk. However this results in formation of unstable \( \text{MO}_5 \) square pyramidal geometry, which should be stabilized by migration of \( \text{O}^{2-} \) from the surface to the oxygen vacancies in the bulk. The second mechanism (Figure 4.14B) proposes that the \( \text{Li}^+ \) are removed from the structure while the \( \text{O}^{2-} \) is removed from the surface, which is energetically more favorable\(^{102} \). This leads again to formation of unstable \( \text{MO}_5 \) coordination, where the structure is stabilized by migration of \( \text{M}^{n+} \) ions from the surface to the bulk, into the cationic vacancies created by removal of \( \text{Li}^+ \) from the transition metal slab, resulting in lattice densification.

The loss of \( \text{Li}_2\text{MnO}_3 \) ordering peaks for the studied compositions confirms that the transition metal ions undergo rearrangement during the first charge, strongly supporting
the second mechanism of oxygen removal from the surface of the layered transition metal oxides that leads to a lattice densification.

Figure 4.13: *Ex situ* synchrotron XRD patterns ($\lambda = 0.7085$ Å) recorded for (A) SLS-00, SLS-10 and SLS-13 pristine powders and for (B) SLS-00, SLS-10 and SLS-13 samples after first charge till 5.0 V vs. Li/Li$^+$. (#) indicates the Li$_2$MnO$_3$ ordering in the transition metal slabs, (*) marks the peaks from the O1 phase.
Figure 4.14: Mechanisms proposed for removal of Li$^+$ and O$^{2-}$ from the layered transition metal oxide structure. Model (A) proposes removal of O$^{2-}$ from the bulk while (B) proposes O$^{2-}$ removal from the surface$^{102}$. 

(A) Oxygen vacancies
O$^{2-}$ ions migration

(B) $M^{n+}$ ions migration
Lattice densification
The \textit{ex situ} synchrotron XRD data also suggests that the rearrangement of cations in the layers, associated with the release of oxygen, possibly destabilizes the structure and triggers the sliding of the slabs leading to the formation of O1 phase at lower potentials for more overlithiated NMC samples. However the appearance of O1 phase could well be a result of creation of defects. This was checked by the analysis of Williamson-Hall plots\textsuperscript{109} for SLS-00, SLS-10 and SLS-13 powders and samples after the first charge till 5.0 V vs. Li/Li\textsuperscript{+}, plotted using the \textit{ex situ} synchrotron XRD patterns. As seen from Figure 4.15, the FWHM*Cos(Theta) vs. Sin(Theta) plots for SLS-00, SLS-10 and SLS-13 powder samples can be fitted using a straight line. From the equation of the straight line the values of strain and crystallite size for SLS-00 were calculated to be 0.0525\% and 177.12 nm respectively, for SLS-10 to be 0.1025\% and 354.25 nm respectively, while that for SLS-13 to be 0.1075\% and 354.25 nm respectively. As expected, the strain in the overlithiated NMC’s is higher than that in the stoichiometric one, owing to the presence of higher amount of monovalent Li\textsuperscript{+} in the transition metal slabs. The calculated crystallite sizes are also close to the values obtained from the SEM images (100-300 \(\mu\)m).

Figure 4.15 also shows the values for [012] and [104] planes for samples after 1\textsuperscript{st} charge. Since in all the cases only 2 reflection orders were available, exact quantitative analysis was not possible. However qualitatively one can observe that the slope of the straight line, i.e. the values of strain along [012] and [104] planes after the first charge for SLS-00 and SLS-10 has certainly increased as compared to the pristine powder samples. This indicates creation of mechanical stress during the charging of the materials. Moreover the strain along [012] and [104] planes is higher for SLS-10 than for SLS-00. This could be linked to formation of larger number of O1 stacking faults in the O3 phase for the SLS-10 sample. However for the SLS-13 sample, the slopes for [012] and [104] planes after 1\textsuperscript{st} charge are lower than for the starting pristine powder. This indicates that the changes in the strain in the material before and after 1\textsuperscript{st} charge are mostly linked to the volumic changes occurring during cycling rather than the formation of O1 phase. These results confirm that the defects in the starting pristine material and in the material after 1\textsuperscript{st} charge are not the foremost reason for formation of O1 phase at lower potentials.
Figure 4.15: Williamson-Hall plot, FWHM*Cos(Theta) vs. Sin(Theta), for (A) SLS-00 (B) SLS-10 and (C) SLS-13 samples. Filled symbols are data for pristine powder and open symbols for sample after 1\textsuperscript{st} charge till 5.0 V vs. Li/Li\textsuperscript{+}. The values have been determined using the ex situ synchrotron XRD patterns shown in Figure 4.13.
To better understand the structural changes occurring in the NMC materials during cycling, *ex situ* NPD measurements were performed on the SLS-10 samples at different stages of lithiation and delithiation. Figure 4.16 shows the electrochemical curve for the SLS-10 sample in a coin-like cell cycled galvanostatically at C/20 rate. The points at which the different cells were stopped and the *ex situ* measurements performed are marked. Despite using 0.12-0.15 g of electrode material without binder, the electrochemical performance of SLS-10 was good. Around 260 mAh/g i.e. 80.6% of the theoretical specific charge (322.5 mAh/g) was obtained on 1st charge of the material till 5.0 V vs. Li/Li*. During the 1st discharge 155 mAh/g could be drawn out of the material, resulting in an irreversible specific charge of 105 mAh/g.

![Figure 4.16: Galvanostatic cycling of SLS-10 in EC/DMC 1M LiPF₆ electrolyte in a coin-like cell. The points at which the cells were stopped and the *ex situ* NPD measurements performed are marked. (X) marks the potential fluctuation due to rest.](image)

The *ex situ* NPD patterns recorded for different samples of SLS-10 are shown in Figure 4.17. The starting SLS-10 powder sample (point 1) shows peaks for the major O3 phase and also for Li₂MnO₃ ordering in the material. On cycling, evolution of intensities and position of the O3 peaks are clearly visible. Over the course of cycling new peaks corresponding to the O1 phase are seen to appear, where the peaks are most prominent in the pattern at the end of 1st charge (point 5). At the end of 1st cycle (point 6), O1 peaks are still visible, though not quite intense. These results are in accordance with the synchrotron XRD data, where the O1 phase is seen to grow until end of 1st charge and then during the 1st discharge the peaks broaden.
Figure 4.17: *Ex situ* NPD patterns ($\lambda = 1.36$ Å) recorded on SLS-10 stopped at different delithiation-lithiation steps during its 1$^{\text{st}}$ cycle between 2.5-5.0 V vs. Li/Li$^+$. Points 1 to 6 are as marked on the curve in Figure 4.16. (+), (*), (X), (C) and (D) represent O3 phase, O1 phase, Li$_2$MnO$_3$ ordering, 1$^{\text{st}}$ charge and 1$^{\text{st}}$ discharge respectively.
On cycling SLS-10, the Li₂MnO₃ ordering peaks are seen to shift and undergo changes in the intensities, however they do not disappear completely as in the case of ex situ synchrotron XRD data. This could be attributed to higher sensitivity of neutrons towards lighter elements, which should detect the presence of Li in the transition metal slabs even in the slightest amounts. In order to analyze the NPD data, firstly pattern matching was performed on all the ex situ NPD patterns, where the values of zero, unit cell parameters and peak width parameters were refined. Having the basic information regarding the unit cell, the atomic positions for starting SLS-10 pattern were refined using the structural model reported in Table 4.2 (page 59). The structural model obtained from the Rietveld refinement of the SLS-10 starting sample (point 1) was then used for the Rietveld refinement of the following samples (point 2 to 6). For refinement of patterns recorded at points 2 to 6, the value of Li in the structure was set to one expected from the electrochemical curve while the occupancies for Mn and Co were fixed to 0.3. The scale factor was refined first and was then fixed during rest of the refinement. The peak width parameters, z value for oxygen, thermal isotropic factors and occupancies were then refined. The thermal isotropic factors for elements in same Wyckoff position were constraint to same value. If the oxygen occupancy in 6c Wyckoff position was refined to a value above 1, this value was fixed to 1. A Li-Ni exchange between 3a and 3b sites was allowed during the refinement. The Rietveld refinements were performed between 2Theta = 30-65° owing to the relatively flat background in this range.

The Rietveld refinement performed on all the 6 points are shown in Figure 4.18. For the points 1 to 4, only two phases viz. the O3 phase in R-3m space group and the Li₂MnO₃ ordering phase in C2/m space group were used. For the pattern at the end of 1st charge (point 5) and at the end of 1st discharge (point 6), additionally peaks corresponding to the O1 phase in P-3m1 space group are seen. However since the intensity of these peaks was too low to be refined, only two phase refinement with O3 phase and Li₂MnO₃ ordering phase were used for these patterns too. As a simultaneous Rietveld refinement of all phases was found to be tedious and resulted in non-converging results, only the most interesting O3 phase was used for the Rietveld refinement, while Li₂MnO₃ ordering peaks were refined using profile matching. All the patterns showed good agreement between the structural models and the experimental data. The results of the Rietveld analyses are summarized in Table 4.3 and 4.4. As the values of occupancies for Mn and Co were fixed to 0.3, they have been excluded from the tables.
Figure 4.18: Rietveld refinement of NPD pattern ($\lambda = 1.36$ Å) for starting SLS-10 powder (point 1), samples charged until 100 mAh/g (point 2), 175 mAh/g (point 3), 199 mAh/g (point 4) and 5.0 V vs. Li/Li$^+$ (point 5) and after complete discharge till 2.0 V vs. Li/Li$^+$. The points are also marked on the electrochemical curve in Figure 4.16 (page 72).
Point 1- \( a = 2.855 \ (1) \ \text{Å}, \ c = 14.197 \ (1) \ \text{Å} \), Nominal Li content = 1.1, refined phases = O3 and Li\(_2\)MnO\(_3\) ordering, \( \chi^2 = 9.16, R_{wp} = 6.0\%, R_B = 1.4\% \)

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Point 2- \( a = 2.819 \ (1) \ \text{Å}, \ c = 14.342 \ (1) \ \text{Å} \), Nominal Li content = 0.79 refined phases = O3 and Li\(_2\)MnO\(_3\) ordering, \( \chi^2 = 4.4, R_{wp} = 13.3\%, R_B = 2.9\% \)

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Point 3- \( a = 2.820 \ (1) \ \text{Å}, \ c = 14.349 \ (1) \ \text{Å} \), Nominal Li content = 0.56, refined phases = O3 and Li\(_2\)MnO\(_3\) ordering, \( \chi^2 = 2.6, R_{wp} = 11.2\%, R_B = 1.0\% \)

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Table 4.3: Results of Rietveld analysis on \( \text{ex situ} \) NPD patterns recorded on starting powder sample (point 1); during 1\(^{st}\) charge till 100 mAh/g (point 2) and 175 mAh/g (point 3). Refined parameters are in italics. Scale factor was fixed during the refinement.
Point 4- $a = 2.820 (1) \text{ Å}$, $c = 14.343 (1) \text{ Å}$, Nominal Li content = 0.48
refined phases = O3 and Li$_2$MnO$_3$ ordering, $\chi^2 = 3.6$, $R_{wp} = 14.2\%$, $R_B = 3.2\%$

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Point 5- $a = 2.823 (1) \text{ Å}$, $c = 14.185 (1) \text{ Å}$, Nominal Li content = 0.30
refined phases = O3 and Li$_2$MnO$_3$ ordering, $\chi^2 = 4.0$, $R_{wp} = 15.5\%$, $R_B = 3.8\%$

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Point 6- $a = 2.843 (1) \text{ Å}$, $c = 14.325 (1) \text{ Å}$, Nominal Li content = 0.76
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Table 4.4: Results of Rietveld analysis on ex situ NPD patterns recorded during 1$^{st}$ charge till 200 mAh/g (point 4), 259 mAh/g (point 5) and at the end of 1$^{st}$ cycle (point 6). Refined parameters are in italics. Scale factor was fixed during the refinement.
Due to short initial data acquisition time of 20 min for the NPD patterns on 0.12-0.15 g materials and the use of small 2Theta range for the refinement, the values for thermal isotropic factor \( (B_{iso}) \) were high. Thus in the Table 4.3 and Table 4.4, \( U_{iso} \) has been reported for clarity, which is the root mean square displacement of an atom from its average position. Slightly higher \( U_{iso} \) values indicate that using the available set of data the atomic positions cannot be pinpointed accurately and longer data acquisition time on larger amount of material is needed for better results. As the goal of this study was to investigate electrochemically cycled samples (with the consequence of having small amounts of material only) and due to limited allocated beamtime at the ILL, Grenoble, this could not be achieved. However, as seen from the Rietveld refinements, the values of reliability factors are low and hence the goodness of fit high. Thus a general trend for the atomic position and occupancy of oxygen can be identified.

The changes in the unit cell parameters, oxygen and lithium content and the Li-Ni exchange in the structure are plotted in Figure 4.19 as a function of the specific charge. The electrochemical cycling curve has also been shown for better comparison of the data. The SLS-10 sample shows similar trend in evolution of unit cell parameters (Figure 4.19B) as for other overlithiated NMC´s studied using in situ synchrotron XRD. SLS-10 shows 2% unit cell volume change between the starting powder and end of 1st charge sample, which is in between the volumic changes shown by SLS-09 and SLS-13 (Figure 4.11, page 65). The Li-Ni exchange in the starting powder (point 1) is 3.0% and is agreement with the results from the ex situ synchrotron XRD on SLS-10 sample. From Figure 4.19C it can be seen that during the course of the first charge, the Li-Ni exchange in the structure increases to above 4%. This increased Li-Ni exchange apparently hinders the slippage of oxygen layers on top of each other and provides stability to the structure.

In case of SLS-10 i.e. \( \text{Li}_{1.1} (\text{Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3})_{0.9} \text{O}_2 \), only 0.7 Li\(^+\) can be extracted by oxidation of all the transition metals to +4 oxidation state. Thus any extra Li\(^+\) removed should be compensated by oxygen removal from the structure. In case of points 1 and 2 i.e. starting powder and sample after charge till 100 mAh/g, refining the oxygen occupancy did not affect the fitting positively. Hence the value of oxygen in these materials was set to 2 (Figure 4.19C). For point 3 i.e. sample after charge till 175 mAh/g, on refining the oxygen occupancy, a value lower than 2 was obtained. This indicates that oxygen has been removed from the structure even though only 0.54 Li\(^+\) has been extracted (from electrochemistry). Thus the oxygen is removed from the structure of the layered oxide even if the transition metals are not completely oxidized.
Figure 4.19: (A) 1\textsuperscript{st} electrochemical cycle of SLS-10 between 2.0-5.0 V vs. Li/Li\textsuperscript{+} (B) evolution of unit cell parameters, and (C) evolution of Li and oxygen content and Li-Ni exchange as a function of specific charge. Points 1 to 6 where the \textit{ex situ} NPD was performed are marked.
For the point 4 i.e. sample after charge till 199 mAh/g, the oxygen occupancy decreased even further to a lower value. Both points 3 and 4 lie on the potential plateau positive to 4.5 V vs. Li/Li⁺, where the evolution of oxygen by activation of the Li₂MnO₃ phase is expected. For point 5 i.e. after complete charge till 5.0 V vs. Li/Li⁺, refining the oxygen occupancy further did not profit the fitting, hence the oxygen occupancy was fixed to the value obtained from refinement of pattern recorded at point 4. During the discharge process no oxidation of O²⁻ and hence no evolution of O₂ is possible. Thus the occupancy of oxygen in this case too was fixed. At the end of 1ˢᵗ charge, the oxygen content in the sample was decreased to 1.94 down from 2 in the starting sample. This oxygen loss corresponds to 0.12 Li⁺ removed from the transition metal slabs. Since the oxygen loss is an irreversible process, around 109 mAh/g specific charge should be irreversibly “lost” during the 1ˢᵗ charge. This value is in good agreement with the irreversible specific charge of 105 mAh/g experimentally seen from the electrochemical curve.

4.4. Proposed mechanism

The results from different studies on stoichiometric and overlithiated NMC, Li₁₊ₓ(Ni₁/₃Mn₁/₃Co₁/₃)₁₋ₓO₂ (0 ≤ x ≤ 0.13) are summarized below along with conclusions drawn from them.

1) During 1ˢᵗ galvanostatic charge till 5.0 V vs. Li/Li⁺, SLS-10 shows long reaction potential plateau positive to 4.5 V vs. Li/Li⁺ and thus delivers higher specific charge than SLS-00.

2) Cyclic voltammogram for SLS-10 shows irreversible oxidative reaction positive to 4.5 V vs. Li/Li⁺.

3) For electrochemical cycling, charge retention of SLS-10 is better than SLS-00 after few cycles.

These results along with the previous information on these materials⁴⁴, suggest that at potential around 4.5 V vs. Li/Li⁺, an irreversible reaction occurs which involves oxygen evolution, leading to structural evolution in the overlithiated NMC (x > 0) resulting in its better electrochemical performance on following cycles.
4) From the *in situ* synchrotron XRD measurements on stoichiometric (x = 0) and several overlithiated (x > 0) NMC, it was seen that O1 phase is formed in all cases during the 1\textsuperscript{st} charge and the potential for its detection decreases with increasing overlithiation.

5) The unit cell volume change during 1\textsuperscript{st} charge is smallest for the most overlithiated SLS-13 NMC.

6) From the *ex situ* synchrotron XRD, Li\textsubscript{2}MnO\textsubscript{3} ordering peaks were seen only for the overlithiated (x > 0) NMC.

7) These Li\textsubscript{2}MnO\textsubscript{3} ordering peaks disappeared at the end of 1\textsuperscript{st} charge till 5.0 V vs. Li/Li\textsuperscript{+} supporting the lattice densification mechanism.

8) Initial strain in the starting material was seen to have no significant effect on the formation of O1 phase.

The detection of Li\textsubscript{2}MnO\textsubscript{3} ordering peaks and the presence of irreversible potential plateau around 4.5 V vs. Li/Li\textsuperscript{+} supports the hypothesis that O\textsubscript{2} is released on activation of Li\textsubscript{2}MnO\textsubscript{3}. Loss of the Li\textsubscript{2}MnO\textsubscript{3} ordering peaks indicate rearrangement of the atoms in the structure, supporting the lattice densification mechanism (mechanism B, Figure 4.14, page 69) for oxygen release from overlithiated (x > 0) layered oxides.

9) From the *ex situ* neutron powder diffraction on SLS-10, it was seen that the occupancy of oxygen in the structure decreases during the 1\textsuperscript{st} charge, confirming the oxygen loss theory.

10) Oxygen evolution is evident only during the irreversible oxidative potential plateau around 4.5 V vs. Li/Li\textsuperscript{+}.

11) The Li-Ni exchange in the structure increases during the 1\textsuperscript{st} charge (delithiation). It decreases slightly after the 1\textsuperscript{st} discharge (lithiation). The increased Li-Ni exchange presumably stabilizes the structure by pillaring effect.

12) Owing to the increased Li-Ni exchange at end of 1\textsuperscript{st} charge, the fact that only around 81% of the theoretical specific charge was drawn out of the material and due to the sensitivity of neutrons to detect Li, complete disappearance of Li\textsubscript{2}MnO\textsubscript{3} ordering peaks was not seen in neutron diffraction patterns as in the case of synchrotron XRD data.
13) Nonetheless, changes in position and intensities of the Li$_2$MnO$_3$ ordering peaks in the NPD data, confirmed its involvement in the reaction mechanism.

Based on above results, following reaction mechanism has been proposed for first electrochemical cycle of SLS-10 (overlithiated 333 NMC) between 2.5-5.0 V vs. Li/Li$^+$, and is illustrated graphically in Figure 4.20:

- The starting sample Li$_{1.1}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{0.9}$O$_2$ (I) has majority of transition metals (M) in the slabs and lithium (Li) in the interslabs, while the Li-Ni exchange results in 3% of Ni to be in the interslabs.

- During the first charge, when the amount of extracted Li$^+$ is less than 0.5 and the potential is negative to 4.4 V vs. Li/Li$^+$, Li is removed from the interslabs resulting in oxidation of transition metals and paving way for higher Li-Ni exchange (II).

- When the amount of extracted Li$^+$ is above 0.5 and the potential is positive to 4.4 V vs. Li/Li$^+$, Li$^+$ are also removed from the slabs, simultaneously releasing oxygen from the surface (III). This results in migration of M$^{n+}$ from the surface into the bulk, resulting in lattice densification.

- On further charge positive to 4.4 V vs. Li/Li$^+$, almost all of the Li$^+$ are removed from the slabs (IV), while simultaneously releasing more oxygen and resulting in lattice densification.

- This structural rearrangement results in sliding of the oxygen planes on top of each other to form the O1 phase at lower potentials. This O1 phase is hence seen for the sample at the end of 1$^{st}$ charge (V).

- During the discharge, the oxygen deficient, lattice densified structure with higher Li-Ni exchange is lithiated, where the Li$^+$ mostly enter the interslabs, resulting in no significant Li$_2$MnO$_3$ ordering in the slabs and hence no oxygen loss on following charge. The lattice densification and increased Li-Ni exchange stabilizes the structure against very positive potential charging during further cycling.
Figure 4.20: Proposed reaction mechanism for first electrochemical cycle of SLS-10 \[\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{0.9}\text{O}_2\] between 2.0-5.0 V vs. Li/Li$^+$. 

- **(I)**: Cationic vacancy (square) and Oxygen ions (red) are present. M oxidation occurs below 0.5 Li$^+$ extracted and below 4.4 V vs. Li/Li$^+$. Slabs and interslabs are shown.
- **(II)**: Li extraction (yellow) results in oxygen evolution (arrows) above 0.5 Li$^+$ extracted and above 4.4 V vs. Li/Li$^+$. M oxidation occurs.
- **(III)**: Oxygen evolution (arrows) continues above 4.4 V vs. Li/Li$^+$. Lattice densification (arrows) occurs.
- **(IV)**: Lattice densification (arrows) continues, leading to structural evolution.
- **(V)**: Lithiation (D) occurs, with M transition metals (blue) and Li lithium (yellow) present.
- **(VI)**: Out-of-plane metal octahedra (triangle) are shown, with Li lithium (yellow) and Ni nickel (blue) present.

Legend:
- C: Charge
- D: Discharge
- M: Transition metals
- Ni: Nickel
- Li: Lithium
- O1 phase defect in O3 phase

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4.5. Discussion

The study of reaction mechanism helped to identify key issues related to the overlithiated 333 NMC materials. It was found that during the course of first charge till 5.0 V vs. Li/Li\(^{+}\), the structure undergoes several structural changes. The structural changes are usually not good for the electrochemistry, however in case of the overlithiated NMC they lead to stabilization of the structure. The study of overlithiated NMC also revealed loss of oxygen on cycling. This oxygen loss could be a major safety concern when the material is used in large batteries for automotive application. However from the neutron diffraction data, loss of only around 0.06 mol O\(^{2-}\) ions or 0.03 mol oxygen per 1 mol of Li\(_{1.1}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{0.9}\text{O}_{2}\) was observed when approximately 80% of the theoretical specific charge is drawn. This is a minor percentage of the gases that are evolved during the 1\(^{st}\) charge of the battery, as a result of formation of Solid Electrolyte Interphase (SEI) on graphite negative electrode. Moreover the usual high specific energy battery design incorporates a safety valve for exhaust of gases in case of pressure build up in the battery. It is also known that the oxygen evolution is limited to 1\(^{st}\) charge alone, which minimizes the risk of evolution of oxygen during several charges.

Thus from the application point of view overlithiated NMC is better than the stoichiometric NMC and can be utilized in different ways:

- Firstly overlithiated NMC can be used as positive electrode material in conventional Li-ion batteries, charging the positive electrode only up to ~4.3 V vs. Li/Li\(^{+}\). Here the specific charge from the overlithiated NMC is restricted; however it plays a major role of acting as a fail-safe. In case of overcharge up to 5.0 V vs. Li/Li\(^{+}\), the overlithiated NMC will release oxygen while still maintaining its structural integrity and not affecting the following cycling performance drastically.

- Overlithiated NMC can also be used in high voltage (5 V) batteries, where it has a definite advantage over stoichiometric NMC in terms of specific charge and cycling stability. However the major issue hindering the use of overlithiated NMC in high voltage batteries is the availability of stable electrolyte.

Nonetheless before actual application of overlithiated NMC´s in batteries, several key parameters need to be understood, especially their thermal stability in charged and discharged states, their rate capability, high and low temperature cycling, etc.
4.6. Conclusion

A study of reaction mechanism of stoichiometric 333 NMC \((x = 0)\) and several overlithiated 333 NMC \((x > 0)\) was conducted between 2.5-5.0 V vs. Li/Li\(^+\), with special focus on \(\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{0.9}\text{O}_2\) (SLS-10). Using the powerful synchrotron and neutron diffraction method, major key structural modifications were identified during the 1\(^{\text{st}}\) charge and 1\(^{\text{st}}\) discharge. The overlithiated \((x > 0)\) NMC undergo 2 irreversible reactions forming the O1 phase and showing loss of \(\text{Li}_2\text{MnO}_3\) ordering. Stoichiometric \((x = 0)\) NMC on the other hand shows only the formation of O1 phase. The loss of \(\text{Li}_2\text{MnO}_3\) ordering was attributed to release of oxygen from the structure, followed by rearrangement of metal ions inside the structure. Usually the O1 phase is formed when sufficient amount of Li is removed from the inter slabs to allow for gliding of oxygen planes on top of each other. In case of overlithiated \((x > 0)\) NMC, the O1 phase was detected at lower potentials as the overlithiation degree increased. This was attributed to the rearrangement of metal ions in the structure, which destabilize the structure resulting in gliding of oxygen planes at lower potentials. From the neutron powder diffraction (NPD) data the Li-Ni exchange was seen to increase during the 1\(^{\text{st}}\) charge. The higher Ni in the inter slabs stabilizes the structure via the pillaring effect and inhibits continuous increase in the amount of O1 phase formed in the overlithiated \((x > 0)\) NMC. The NPD data also confirmed that the oxygen content decreases during the first charge. Combining all the available information a reaction mechanism has been proposed for cycling of overlithiated 333 NMC \(\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{0.9}\text{O}_2\) (SLS-10). From this study it can concluded that although two irreversible reactions occur during the charging of the overlithiated \((x > 0)\) NMC compounds, they still deliver better cycling stability than the stoichiometric \((x = 0)\) NMC and hence are better for practical use in the very positive potential range.
Chapter 5

Electrochemical and structural study of $M_{0.5}TiOPO_4$ ($M = \text{Ni, Cu, Mg}$)
5.1. Introduction

The demand for safer negative electrode materials enabling higher specific energy of the battery is leading researchers away from the graphite electrodes. Though graphite works very well delivering a specific charge of 372 mAh/g, it has working potential (0.1-0.2 V vs. Li/Li$^+$) close to that of Li$^+$ reduction. Thus if a battery is charged at high rates the potential of the negative graphite electrode can drop below that of Li and hence lead to Li plating on graphite. This raises a major safety concern for use of graphite in high power application. Thus electrode materials with redox potential positive to that of graphite are required. $\text{M}_{0.5}\text{TiOPO}_4$ (M = Ni, Co, Fe) are novel candidates for negative electrode materials that have positive redox potential (1.0-2.0 V vs. Li/Li$^+$) and higher specific charge (~420 mAh/g) than graphite. However the reaction mechanism in these types of materials is not yet understood. It is also not known how the presence of M in the structure and particle size affects the electrochemistry of the material. The goal of this study is hence to investigate the effect of M and particle size on the electrochemical behavior of $\text{M}_{0.5}\text{TiOPO}_4$ (M = Ni, Cu, Mg) and to understand the reaction mechanism of Li insertion in this family of compounds, using $\text{Ni}_{0.5}\text{TiOPO}_4$ as an example.

5.2. Effect of M and particle size on $\text{M}_{0.5}\text{TiOPO}_4$ (M = Ni, Cu, Mg)

5.2.1. Experimental

Synthesis: In the literature two synthesis routes have been described for the synthesis of $\text{M}_{0.5}\text{TiOPO}_4$ compound viz. solid state synthesis and solution route synthesis. The solid state synthesis uses a mixture of metal oxide, $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{TiO}_2$ in stoichiometric ratio which is subjected to ball milling and various heat treatment$^{61}$. In case of the solution route synthesis, a solution of metal nitrate in water (I), $\text{NH}_4\text{H}_2\text{PO}_4$ in water (II) and $\text{TiCl}_4$ added to ethanol in air (III) are used in stoichiometric ratio; whereby solution (III) is added to the mixture of (I)+(II) drop wise, dried and then subjected to different heat treatment steps$^{110}$. With the goal of obtaining $\text{M}_{0.5}\text{TiOPO}_4$ sample, both the synthesis routes were explored here. However it was found that the solid state route always resulted in formation of large quantities of $\text{TiO}_2$ impurity. For solution route on the other hand, difficulties were encountered to obtain titanium in the stoichiometric ratio. The solution route described earlier utilizes $\text{TiCl}_4$ as the titanium precursor, which is highly reactive with moisture giving corresponding hydroxide and HCl gas. As the solution of $\text{TiCl}_4$ in ethanol
(III) has to be made in air, the amount of titanium precursor is difficult to control precisely and hence this method is highly irreproducible. Thus a reliable and reproducible synthesis route for M_{0.5}TiOPO_4 was needed.

Hence a more stable TiCl_4·2THF complex was synthesized using TiCl_4 and Tertrahydrofuran (THF) (both from Sigma-Aldrich, U.S.A.), employing a method similar to one described elsewhere\textsuperscript{111}. For the synthesis of TiCl_4·2THF, 4 mol THF was taken in a round bottom flask under Ar and was cooled down using ice bath. 1 mol TiCl_4 was added drop wise to the round bottom flask containing THF under reflux. Yellow colored TiCl_4·2THF precipitated in the flask. Care was taken as to avoid excessive heating of the reaction mixture, which leads to polymerization of THF giving an undesirable orange colored precipitate. After addition of complete amount of TiCl_4, the reaction mixture was stirred for 1-2 h, after which it was transferred into a fritted filter funnel. The TiCl_4·2THF complex was separated from the excess THF via filtration under Ar-flow. The TiCl_4·2THF was then transferred into another round bottom flask, where the sample was dried under vacuum. Extreme care was taken to avoid exposure of the reaction mixture or the reaction product to air. The purity of the dry TiCl_4·2THF complex was confirmed using X-ray diffraction in transmission mode using a capillary at STOE STADI P powder diffractometer equipped with a Cu anti-cathode. TiCl_4·2THF complex is less reactive in air than TiCl_4 and hence allows for the titanium precursor to be used in stoichiometric ratio. For the synthesis of Ni_{0.5}TiOPO_4 using the modified solution route, solution of Ni(NO_3)_2 in water (I), NH_4H_2PO_4 in water (II) and TiCl_4·2THF in ethanol (III) were made in air in stoichiometric ratio. Solution (III) was added drop wise to the mixture of (I)+(II) under stirring. This resulted in the formation of gelatinous green colored precipitate. The solution mixture was stirred overnight, dried and then subjected to a heat treatment step at 250°C/12 h and 500°C/24 h in order to decompose the ammonium salt. The sample was then heat treated at 1000°C/48 h at a heating and cooling rate of 100°C/h. Intermediate grinding of the powders was performed in between different heat treatment steps in a mortar. The obtained sample was a light green colored pellet, which was crushed and grinded again in a mortar. For synthesis of Cu_{0.5}TiOPO_4, Cu(NO_3)_2 in water (I) was used as the metal precursor. Rest of the synthesis steps were same except for the additional heat treatment step at 700°C/24 h and final step at 950°C/24 h. In case of Mg_{0.5}TiOPO_4, MgO in dil. HNO_3 (I) was used as the precursor and synthesis included additional heat treatment steps at 700°C/24 h, 800°C/24 h and a final step at 900°C/24 h. The heat treatments steps above
500°C were performed to facilitate crystallization of the materials, and were chosen on the basis of previous tests performed to obtain pure samples.

Generally heat treatment at such high temperatures results in fusing together of the primary particles. Thus the as synthesized samples were ball milled in a ZrO$_2$ vial for 8h using the Fritsch Pulverisette 7 ball miller, in order to reduce the particle size.

**Characterization:** The purity of as synthesized $\text{M}_0.5\text{TiOPO}_4$ ($\text{M} = \text{Ni, Cu, Mg}$) samples was checked using X-ray diffraction at Brucker D8 diffractometer equipped with Cu anti-cathode ($\lambda = 1.5406$ Å). Particle size analysis was performed on the as synthesized $\text{M}_0.5\text{TiOPO}_4$ samples (MTOP-AS) and $\text{M}_0.5\text{TiOPO}_4$ sample after 8h of ball milling (MTOP-BM8h) using Horiba LA-950 particle analyzer. Brunauer-Emmett-Teller (BET) specific surface area was measured for all the MTOP-AS and MTOP-BM8h samples ($\text{M} = \text{Ni, Cu, Mg}$) using N$_2$ physisorption with Quantachrome instruments Autosorb-1 machine.

**Electrochemical study:** For the electrochemical study, MTOP-AS ($\text{M} = \text{Ni, Cu, Mg}$) samples were mixed in a mortar with Super-P carbon (TIMCAL, Switzerland) and then mixed with Kynar Flex® 2801 binder in ratio 60:20:20 by weight. Slurries of these mixtures were prepared in NMP and then doctor-bladed on Cu current collector. The slurries were allowed to dry at 80°C overnight in vacuum, upon which 13 mm electrodes were cut out of it. The electrodes were then heated at 120°C overnight under vacuum before making the electrochemical cell. The MTOP-BM8h ($\text{M} = \text{Ni, Cu, Mg}$) samples were ball milled for 2h with Super-P carbon in ratio 3:1 by weight to achieve good mixing between the active material and conductive additive. Kynar Flex® 2801 was added to the mixture of MTOP-BM8h and Super-P carbon to obtain the active material, Super-P carbon and binder in ratio 60:20:20 by weight (MTOP-SPC). Electrodes were made for MTOP-SPC ($\text{M} = \text{Ni, Cu, Mg}$) as described earlier.

The dried electrodes of different samples were then used to assemble cells inside an Ar-filled glove box using lithium as the counter electrode. A glass fiber soaked in ethylene carbonate (EC): dimethyl carbonate (DMC) 1M LiPF$_6$ electrolyte (Ferro, USA) was used as the separator. At least two cells were cycled each at C/20, C/10, C/5 and 1C rate with respect to the observed specific charge from 3 Li$^+$ insertion in the material. Cyclic voltammetric studies were also performed for all the samples at a potential sweep rate of 0.01 mV/s. The potential range for cycling of different samples was chosen on the basis of
preliminary cyclic voltammetric studies on MTOP-AS (M = Ni, Cu, Mg) samples, so as to achieve ~3 Li$^+$ insertion during 1$^{st}$ lithiation step. Thus the NiTOP-AS and NiTOP-SPC were cycled between 0.5-3.5 V vs. Li/Li$^+$, the CuTOP-AS and CuTOP-SPC between 0.2-3.5 V vs. Li/Li$^+$ and the MgTOP-AS and MgTOP-SPC samples between 0.1-3.5 V vs. Li/Li$^+$.

5.2.2. Results and discussion

The XRD pattern for TiCl$_4$·2THF (Figure 5.1) shows that all the recorded peaks could be indexed with the $P2_12_12_1$ space group. No extra peaks from TiO$_2$ or Ti(OH)$_2$ were visible indicating the purity of the titanium precursor. This purity is directly reflected in the final compounds (Figure 5.2), where the XRD patterns of NiTOP-AS and CuTOP-AS reveal only the presence of expected Ni$_{0.5}$TiOPO$_4$ and Cu$_{0.5}$TiOPO$_4$ phases respectively. The CuTOP-AS was seen to be a mixture of two polymorphs viz. $\alpha$ and $\beta$ phases, which is in accordance with the literature$^{112}$. These two phases always coexist in the as synthesized powder and can only be separated as crystals, after heat treatment of the powder at 1000°C followed by slow cooling over 7 days$^{113}$. Thus for the electrochemical studies, CuTOP-AS sample with a mixture of $\alpha$ and $\beta$ phases was used.

![Figure 5.1: Experimental and calculated ($P2_12_12_1$) X-ray powder diffraction pattern ($\lambda = 1.5406$ Å) for TiCl$_4$·2THF complex.](image)

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The MgTOP-AS sample on the other hand was seen to be a mixture of $\text{Mg}_{0.5}\text{TiOPO}_4$ and NASICON $[\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3]$ phases. This is probably owing to the fact that the final heat treatment step for $\text{Mg}_{0.5}\text{TiOPO}_4$ has to be precisely controlled, as below 900°C NASICON phase is seen to exist\textsuperscript{114}. However even after heat treatment at 900°C\textsuperscript{114} for 24 h as indicated in literature, and trying different final heat treatment temperatures (950°C and 1000°C) with varying heat treatment time, pure $\text{Mg}_{0.5}\text{TiOPO}_4$ phase could not be obtained. Thus for the electrochemical studies, the MgTOP-AS sample was used as such.

![XRD patterns](image)

**Figure 5.2:** XRD patterns ($\lambda = 1.5406$ Å) recorded for as synthesized samples of $\text{Ni}_{0.5}\text{TiOPO}_4$, $\text{Cu}_{0.5}\text{TiOPO}_4$ and $\text{Mg}_{0.5}\text{TiOPO}_4$ at a laboratory diffractometer.

The results of the particle size analysis for different MTOP-AS and MTOP-BM8h ($M = \text{Ni}, \text{Cu}, \text{Mg}$) is seen in Figure 5.3. As expected from the high temperature heat treatment, the particle sizes for NiTOP-AS and MgTOP-AS is in the range of 10-300 µm. The CuTOP-AS on other hand showed lognormal particle size distribution in the range of 2-15 µm. On ball milling, the particle size of the entire sample was reduced. For CuTOP-BM8h and MgTOP-BM8h, the particle sizes are reduced to 1-2 µm with around 17.5% particles in range of 60-300 nm. The majority of particles in NiTOP-BM8h were even smaller. The results for particle size analyses and BET specific surface area for all the samples have been summarized in Table 5.1.
Having confirmed the purity and particle sizes for all the samples, electrochemical studies were performed on them. Figure 5.4 shows the 1st and 5th galvanostatic cycle for various MTOP-AS and MTOP-SPC (M = Ni, Cu, Mg) samples at C/20 rate between different potential limits. Cu$_{0.5}$TiOPO$_4$ and Mg$_{0.5}$TiOPO$_4$, like Ni$_{0.5}$TiOPO$_4$, too can be lithiated during the 1st lithiation step to deliver specific charge close to their expected values of 422 mAh/g and 470 mAh/g respectively (3 Li$^+$ insertion). On the 1st delithiation up to 3.5 V vs. Li/Li$^+$ the samples reversibly extract 2 Li$^+$. Same is true for all the MTOP-SPC (M = Ni, Cu, Mg) samples.
Table 5.1: Information regarding the particle size and BET specific surface area for various as synthesized (AS) and ball milled samples (BM8h). The BET specific surface area for Super-P carbon and Super-P carbon ball milled 2 h alone is also reported.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mean size (µm)</th>
<th>Median size (µm)</th>
<th>BET Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiTOP-AS</td>
<td>104.8</td>
<td>85.5</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>NiTOP-BM8h</td>
<td>2.5</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td>CuTOP-AS</td>
<td>5.7</td>
<td>5.4</td>
<td>1.1</td>
</tr>
<tr>
<td>CuTOP-BM8h</td>
<td>3.9</td>
<td>3.5</td>
<td>1.5</td>
</tr>
<tr>
<td>MgTOP-AS</td>
<td>93.7</td>
<td>71.9</td>
<td>0.9</td>
</tr>
<tr>
<td>MgTOP-BM8h</td>
<td>4.8</td>
<td>4.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Super-P Carbon</td>
<td>-</td>
<td>-</td>
<td>90.0</td>
</tr>
<tr>
<td>Super-P carbon ball milled 2 h alone</td>
<td>-</td>
<td>-</td>
<td>83.0</td>
</tr>
</tbody>
</table>

If one concentrates on the as synthesized NiTOP-AS and MgTOP-AS, both the samples show completely different delithiation profile after the initial lithiation step, with the charge-discharge profile for the 5th cycle matching that of the 1st delithiation step. This is in accordance with the reports on Ni₀.₅TiOPO₄ and Co₀.₅TiOPO₄[61, 62]. This indicates that both Ni₀.₅TiOPO₄ and Mg₀.₅TiOPO₄ undergo structural changes during the 1st lithiation step that results in reversible cycling of only 2 out of the 3 Li⁺ that initially react with the material. For CuTOP-AS on the other hand, similarities can be seen between the 1st lithiation and 1st delithiation step. Reversible reactions occur between 1.5-1.7 V vs. Li/Li⁺ for the CuTOP-AS sample, while the 1st lithiation plateau at 1.8 V vs. Li/Li⁺ and the plateau at 0.8 V vs. Li/Li⁺ corresponding to electrolyte degradation on Super-P carbon, remain irreversible. On 5th cycle, the potential plateau between 1.5-1.7 V vs. Li/Li⁺ is still visible and reversible. As the CuTOP-AS sample is a mixture of α and β phases and owing to the fact that the material reacts with the expected 3 Li⁺, it can be concluded that both α and β phases are electrochemically active.
Figure 5.4: 1\textsuperscript{st} (solid line) and 5\textsuperscript{th} (dash line) galvanostatic cycle of (A) NiTOP-AS, NiTOP-SPC (B) CuTOP-AS, CuTOP-SPC and (C) MgTOP-AS, MgTOP-SPC, at C/20 rate between 0.5-3.5 V, 0.2-3.5 V and 0.1-3.5 V vs. Li/Li\textsuperscript{+} respectively.
For the MTOP-SPC (M = Ni, Cu, Mg) samples, owing to the smaller particle size, the lithiation starts at positive potentials as opposed to the as synthesized samples. Moreover the higher specific surface area for the MTOP-SPC (M = Ni, Cu, Mg) samples, results in higher measured specific charge during the 1st lithiation step due to electrolyte degradation. However only 2 Li$^+$ are reversibly extracted from NiTOP-SPC and CuTOP-SPC. The 5th cycle profile for these samples resembles their 1st delithiation profile, showing no distinct flat plateaus but a rather solid-solution type behavior. For the MgTOP-SPC on the other hand a large specific charge of 850 mAh/g is obtained during the 1st lithiation step, which is much higher than the expected 470 mAh/g. On delithiation, around 475 mAh/g is reversibly extracted from the material. During the 5th cycle, 460 mAh/g is still reversibly achieved. This behavior of MgTOP-SPC sheds light on the possible reaction mechanism in this family of compounds. Magnesium is known to form an alloy with Li$^+$ below 0.2 V vs. Li/Li$^{+115, 116}$. The high specific charge on the 1st lithiation and higher reversible specific charge on cycling suggests that Mg$^0$ is formed during the course of 1st lithiation, which presumably alloys reversibly with Li$^+$. This alloying reaction seems to be more favored for the ball milled samples with smaller particle size, as more Mg$^0$ can be present on the surface to react with Li$^+$. Another possible explanation for the high specific charge could be the activation of the impurities. Although same NASICON impurity [Mg$_{0.5}$Ti$_2$(PO$_4$)$_3$] is present in the MgTOP-AS and the MgTOP-SPC samples, the ball milling could also result in reduction of the particle size for the impurity and hence increase its reaction kinetics. However preliminary low rate (C/50) galvanostatic studies and the cyclic voltammetric studies at scan rate of 0.01 mV/s on these materials showed that even at such slow electrochemical cycling, the MgTOP-SPC shows higher specific charge than MgTOP-AS. Thus formation of Mg$^0$ and hence an alloy with Li$^+$ seems to be the more probable explanation. This alloying reaction is not seen for NiTOP-SPC and CuTOP-SPC as Ni and Cu do not alloy with Li$^+$.

To confirm that the difference in the reaction potential between the as synthesized samples and samples ball milled with Super-P Carbon are due to differences in the particle sizes, Galvanostatic Intermittent Titration Technique (GITT) measurements were performed on the pure single phase Ni$_{0.5}$TiOPO$_4$. For the GITT measurement, NiTOP-AS and NiTOP-SPC were cycled at C/100 rate for 2.5 h, followed by a rest period for 10 h and 25 h respectively, during which the cells reached quasi-equilibrium state. The results are presented in Figure 5.5. The NiTOP-AS cell shows large relaxation until 350 mAh/g,
showing similar open circuit potential as that for NiTOP-SPC. This result confirms that the differences in the reaction potential are indeed an effect of reduced particle size.

Figure 5.5: GITT curves for (A) NiTOP-AS and (B) NiTOP-SPC.

Figure 5.6 shows the cyclic voltammograms for different MTOP-AS and MTOP-SPC (M = Ni, Cu, Mg) samples. The potential for 1\textsuperscript{st} lithiation step between different samples is different as is the reaction potential for further cycles. This reveals that changing the M in M\textsubscript{0.5}TiOPO\textsubscript{4} can help tune the reaction potential. In accordance with the galvanostatic cycling data, the 1\textsuperscript{st} lithiation in most of the samples shows different profile than the following cycles. In case of CuTOP-AS the charge-discharge profiles show many similarities, which indicates that the structural changes in Cu\textsubscript{0.5}TiOPO\textsubscript{4} are not as drastic as in case of Ni\textsubscript{0.5}TiOPO\textsubscript{4} and Mg\textsubscript{0.5}TiOPO\textsubscript{4} and are partially reversible.
Figure 5.6: Cyclic voltammograms of (A) NiTOP-AS, NiTOP-SPC (B) CuTOP-AS, CuTOP-SPC and (C) MgTOP-AS, MgTOP-SPC during 1st cycle (solid line) and 2nd lithiation step (dash line) at sweep rate of 0.01 mV/s between 0.5-3.5 V, 0.2-3.5 V and 0.1-3.5 V vs. Li/Li$^+$ respectively.
The charge retention curves for all the samples are shown in Figure 5.7. In all the cases the as synthesized samples show better charge retention over many cycles. Despite the smaller particle size and good mixing between the active material and Super-P carbon, the specific charge for all the MTOP-SPC (M = Ni, Cu, Mg) samples drops after few cycles. Similar results are obtained from the rate capability studies (Figure 5.8, page 99), where the MTOP-AS show better performance than the MTOP-SPC (M = Ni, Cu, Mg) samples. The MTOP-AS (M = Ni, Cu, Mg) show more than 200 mAh/g even at 1C rate, while the values for MTOP-SPC (M = Ni, Cu, Mg) samples drop down to almost zero. Amongst the different MTOP-AS (M = Ni, Cu, Mg) samples, CuTOP-AS shows the best charge retention and rate capability. This better performance of the CuTOP-AS could be attributed to its smaller particle size as opposed to NiTOP-AS or MgTOP-AS samples. However it could also be a structural effect. CuTOP-AS is a mixture of α and β phases, where α phase has similar unit cell parameters and atomic arrangement as for NiTOP-AS and MgTOP-AS, resulting in presence of narrow straight channels along c-axis in the initial structure for Li\(^+\) insertion. The β phase on the other hand has a distorted structure, resulting in formation of broader path for Li\(^+\) insertion. These broad channels in β-phase should result in better electrochemistry for CuTOP-AS. In case of MgTOP-AS, from the electrochemistry, a reversible alloying of Mg\(^0\) with Li is expected. The alloying reactions are known to be kinetically hindered, which explains poor rate capability of MgTOP-AS as opposed to NiTOP-AS sample.

In case of MTOP-SPC (M = Ni, Cu, Mg) samples, the poor electrochemical behavior could be attributed to their higher specific surface area. At such low potentials versus lithium, a Solid Electrolyte Interphase (SEI) should grow on both the electrode material and the Super-P carbon additive. For smaller particles with higher specific surface area undergoing different phase transformations during the 1\(^{st}\) lithiation step, the SEI formed could evolve during the course of cycling, impeding the performance of the ball milled samples. However since the goal of this work was to study the electrochemical performance of various M\(_{0.5}\)TiOPO\(_4\) (M = Ni, Cu, Mg), further studies in this direction were not conducted.
Figure 5.7: Charge retention curves for delithiation of (A) NiTOP-AS, NiTOP-SPC (B) CuTOP-AS, CuTOP-SPC and (C) MgTOP-AS, MgTOP-SPC, cycled at various rates between 0.5-3.5 V, 0.2-3.5 V and 0.1-3.5 V vs. Li/Li$^+$ respectively.
Figure 5.8: Rate capability for delithiation of as synthesized samples (filled symbols) and samples ball milled with Super-P carbon (open symbols), for $\text{Ni}_{0.5}\text{TiOPO}_4$ (NiTOP), $\text{Cu}_{0.5}\text{TiOPO}_4$ (CuTOP) and $\text{Mg}_{0.5}\text{TiOPO}_4$ (MgTOP) cycled at different rates between 0.5-3.5 V, 0.2-3.5 V and 0.1-3.5 V vs. Li/Li$^+$ respectively.

Figure 5.9: Galvanostatic cycling of NiTOP-AS between (A) 1.25-3.5 V (B) 1.0-3.5 V (C) 0.5-3.5 V vs. Li/Li$^+$ at C/10 rate and (D) their charge retention curves for delithiation.
To study the effect of amount of lithium reacting during the 1st lithiation step on the following cycles, NiTOP-AS cells were cycled versus lithium between different potential windows corresponding to reaction with 1 Li⁺, 2Li⁺ and ~3 Li⁺ respectively (Figure 5.9). It can be seen that even after reaction with 1 Li⁺, the electrochemical profile of 1st lithiation step is completely different than for the following cycles. This indicates that the structural changes already start occurring even after reaction with 1 Li⁺. The charge retention curves reveal (Figure 5.9D) that the cell that has been cycled between 0.5-3.5 V vs. Li/Li⁺ delivers the best results in terms of specific charge.

5.2.3. Conclusion

It was successfully proven that the reversible reaction of M₀.₅TiOPO₄ (M = Cu, Mg) versus lithium is possible. Different M₀.₅TiOPO₄ (M = Ni, Cu, Mg) samples react at different potentials versus lithium, showing different charge-discharge profiles, which indicates that the reaction potential for this family of compounds can be tuned by choosing the right M in M₀.₅TiOPO₄. Particle size, too, was seen to have an effect on the reaction potential for the various samples. Smaller particle size splits the 1st lithiation plateau in MTOP-SPC (M = Ni, Cu) into several steps. However it adversely affects the long term cycling and rate capability of the materials. For MgTOP-SPC, smoother solid-solution type behavior was observed, which delivers very high reversible specific charge. In case of Mg₀.₅TiOPO₄ the extra reversible specific charge from the material, hints to formation of Mg⁰ during the course of 1st lithiation, which presumably alloys reversibly with lithium. In all the cases as synthesized samples showed better charge retention as compared to ball milled samples. Moreover the electrochemical studies on NiTOP-AS suggest that the phase transformation starts even after reaction with 1 Li⁺. Hence the electrochemical studies also gave clues to understand the reaction mechanism in this family of compounds.

5.3. Study of reaction mechanism for Ni₀.₅TiOPO₄

5.3.1. Introduction

It was found that of the three M₀.₅TiOPO₄ (M = Ni, Cu, Mg) synthesized using the modified solution route, Ni₀.₅TiOPO₄ was present as a single phase with no other impurities, as seen from XRD measurements at a laboratory diffractometer. Hence Ni₀.₅TiOPO₄ was used for the study of reaction mechanism. From the electrochemical studies it is evident that although ball milling is not good for long term cycling and rate
capability, it results in splitting of the 1\textsuperscript{st} lithiation step into several plateaus. As a clear distinction between different processes is usually desired in the study of reaction mechanism, ball milled Ni\textsubscript{0.5}TiOPO\textsubscript{4} sample was used for this purpose.

5.3.2. Experimental

5.3.2.1. Material characterization

\textbf{Synthesis:} Ni\textsubscript{0.5}TiOPO\textsubscript{4} sample was prepared using modified solution route synthesis, as described in section 5.2.1. The as synthesized Ni\textsubscript{0.5}TiOPO\textsubscript{4} (NiTOP-AS) was ball milled 8 h (NiTOP-BM8h) to reduce the particle size and then ball milled again with conductive Super-P carbon in ratio (3:1). Kynar Flex\textsuperscript{®} 2801 was added to this mixture, to obtain active material, Super-P carbon and binder in ratio 60:20:20 by weight (NiTOP-SPC). Electrodes and cells were prepared as described in section 5.2.1.

\textbf{Structural characterization:} To check the purity of the sample, NiTOP-BM8h was studied using synchrotron XRD at the Materials Science (X04SA) beamline of SLS at PSI Villigen. For the synchrotron diffraction measurement, the NiTOP-BM8h sample was pressed between two self adhesive Kapton\textsuperscript{®} tapes and the measurement was performed for 8 min in transmission mode at a wavelength of 0.7085 Å using a focused monochromatic beam of 0.5 mmx0.5 mm area. Neutron diffraction pattern was also recorded for the NiTOP-BM8h sample at the HRPT beam line of SINQ, PSI Villigen. For the neutron diffraction measurement, the NiTOP-BM8h sample was filled in an air tight 2.5 cm\textsuperscript{3} vanadium tube, which was sealed in an Ar-filled glovebox. In order to prevent incoherent air scattering of the diffracted beam from the sample to the detector, the sealed vanadium tube was placed inside a vanadium drum that was under vacuum. Neutron diffraction measurement was performed in transmission mode at 1.494 Å wavelength for 8 h. In both the cases Rietveld refinement was performed.

\textbf{Morphology:} To study the morphology, Scanning Electron Microscope (SEM) images were recorded for the NiTOP-AS, NiTOP-BM8h and NiTOP-SPC sample using the Carl Zeiss Ultra\textsuperscript{TM} 55 machine at 5 KV tension using the in lens detector. Energy Dispersive X-ray Spectroscopy (EDX) measurements were also performed during the SEM studies to check the elemental composition of the samples.
5.3.2.2. Study of reaction mechanism

**Electrochemistry:** For most of the following analytical studies, NiTOP-SPC was used. In cases where the presence of binder is undesired, only the ball milled mixture of Ni$_{0.5}$TiOPO$_4$ with Super-P carbon (3:1 by weight), without binder, was used and is mentioned accordingly. For the study, standard electrochemical cells were cycled between 0.5-3.2 V vs. Li/Li$^+$ at C/50 rate with respect to the observed specific charge of 426 mAh/g (3 Li$^+$). Different cells were stopped after 1, 2, 3 Li$^+$ insertion down to complete lithiation till 0.5 V, after which a complete delithiation till 3.2 V vs. Li/Li$^+$ was performed. The following investigations were mainly performed on cells stopped at the above mentioned values of Li or potential. If measurements were performed at extra points, they have been mentioned accordingly.

**In situ/ex situ synchrotron XRD:** For the *in situ* synchrotron XRD measurements “coffee bag” cells without and with hole covered with a Kapton® tapes were used. The electrodes and the “coffee bag” cells were prepared as described in section 2.2. The active material, Super-P carbon, Kynar Flex® 2801 were used in ratio 60:20:20 by weight. The “coffee bag” cells were cycled between 3.2-0.4 V vs. Li/Li$^+$ at C/20 rate in PC/DMC 1M LiPF$_6$ electrolyte against Li as the counter electrode. A lower potential limit was chosen owing to the fact that the mechanical pressure in the “coffee bag” cell is not the same as in the standard coin-like cells, which leads to a higher internal resistance in the former. The *in situ* synchrotron XRD patterns were recorded at a wavelength of 0.7085 Å using a focused monochromatic beam in transmission mode at the MS-powder beamline of SLS, PSI Villigen. For the *ex situ* synchrotron XRD measurements, the cells stopped at different stages of lithiation or delithiation were disassembled, samples washed, dried and the material held between two self adhesive Kapton® tapes.

**Ex situ Raman spectroscopy:** Raman spectra were acquired at Horiba-Jobin Yvon Labram HR800 machine using a Helium-Neon laser (0.6328 Å) under confocal conditions. For the measurement a D1 intensity filter and an X 50 objective with a spatial resolution of 2-3 um$^3$ was used. For NiTOP-AS and NiTOP-SPC powder without binder, measurements were performed over 200-1700 cm$^{-1}$ for 20-30 sec each and integrated over 3 scans. The NiTOP-SPC powder without binder was cycled till different steps, the cells stopped, material washed with DMC, dried and then used for the *ex situ* Raman measurement. The measurements on the lithiated powder samples were performed under Ar using an air tight *ex situ* Raman cell. For the cycled samples the measurement were performed between
200-1000 cm\(^{-1}\) for 150 sec each and integrated over 3 scans. This process was repeated several times at various spots in the electrode material. A smaller wavenumber range was selected for the cycled sample, as this was the range of interest where the peaks from Ni\(_{0.5}\)TiOPO\(_4\) are visible. Limiting the range also reduced the data acquisition time drastically.

**SQUID:** Temperature (T) loops were performed on the Ni\(_{0.5}\)TiOPO\(_4\) samples at different steps. For this purpose Zero Field Cooled (ZFC) measurements were performed where the sample was cooled down from 300 K to 2 K without magnetic field. After this Field cooled (FC) measurements were performed where the sample was taken back to 300 K and down to 2 K at a constant magnetic field of 1000 Oe. For the magnetic field (B) loops the samples were maintained at 5 K and the field was changed between 5000 Oe to -5000 Oe. The measurements were performed under Ar atmosphere using a sealable quartz tube at ETH Zürich. The help from Christian Mensing for performing the SQUID measurements is acknowledged.

**HRTEM:** HRTEM and ED measurements were performed on NiTOP-SPC powder without binder and sample after complete lithiation till 0.5 V. The sample preparation had to be done in air due to lack of availability of a transfer chamber to the TEM machine. Thus the samples were exposed to air for approximately 3-5 min. For sample preparation, the electrode material was dispersed in ethanol and some droplets were deposited on a holey copper mesh. HRTEM investigation were performed on the Tecnai F30 microscope (FEI, field emission gun (FEG)) at ETH Zürich operated at 300 kV. The help from Dr. Frank Krumeich for performing the HRTEM/ED measurements is acknowledged.

**Post-mortem SEM:** SEM images were recorded for the NiTOP-SPC electrode and compared with the samples after reaction with 1, 2 and 3 Li\(^+\). The sample preparation in all the cases was done in an Ar-filled glovebox and the samples transferred using the transfer chamber into the SEM under Ar atmosphere. The SEM images were recorded at the Carl Zeiss Ultra™ 55 machine using the in lens detector.

**\(^7\)Li MAS NMR:** \(^7\)Li MAS NMR were recorded at different steps during 1\(^{st}\) lithiation and 1\(^{st}\) delithiation of NiTOP-SPC powder. The measurements were performed under Ar atmosphere at 4.7 T (corresponding to a resonance frequency of 77.77 MHz) with spinning speed of 60 KHz at Brucker Avance Widebore NMR spectrometer equipped with a 1.3 mm high speed H-X MAS probe head with 1.3 mm Zirconia rotors. The reference used was
1 M aqueous solution of LiCl (chemical shift 0 ppm). For the measurement a Hahn spin echo method was used. The measurements were done at the Karlsruhe Institute of Technology, Germany. The help from Dr. Sylvio Indris for the \(^7\)Li MAS NMR measurements and data analyses is acknowledged.

**X-ray Photoelectron Spectroscopy (XPS):** XPS measurements were performed on the NiTOP-SPC powder sample and sample after complete lithiation down to 0.5 V vs. Li/Li\(^+\). The measurements were performed at the Thermo Scientific ESCALAB 220iXL instrument using Al-K\(\alpha\) (1486.6 eV) radiation. For the measurements of the powder samples, a graphite disk with scratched surface was used. The powder samples were pressed in the cavities of the graphite disk in an Ar-filled glove box. Due to lack of an appropriate transfer chamber from the glove box to the XPS machine, the powder samples were exposed to air for 2-3 min.

### 5.3.3. Results and discussion

The SEM images recorded for NiTOP-AS, NiTOP-BM8h and NiTOP-SPC are shown in Figure 5.10. The size of primary particles for NiTOP-AS ranges from 0.07 µm to 1.5 µm, with most of the primary particles in the range of 0.3-0.5 µm. It is seen for NiTOP-AS that the primary particles show well defined facets indicating its good crystallinity. On ball milling, however, no distinct features are visible for the NiTOP-8h and NiTOP-SPC samples. Except for the presence of Super-P carbon on the surface, no significant morphological changes are seen between these two samples. An EDX measurement performed on the NiTOP-SPC sample shows peaks only from the expected elements viz. Ni, Ti, O, P and C. No extra peaks corresponding to Cl or Zr are visible. Thus it can be said with in the sensitivity of the technique that no impurities are introduced into the final product, either by using a different titanium precursor (TiCl\(_4\cdot 2\)THF) than reported in the literature or by ball milling the sample in ZrO\(_2\) vial.
Figure 5.10: SEM images for (A) NiTOP-AS, (B) NiTOP-BM8h, (C) NiTOP-SPC, and (D) EDX measurement on the NiTOP-SPC powder sample.

Rietveld refinement of NiTOP-BM8h neutron diffraction pattern was performed using the structural model described by P. Gravereau et al.\textsuperscript{117} and is shown in Figure 5.11A. Due to the sensitivity of neutrons to detect lighter elements like oxygen, the structural model obtained from the Rietveld analyses of the neutron powder diffraction pattern was used to refine the synchrotron XRD pattern (Figure 5.11B). The use of high intensity neutron and X-ray sources, revealed impurity peaks in the NiTOP-BM8h sample. This impurity was identified to be the rutile TiO\textsubscript{2} phase in $P4_2/mnm$ space group with $a = 4.554$ (1) Å, $b = 4.554$ (1) Å, $c = 2.835$ (1) Å and was quantified to only 1.6% by weight.
Figure 5.11. Rietveld refinement of (A) neutron powder diffraction ($\lambda = 1.494$ Å) and (B) synchrotron X-ray diffraction pattern ($\lambda = 0.7085$ Å) recorded for Ni$_{0.5}$TiOPO$_4$ ball milled for 8 h (NiTOP-BM8h).

Only the Rietveld analysis for the neutron powder diffraction data is reported in Table 5.2. From the Rietveld analysis, a slight variation of the atomic positions is seen as compared to those reported by P. Gravereau et al.$^{117}$ These small changes in atomic positions translate in slightly different bonds lengths and angles, which are reported in Table 5.3 along with the values obtained from literature$^{117}$. 
Ni$_{0.5}$TiOPO$_4$, $P2_1/c,$

\[ a = 7.3763 \, \text{(1) Å}, \quad b = 7.3296 \, \text{(1) Å}, \quad c = 7.3508 \, \text{(1) Å}, \quad \beta = 120.288 \, \text{(1) Å}, \quad V = 343.18 \, \text{(1) Å}^3 \]

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Wavelength/ Measurement time: 1.494 Å/ 8 h

2Theta range/ Step increment: 4°-165° / 0.05°

Refinement program: Fullprof suite version 2007

Number of measured reflections: 881

Reflections used for refinement: 833

Number of refined parameters: 66

Zero shift: 0.0208°

Peak width parameters: $u = 0.14361$, $v = -0.32206$, $w = 0.13197$

Phases and weight percentages: Ni$_{0.5}$TiOPO$_4$ 98.4%, TiO$_2$ rutile 1.6%

Reliability factors: $R_p = 5.11\%$, $R_{wp} = 6.83\%$, $R_{exp} = 2.34\%$, $\chi^2 = 8.52$

Table 5.2: Rietveld analysis of neutron diffraction pattern recorded for Ni$_{0.5}$TiOPO$_4$ sample ball milled for 8 h. Refined parameters are in italics.
Table 5.3: Comparison of bond distances (Å) and angles (°) for Ni_{0.5}TiOPO_{4} obtained from the structural data reported in Table 5.2 (italics) and for those reported by P. Gravereau et al.\textsuperscript{117}. Angles are above the underlined diagonal, bond lengths are highlighted in grey.

As a consequence the [NiO_{6}]_{td} is more symmetrical at the expense of [TiO_{6}]_{td} and [PO_{4}]_{td} that are more distorted than was thought earlier. This precise data could only be obtained due to the use of high quality neutron diffraction pattern.
The electrochemistry of NiTOP-SPC sample used for the study of reaction mechanism using several different analytical techniques is shown in Figure 5.12. As expected the 1st lithiation step splits into different potential plateaus. The points where the different cells were stopped for the studies are marked on the curve.

![Figure 5.12: 1st galvanostatic cycle of NiTOP-SPC between 0.5-3.2 V vs. Li/Li⁺. The points where the cells were stopped and material analyzed are marked.](image)

The first analytical technique used for the study of the reaction mechanism was the synchrotron XRD. From the *in situ* synchrotron XRD (Figure 5.13A) it can be seen that new peaks appear during the course of lithiation. At the end of the delithiation step (j 3.2 V) the new peaks are broad and lower in intensity. This hints that the phase transformation to the new phase is partially reversible. After a careful analysis, it was determined that these new peaks could be fitted with the same monoclinic space group ($P2_1/c$) as the starting compound but with different unit cell parameters, $a = 7.667$ (1) Å, $b = 7.520$ (1) Å, $c = 7.354$ (1) Å, $\beta = 118.56$ (2)°, $V = 372.46$ (9) Å$^3$. Owing to the lower mechanical pressure in the “coffee bag” cells a complete reaction was not achieved in the *in situ* cell, thus *ex situ* measurements were performed. The *ex situ* synchrotron XRD patterns (Figure 5.13B) recorded on NiTOP-SPC revealed amorphization on lithiation, which pertained even after delithiation.
Figure 5.13: (A) *In situ* synchrotron XRD patterns ($\lambda = 0.7085$ Å) recorded for NiTOP-SPC in a “coffee bag” cell and (B) *ex situ* synchrotron XRD measurements ($\lambda = 0.7085$ Å) performed on NiTOP-SPC powder without binder. (*) marks the peaks from new phase.
Thus the conventional diffraction method of following the structural changes in order
to understand the reaction mechanism could not be successfully employed in this case.
Nonetheless the XRD measurements delivered two important pieces of information:

- Part of the lithiated phase crystallizes in the same $P2_1/c$ space group as the
  starting Ni$_{0.5}$TiOPO$_4$ sample but with different unit cell parameters resulting in
  8.5% unit cell volume expansion.

- The sample undergoes amorphization on lithiation, with some part still in partially
  crystalline state as seen from the broad peaks in the \textit{ex situ} synchrotron XRD
  patterns.

In order to take a deeper look at the reaction mechanism, \textit{ex situ} Raman
measurements were performed on the NiTOP-SPC powder without binder. The NiTOP-AS
and NiTOP-SPC powder (Figure 5.14) sample show identical peaks attributed to P-O
bending, Ti-O stretching and P-O stretching. The NiTOP-SPC powder also shows
additional carbon structural vibrations for the Super-P carbon used in the electrode
mixture. \textit{Ex situ} Raman measurements revealed loss of Raman signal after reaction with
$1^{st}$ Li$^+$, which pertained on further cycling. This behavior of sample turning Raman inactive
could be due to increased electronic conductivity ($\sigma$) of the sample, which leads to
decreased optical skin depth ($\delta$) of the laser beam. These two parameters are related to
each other by following equation$^{118}$.

$$\delta = \sqrt{2 / \sqrt{\mu \sigma \omega}}$$

where $\mu$ and $\omega$ are the magnetic permeability and inverse of the wavelength respectively.

Increase in electronic conductivity has also been reported to induce loss of Raman
activity in other materials like Li$_4$Ti$_5$O$_{12}$$^{119}$. In case of Li$_4$Ti$_5$O$_{12}$, on lithiation to Li$_7$Ti$_5$O$_{12}$,
three of the Ti originally in +4 oxidation state are reduced to +3 oxidation state. This
presence of Ti$^{+4}$/Ti$^{+3}$ mixed valence results in increased electronic conductivity of the
lithiated Li$_7$Ti$_5$O$_{12}$ sample$^{120, 121}$. It is also known that for certain Ti$_n$O$_{2-n}$, the ordering of
oxygen deficiency leads to formation of adjacent face-shared [TiO$_6$] octahedra. These face
shared [TiO$_6$]$_{\text{old}}$ result in increased electronic interaction between the adjacent titanium
ions and hence resulting in increased electrical conductivity$^{122}$. In case of Ni$_{0.5}$TiOPO$_4$, the
3D structure consists of chains of [TiO$_6$]$_{\text{old}}$ running along c axis connected together by
corner sharing [PO$_4$]$_{\text{tld}}$ and face and corner sharing [NiO$_6$]$_{\text{tld}}$. During the lithiation step, the
Ti$^{+4}$ in the structure is expected to reduce to Ti$^{+3}$ oxidation state, resulting in Ti$^{+4}$/Ti$^{+3}$ mixed valence. It is also possible that there occurs certain Ni-Ti atomic exchange during lithiation, resulting in presence of face sharing [TiO$_6$]$_{tot}$ with Ti in +4 and +3 oxidation state. In both the cases the end result would be increase in the electronic conductivity.

Another possibility for loss of Raman signal is that during the course of lithiation, Ni$^{+2}$ in Ni$_{0.5}$TiOPO$_4$ is reduced to Ni$^{0}$ and hence is extruded out of the structure. If the conducting Ni$^{0}$ is present on the surface of the oxyphosphate as a continuous reflective layer, no Raman signal would be obtained. However formation of smooth continuous Ni$^{0}$ layer on the surface seems to be unlikely.

Figure 5.14: Raman spectra for NiTOP-AS, NiTOP-SPC powder and samples after different lithiation and delithiation steps.

To test the hypothesis that Ti$^{+4}$ and Ti$^{+3}$ are present in face sharing octahedra, X-ray Absorption Spectroscopy (XAS) measurements would be necessary to test the oxidation state and the local structure of the Ti. Unable to receive beam time for XAS measurement.
during desired period, the local structure of Li$^+$ was probed using $^7$Li MAS NMR measurements to gain more insight into the reaction mechanism. Figure 5.15 shows the $^7$Li MAS NMR spectra for samples after various lithiation and delithiation steps. After reaction with 0.5 (b) and 1.0 (c) Li$^+$, the spectra show slight negative and positive ppm shift. The positive ppm shift was attributed to direct Li-O-Ni bond. However, the negative shift could be attributed to either a Li-O-Ti$^{+3}$ bond or Ni present in the second coordination shell of Li. As the negative ppm shift was not observed upon reaction with more than 1 Li$^+$ (d to j), it was ascribed to Ni in the second coordination shell. Thus, it can be concluded that up to reaction with 1 Li$^+$, a direct Li-O-Ni bond is expected in the structure\textsuperscript{1}. On further lithiation only a peak at 0 ppm corresponding to hyperfine interaction of Ni with Li is seen. This indicates that the Ni is no longer in the immediate surrounding of the Li$^+$ and probably is extruded out. On complete delithiation (j) the 0 ppm peak is sharper than the earlier peaks indicating possible reoxidation of Ni$^0$.

**Figure 5.15:** $^7$Li MAS NMR spectra for NiTOP-SPC sample at different stages of lithiation and delithiation. (*) marks the positive and negative ppm peak shifts corresponding to a direct Li-O-Ni bond.

\textsuperscript{1}$^7$Li MAS NMR data analysis performed by Dr. Sylvio Indris, KIT, Germany
In order to test the hypothesis that Ni$^0$ is formed during the course of lithiation, SQUID measurements were performed on the different samples. Slightest changes in the magnetic moment can be identified using the B-loop of the SQUID, while the T-loops help in calculation of the oxidation state. The anticipated reduction of Ni$^{+2}$ to ferromagnetic face centered cubic (fcc) Ni$^0$ is expected to lead to an increased magnetic moment for the lithiated samples. However as seen from Figure 5.16, the magnetic moment drops on reaction with 1 Li$^+$ and keeps on decreasing as the amount of reacted Li$^+$ increases. On delithiation (j) the magnetic moment increases slightly.

These unexpected results might be explained as follows:

- Firstly, instead of formation of stable fcc Ni$^0$, it is possible that the Ni$^0$ exists in a metastable hexagonal close packed (hcp) form, which has different magnetic properties than former$^{123}$.

- The surface layer on the Ni$^0$ too is seen to affect its magnetic properties. It is possible that Ni$^0$ formed in the material is trapped in between other phases for e.g. as in the case of Ni$^0$ in TiO$_2$$^{124}$ or Co$^0$ in SiO$_2$ phase$^{125}$. 

Figure 5.16: SQUID B-loops for NiTOP-SPC samples at different stages of lithiation and delithiation. Inset shows the T-loops for starting (a) and end of lithiation sample (g).
The T-loops (inset of Figure 5.16) for starting powder sample (a) and sample at end of 1st lithiation step (g) show non-linear curves for paramagnetic materials. The strong coupling between Ni and Ti makes it impossible to fit the Curie-Weiss law and hence does not allow for direct calculation of the oxidation state of Ni. However the SQUID measurements do not exclude the formation of Ni⁰ on lithiation.

In order to check the oxidation state of Ni in Ni₀.₅TiOPO₄, XPS analysis was performed on the starting NiTOP-SPC powder sample and sample at the end of 1st lithiation step using the Ni 2p spectra. For the analysis of the oxidation states only the Ni 2p₃/₂ was used. Spectra for NiTOP-SPC powder sample (Figure 5.17a) reveals that the Ni in the structure is present in +2 oxidation state at a binding energy of 856.7 eV^{126}. On lithiation however the peak position of the Ni 2p₃/₂ shifts to binding energy of 853.6 eV corresponding to that of Ni⁰^{127}. Thus the XPS measurements confirmed that the Ni⁺² in Ni₀.₅TiOPO₄ is indeed reduced to Ni⁰ during the course of lithiation. From the XPS measurements on the Ti 2p and P 2p spectra no significant changes in the peak position were visible (Figure 5.18A and B). For the O 1s and C 1s spectra (Figure 5.18C and D) on the other hand, significant changes were observed, with formation of new peaks, presumably corresponding to formation of SEI on the surface of the electrode material.

![Figure 5.17: XPS measurements showing Ni 2p spectra for NiTOP-SPC starting powder sample (a) and sample after the complete lithiation step (g) down to 0.5 V vs. Li/Li⁺.](image-url)
Figure 5.18: XPS measurements showing (A) Ti 2p (B) P 2p (C) O 1s, and (D) C 1s spectra for NiTOP-SPC starting powder sample (a) and sample after the complete lithiation step (g) down to 0.5 V vs. Li/Li$^+$. XPS measurements at the end of 1$^{st}$ delithiation step proved to be very difficult, firstly due low conductivity of the sample and presence of large (25%) amount of Super-P carbon in NiTOP-SPC powder where a SEI is seen to grow on the surface. This is obviously the reason for poor peak to background ratio of spectra for the cycled samples.

To confirm the formation of Ni$^0$ particles HRTEM images were recorded for NiTOP-SPC powder (a) and sample after complete lithiation (g). The HRTEM image (Figure 5.19A) for NiTOP-SPC powder shows well defined lattice fringes indicating its good crystallinity. The ED for this sample supports this fact. On complete lithiation, most of the sample turns amorphous, while a part of the bulk is still slightly crystalline, as was expected from the synchrotron XRD measurements. This crystalline part is trapped
between amorphous matrix, which also covers the surface. The ED for completely lithiated sample confirms the amorphization of the sample. Within the magnification of the machine no clear aggregates of Ni\(^0\) particles were visible. Electron Energy Loss Spectroscopy (EELS) measurements could not be performed on the samples to determine the oxidation states of the elements owing to the thickness of the particles in micrometer range.

![Figure 5.19: (A) HRTEM (B) ED measurements for NiTOP-SPC starting powder (a). (C) HRTEM and (D) ED measurements for completely lithiated NiTOP-SPC sample (g).](image)

Post-mortem SEM images were recorded for NiTOP-SPC electrodes after reaction with 1, 2 and 3 Li\(^+\) respectively. The SEM images (Figure 5.20), too, show no drastic morphological changes during the 1\(^{st}\) lithiation step. No Ni\(^0\) aggregates could be identified.
The EDX mapping of the lithiated sample (Figure 5.21) showed that all the elements viz. Ni, Ti, O and P are well distributed over the surface of the sample. Moreover the C from the Super-P carbon conductive additive and F from the Kynar® Flex 2801 (PVdF-HFP) polymeric binder used in the electrode are also well distributed within the electrode.

Figure 5.20: SEM images of (A) NiTOP-SPC electrode, and NiTOP-SPC after reaction with (B) 1 Li⁺ (C) 2 Li⁺ and (D) 3 Li⁺.

5.3.4. Reaction mechanism

Through the study of Ni_{0.5}TiOPO_4 material using several analytical methods, much critical information could be obtained, which has been summarized in Table 5.4 (page 120) along with conclusions drawn from them. The most important information obtained is that after reaction with 1 Li⁺, a direct Li-O-Ni bond exists, which is broken on further lithiation resulting in formation of Ni⁰ particles.
Figure 5.21: (A) Secondary electron image of lithiated Ni$_{0.5}$TiOPO$_4$ sample. EDX mapping performed for different elements is shown. Fluorine is from the PVdF-HFP binder.
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<td>Part of lithiated phase in the same space group as the starting compound showing 8.5% volumic changes</td>
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<tr>
<td>Raman spectroscopy</td>
<td>Sample Raman inactive after reaction with 1 Li⁺</td>
<td>Possibly increased electronic conductivity by either presence of Ti⁺⁴/Ti⁺³ mixed valence, formation of face sharing [TiO₆]₉oct and/or formation of Ni⁰ layer on the surface of the material</td>
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<tr>
<td>$^7$Li MAS NMR</td>
<td>Positive and negative ppm shift until reaction with 1 Li⁺ after which only 1 peak at 0 ppm visible</td>
<td>Direct Li-O-Ni bond until reaction with 1 Li⁺ after which Ni no longer in immediate surrounding of Li⁺</td>
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<td>XPS</td>
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<td>SQUID</td>
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<td>Ni⁰ either in metastable hcp packing rather than stable fcc packing or Ni⁰ covered with surface layer</td>
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<td>HRTEM/ED</td>
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<td>Crystalline part trapped in amorphous matrix</td>
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<tr>
<td>SEM/EDX</td>
<td>No drastic changes in morphology after 1st cycle</td>
<td>No Ni⁰ clusters found on the surface</td>
</tr>
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Table 5.4: Summary of results obtained from the study of reaction mechanism of Ni₀.₅TiOPO₄ and conclusions drawn from them.
Combining all the available information, following reaction mechanism has been proposed, schematic for which is shown in Figure 5.22:

- During reaction with around 1 Li\(^+\) there occurs a partial reduction of Ti\(^{4+}\) to Ti\(^{3+}\), along with partial reduction of Ni\(^{2+}\) to Ni\(^0\). This results in transformation of crystalline Ni\(_{0.5}\)TiOPO\(_4\) (I) to partially crystalline, lithiated Li\(_a\)Ni\(_{0.5-x}\)TiOPO\(_4\) and Ni\(^0\) phases (II). This phase transformation results in formation of a direct Li-O-Ni bond in the structure Li\(_a\)Ni\(_{0.5-x}\)TiOPO\(_4\), while increasing the electronic conductivity of the material.

- On further lithiation, whole of Ni\(^{2+}\) in the structure is reduced to Ni\(^0\), forming a lithiated titanium rich phase, Ni\(^0\) and some unreacted part still as lithiated nickel titanium oxyphosphate (III).

- During the 1\(^{st}\) delithiation step, the material is cycled only between (II) and (III) as no evidence for restoration of Ni\(_{0.5}\)TiOPO\(_4\) structure is observable.

Figure 5.22: Schematic of proposed reaction mechanism for Ni\(_{0.5}\)TiOPO\(_4\). C and D stand for charge (lithiation) and discharge (delithiation) respectively.
5.4. General discussion

The goal of this entire study was to test the electrochemistry of model $M_{0.5}\text{TiOPO}_4$ ($M = \text{Ni, Cu, Mg}$) materials and to understand the reaction mechanism in this family of compounds using $\text{Ni}_{0.5}\text{TiOPO}_4$ in order to support the design of better performance negative electrode materials. It was found that all of the studied $M_{0.5}\text{TiOPO}_4$ ($M = \text{Ni, Cu, Mg}$) deliver more specific charge at positive potentials than graphite. However in terms of practical application only 200-300 mAh/g specific charge could be drawn from these materials. Moreover only the potential of the $1^{\text{st}}$ lithiation step is distinctly affected by the $M$ in $M_{0.5}\text{TiOPO}_4$ ($M = \text{Ni, Cu, Mg}$). For following cycles the lithiation-delithiation processes for different $M_{0.5}\text{TiOPO}_4$ ($M = \text{Ni, Cu, Mg}$) are in the similar potential range. Thus despite the different $M$ in $M_{0.5}\text{TiOPO}_4$ ($M = \text{Ni, Cu, Mg}$), the structural changes in all the samples seem to be similar. In case of $\text{Ni}_{0.5}\text{TiOPO}_4$ and $\text{Mg}_{0.5}\text{TiOPO}_4$ the electrochemical profile after few cycles shows solid-solution type reaction, which is normally undesirable for practical applications. Moreover the higher specific charge from $\text{Mg}_{0.5}\text{TiOPO}_4$ suggests formation of $\text{Mg}^0$ during lithiation, which undergoes an alloying reaction. A material that undergoes several phase transformations ending in formation of alloy with lithium can lead to many safety issues. This coupled with the fact that the upper potential limit for cycling of these materials is 3.5 V vs. Li/Li$^+$, makes them undesirable in Li-ion batteries.

The only promising candidate of the three studied oxyphosphates is $\text{Cu}_{0.5}\text{TiOPO}_4$. $\text{Cu}_{0.5}\text{TiOPO}_4$ shows similar lithiation and delithiation profile over several cycles, between 1.5-1.8 V vs. Li/Li$^+$, which could be due to the fact that it is a mixture of 2 polymorphs ($\alpha$ and $\beta$ phases). This positive reaction potential of $\text{Cu}_{0.5}\text{TiOPO}_4$ is an advantage in terms of safety, but at the expense of specific energy. The material shows very stable cycling over hundreds of cycles, with good rate capabilities. Thus, if the reason for “loss” of 1 Li$^+$ on cycling can be understood and resolved, $\text{Cu}_{0.5}\text{TiOPO}_4$ as such might be interesting for Li-ion batteries.

To understand the reaction mechanism of lithiation and delithiation in this family of compounds, several studies were conducted using $\text{Ni}_{0.5}\text{TiOPO}_4$. It was proved that part of the specific charge in $\text{Ni}_{0.5}\text{TiOPO}_4$ is provided by reduction of Ni$^{+2}$ to Ni$^0$, while part probably from reduction of Ti$^{+4}$ to Ti$^{+3}$, as originally expected from these materials. Reduction of both 0.5 Ni$^{+2}$ and 1 Ti$^{+4}$ explain reaction of material with 2 Li$^+$, but there still remains the question of 3$^{\text{rd}}$ Li$^+$. In order for the 3$^{\text{rd}}$ Li$^+$ to react with the material, either the Ti$^{+3}$ formed has to reduce further to Ti$^{+2}$ or P$^{+5}$ in the structure has to be reduced. The
oxygen in the structure is already in -2 oxidation state and hence cannot be reduced further. Thus to completely understand the reaction mechanism in this family of compounds, XAS measurements are considered necessary and are suggested for future work. However if one understands the complete reaction mechanism in this family of compounds, even better electrode materials could be designed.

5.5. Conclusion

It was shown in this thesis that similar to Ni$_{0.5}$TiOPO$_4$, Cu$_{0.5}$TiOPO$_4$ and Mg$_{0.5}$TiOPO$_4$ react reversibly versus lithium and that the reaction potential is dependent on the M in M$_{0.5}$TiOPO$_4$ (M = Ni, Cu, Mg). Moreover the electrochemistry is affected by the particle size of the material. However in terms of long term cycling and rate capabilities, the as synthesized samples with larger particle sizes were superior to the ball milled samples. Amongst the different studied materials, Cu$_{0.5}$TiOPO$_4$ showed most promising results in terms of electrochemistry. For the study of reaction mechanism in this family of compounds, Ni$_{0.5}$TiOPO$_4$ was chosen due to its high purity. Several analytical techniques like synchrotron XRD, SQUID measurements, $^7$Li MAS NMR, XPS measurements, etc. were employed for this purpose. It was found that lithiation results in reduction of Ni$^{+2}$ to Ni$^0$ oxidation state. Combining this with all the available information from various analytical techniques, a plausible reaction mechanism has been proposed.
Chapter 6

General conclusion and outlook
6.1. Conclusion

This thesis is subdivided into three interrelated parts; one on the development of an \textit{in situ} neutron diffraction cell for facilitating the study of reaction mechanism in materials for Li-ion batteries, other involving a study of reaction mechanism of a positive electrode material, and last one on the study of reaction mechanism of a novel negative electrode material.

For the first part, the electrode preparation for the rectangular \textit{in situ} neutron diffraction cell was first optimized. Model material Li$_4$Ti$_5$O$_{12}$ was investigated \textit{in situ} at the HRPT beamline, PSI, Villigen. This study revealed that optimizing the electrode formulation results in faster electrochemical cycling of the electrode material; however the rectangular cell design itself leads to uneven absorption of the diffracted neutron beams, rendering the Rietveld refinement of the neutron diffraction data very difficult. Moreover the large amount of electrode material (3 g) needed and long data acquisition time needed (9 h), result in large electrochemical polarization in the cell and low time resolution. Thus a circular \textit{in situ} neutron diffraction cell was developed, for use at the high intensity D20 beamline at ILL, Grenoble. This cell utilizing only 0.2-0.3 g of electrode material, resulted in better electrochemical performance. By moving to a powerful neutron source the data acquisition time was reduced down to 10-20 min, while the use of circular design allows for the Rietveld refinement over the complete 2Theta range when a deuterated electrolyte is used. Hence the circular design overcomes the problems of the rectangular \textit{in situ} neutron diffraction cell design. The first \textit{in situ} neutron diffraction measurements were successfully performed on LiFePO$_4$ model electrode material. The evolution of peaks corresponding to different phases could be qualitatively followed. Second study involving graphite, conducted using the circular cell developed with in this thesis, showed very good electrochemical performance, while presenting many peak evolutions in the \textit{in situ} neutron diffraction patterns. Thus a reliable, small, circular \textit{in situ} neutron diffraction cell capable of electrochemically cycling small amount of electrode material and delivering very good time resolution for the diffraction measurements was successfully developed.

The second part of this thesis involved investigation of structural changes occurring in Li$_{1+x}$(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_{1-x}$O$_2$ ($0 \leq x \leq 0.13$), NMC materials, when charged positive to 4.4 V vs. Li/Li$^+$. For this purpose a range of NMC materials ($0 \leq x \leq 0.10$, varied by 0.01 and $x = 0.13$) were synthesized and studied using \textit{in situ} synchrotron XRD measurements. From this study it was found that all the samples undergo similar structural changes,
showing formation of O1 phase during the 1\textsuperscript{st} charge. However the potential for detection of the O1 phase in the \textit{in situ} synchrotron XRD data was found to be lowered with increasing overlithiation content (x) in the structure. Thus more amount of O1 phase was formed at the end of 1\textsuperscript{st} charge till 5.0 V vs. Li/Li\textsuperscript{+} for more overlithiated samples. The \textit{in situ} synchrotron XRD also revealed that as the overlithiation in the sample increases, it undergoes lower volumic changes during the 1\textsuperscript{st} charge. From the \textit{ex situ} synchrotron XRD measurements on starting powder samples of stoichiometric NMC (x = 0) and two overlithiated NMC (x = 0.10 and 0.13), Li\textsubscript{2}MnO\textsubscript{3} ordering peaks were observed only for the overlithiated NMC’s indicating preferential arrangement of transition metal ions around Li\textsuperscript{+} in the transition metal slabs. These Li\textsubscript{2}MnO\textsubscript{3} ordering peaks disappeared at the end of 1\textsuperscript{st} charge as seen from \textit{ex situ} synchrotron XRD patterns, the loss of which is supposed to result in O\textsubscript{2} evolvement from the structure of layered oxide. In all the cases O1 phase peaks were detected at the end of 1\textsuperscript{st} charge, which was in accordance with the \textit{in situ} synchrotron XRD data. To understand in more detail the structural changes occurring in these types of compounds, \textit{ex situ} neutron powder diffraction was performed for overlithiated NMC (x = 0.1) at different stages of lithiation and delithiation. The Rietveld refinement of the neutron diffraction patterns revealed decrease in oxygen occupancy during the first charge, confirming the O\textsubscript{2} loss theory. The Li-Ni exchange in the structure was also seen to increase during the course of 1\textsuperscript{st} charge. Based of these observations, a reaction mechanism was proposed for the high potential charging of overlithiated (x = 0.1) NMC. It was proposed that during the course of 1\textsuperscript{st} charge, the O\textsuperscript{2-} is removed from the surface of the NMC followed by migration of M\textsuperscript{II} ions into the bulk of the material, resulting in lattice densification. This structural change also results in slippage of oxygen layers on top of each other to form the O1 phase at lower potentials. However the increased Li-Ni exchange and lattice densification render stability to the structure allowing for its better charge retention during cycling. Thus it was concluded that for use in high potential range, overlithiated NMC (x > 0) is better as a positive electrode material in terms of practical application as opposed to stoichiometric (x = 0) NMC.

On the negative side of the Li-ion cell, M\textsubscript{0.5}TiOPO\textsubscript{4} (M = Ni, Cu, Mg) was studied as a novel candidate electrode material. It was known that M\textsubscript{0.5}TiOPO\textsubscript{4} (M = Ni, Co) undergoes reaction with 3 Li\textsuperscript{+} as opposed to 1 Li\textsuperscript{+} expected from the structure, of which only 2 Li\textsuperscript{+} are reversibly cycled. Thus M\textsubscript{0.5}TiOPO\textsubscript{4} (M = Cu, Mg) were tested electrochemically and were found to react in a similar manner. The M in M\textsubscript{0.5}TiOPO\textsubscript{4} (M = Ni, Cu, Mg) was seen to affect the reaction potential of the 1\textsuperscript{st} lithiation step, however did not have drastic effect on
the reaction potential of the following cycles, which had different electrochemical profiles than the 1\textsuperscript{st} lithiation step. Of all the three samples, Cu\textsubscript{0.5}TiOPO\textsubscript{4} showed the best electrochemical performance. This was presumably due to presence of a mixture of 2 polymorphs in the material, one of which possibly has broader channels for Li\textsuperscript{+} insertion. The study of influence of the particle size on the electrochemistry of different M\textsubscript{0.5}TiOPO\textsubscript{4} (M = Ni, Cu, Mg) indicated that the as synthesized samples with larger particle size had better electrochemical performance than the smaller particles. This was probably due to the fact that lower particle size and hence larger specific surface area of the samples leads to thick and dynamic SEI formation which impedes its electrochemical performance. Of the three samples, Ni\textsubscript{0.5}TiOPO\textsubscript{4} was chosen for the study of reaction mechanism owing to the fact that it was the purest sample available. Several analytical techniques were used for the study of the reaction mechanism. The synchrotron XRD measurements revealed that the sample turns amorphous on cycling with some part still crystalline. This crystalline part is trapped in an amorphous matrix, as was evident from HRTEM images. The \textsuperscript{7}Li MAS NMR measurements confirmed that Li\textsuperscript{+} insertion in the material leads to formation of direct Li-O-Ni bond up to insertion of 1 Li\textsuperscript{+}, after which this bond is broken. The XPS measurements confirmed the reduction of Ni\textsuperscript{+2} in the structure to Ni\textsuperscript{0} on lithiation. Combining all the available information a possible reaction mechanism for lithiation and delithiation in Ni\textsubscript{0.5}TiOPO\textsubscript{4} has been proposed.

6.2. Outlook

This thesis undertook the study of different electrode materials and developed an \textit{in situ} neutron diffraction cell, which paves the way for further investigations and material development. Listed below are some suggestions for future work.

\textit{In situ} neutron diffraction cell:

- Application of the developed \textit{in situ} neutron diffraction technique to solve unknown reaction mechanisms.

- Replacing the Al/Ti sample holder for the circular cell with null matrix Ti-Zr alloy or V coated with thin layer of Ti to avoid or minimize the diffraction peaks from the sample holder respectively.
• Constructing an automatic sample changer for use at D20 beamline of ILL, Grenoble, allowing for sequential *in situ* neutron diffraction measurements using two or more circular cells.

**NMC positive electrode material:**

• Using the circular *in situ* neutron diffraction cell, developed in this thesis, to study the oxygen evolution mechanism in further detail.

• Correlating the potential for release of oxygen to the formation of O1 phase.

• Understanding the effect of varying ratio of transition metals on the electrochemistry and the reaction mechanism.

• Based on the above information, designing a better positive electrode material.

**M_{0.5}TiOPO_4 (M = Ni, Cu, Mg) negative electrode material:**

• Studying the Ni_{0.5}TiOPO_4 and Cu_{0.5}TiOPO_4 using XAS measurements to understand the changes in the oxidation state and the coordination.

• Performing ^31^P MAS NMR to understand the changes occurring in the local environment of P.

• Synthesizing Fe_{0.5}TiOPO_4, Ti_{0.25}TiOPO_4, etc. and based on their electrochemical performances, designing a mixed metal titanium oxyphosphate with better electrochemical performance.
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63. F. Rosciano, *In situ synchrotron and neutron diffraction based methods for the characterization of cathodic materials for lithium-ion batteries*, Eidgenössische Technische Hochschule (ETH) Zürich, Zürich, **2008**.


List of publications


List of oral presentations

- V. A. Godbole, J.-F. Colin, and P. Novák, *In situ* synchrotron diffraction study of stoichiometric and overlithiated NMC \( [\text{Li}_{1+x} (\text{Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3})_{1-x}] \text{O}_2 \), European Powder Diffraction Conference 12 (2010), Darmstadt, Germany.

- V. A. Godbole, C. Villevieille, H. Sommer, P. Verma, Sylvio Indris, and P. Novák, Structural and electrochemical studies of \( \text{M}_{0.5}\text{TiOPO}_4 \) (\( \text{M} = \text{Ni, Cu, Mg} \)) synthesized using modified solution route, *Lithium Batteries Discussion* (2011), Arcachon, France.

- T. Sasaki, J.-F. Colin, V. Godbole, Y. Takeuchi, Y. Ukyo, and P. Novák, Crystal structure changes during overcharge of Mg-Substituted \( \text{Li} (\text{Ni,Co,Al}) \text{O}_2 \) by *in situ* synchrotron X-ray diffraction, 15th International Meeting on Lithium Batteries (2010), Montreal, Canada.

- T. Sasaki, V. Godbole, H. Sommer, Y. Takeuchi, Y. Ukyo, and P. Novák, Structural and morphological changes of Mg-substituted \( \text{Li} (\text{Ni, Co, Al}) \text{O}_2 \) during overcharge reaction, 218th Electrochemical Society Meeting (2010), Las Vegas, U.S.A.

- J.-F. Colin, V. Godbole, and P. Novák, *In situ* neutron diffraction of \( \text{Li}_4\text{Ti}_5\text{O}_{12} \), 42nd IUPAC Congress (2009), Glasgow, U.K.
List of poster presentations

- V. Godbole J.-F. Colin, and P. Novák, *In situ* neutron and synchrotron diffraction studies of electrode materials for Li-ion batteries, 25th One Day Symposium on Topics in Electrochemistry (2009), PSI Villigen, Switzerland.

- V. Godbole J.-F. Colin, and P. Novák, *In situ* neutron and synchrotron diffraction studies of electrode materials for Li-ion batteries”, 8th PSI Summer School on Condensed Matter Research (2009), Zuoz, Switzerland.

- V. A. Godbole, C. Villevieille, H. Sommer, P. Verma, Sylvio Indris, and P. Novák, Structural and electrochemical studies of M_{0.5}TiOPO_{4} (M=Ni, Cu, Mg) synthesized using modified solution route, Lithium Batteries Discussion (2011), Arcachon, France.
# Curriculum Vitae

## Personal details

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<th>Name</th>
<th>Vikram Anil GODBOLE</th>
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## Education

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<th>Degree/ Year(s)</th>
<th>Doctor of Sciences/ 2008-2011</th>
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<tr>
<td>Advisors</td>
<td>Prof. Dr. Petr Novák and Prof. Dr. Alexander Wokaun</td>
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<td>Topic</td>
<td>Elucidating the reaction mechanism of electrode materials for Li-ion batteries using &lt;em&gt;in situ&lt;/em&gt; structural characterization</td>
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<td>Institution/Degree awarding University</td>
<td>Paul Scherrer Institute (PSI) and Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland</td>
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<td>Degree/ Year(s)</td>
<td>Erasmus Mundus European Master in `Materials for Energy Storage and Conversion´ (M.E.S.C)/ 2006-2008</td>
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<td>Degree awarding universities</td>
<td>Université Paul Sabatier, Toulouse (France), Université de Provence, Marseille (France), Warsaw University of Technology, Warsaw (Poland), Université de Picardie Jules Verne, Amiens (France), Universidad de Córdoba, Córdoba (Spain)</td>
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<td>Master thesis/ Date(s)</td>
<td>`Metal hydrides as negative materials for Li-ion batteries´ supervised by Dr. Luc Aymard and Prof. Dr. Jean-Marie Tarascon in LRCS laboratory, Amiens (France), February-September 2008</td>
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<td>Degree/ Year(s)</td>
<td>Bachelor of Science (Honours) Chemistry/ 2003-2006</td>
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<td>University of Delhi, New Delhi (India)</td>
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