Cooperative Lithium-Ion Insertion Mechanisms in Cathode Materials for Battery Applications

BY

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ABSTRACT


Understanding lithium-ion insertion/extraction mechanisms in battery electrode materials is of crucial importance in developing new materials with better cycling performance. In this thesis, these mechanisms are probed for two different potential cathode materials by a combination of electrochemical and single-crystal X-ray diffraction studies. The materials investigated are V$_6$O$_{13}$ and cubic LiMn$_2$O$_4$ spinel.

Single-crystal X-ray diffraction studies of lithiated phases in the Li$_x$V$_6$O$_{13}$ system (x=2/3 and 1) exhibit superlattice phenomena and an underlying Li$^+$ ion insertion mechanism which involves the stepwise addition of Li$^+$ ions into a two-dimensional array of chemically equivalent sites. Each successive stage in the insertion process is accompanied by a rearrangement of the Li$^+$ ions together with an electron redistribution associated with the reduction of specific V-atoms in the structure. This results in the formation of electrochemically active sheets in the structure. A similar mechanism occurs in the LiMn$_2$O$_4$ delithiation process, whereby lithium is extracted in a layered arrangement, with the Mn atoms forming charge-ordered Mn$^{3+}$/Mn$^{4+}$ layers.

Lithium-ion insertion/extraction processes in transition-metal oxides would thus seem to occur through an ordered two-dimensional arrangement of lithium ions extending throughout the structure. The lithium ions and the host structure rearrange cooperatively to form superlattices through lithium and transition-metal ion charge-ordering. A picture begins to emerge of a universal two-dimensional lithium-ion insertion/extraction mechanism analogous to the familiar staging sequence in graphite.

Key words: Li-ion battery, cathode materials, single-crystal, X-ray diffraction, delithiation, superlattice, phase transformation, charge-ordering

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Inte mycket håller mättet
bela levnadshoppet ut.
Staden med det röda slottet
är dock min till livets slut.

Bland dess gamla hus och gränder
brann mitt ljus i tio år.
Och längs Fyris fågelstränder
sökte jag min framtidens spår.

Oss kan intet hinder skilja,
vårstad än i ålderns höst,
ty en kungsängslilja
blommar ständigt i mitt bröst.

-Einar Malm
PREFACE

This thesis is a summary of the following papers, referred to in the text by their roman numerals I-V.

I. The structure of \([\text{Li}_{0.91}\text{Mn}_{0.09}]\text{Mn}_2\text{O}_4\)
   H. Björk, H. Dabkowska, J.E. Greedan, T. Gustafsson and J.O. Thomas
   *Acta Cryst.*, **C57** (2001) 331

II. Superlattice formation in the lithiated vanadium oxide phases \(\text{Li}_{0.67}\text{V}_6\text{O}_{13}\)
   and \(\text{LiV}_6\text{O}_{13}\)
   H. Björk, S. Lidin, T. Gustafsson and J.O. Thomas
   *Acta Cryst.*, **B57** (2001) 759

III. Single-crystal studies of electrochemically delithiated \(\text{LiMn}_2\text{O}_4\)
    H. Björk, T. Gustafsson and J.O. Thomas

IV. Long-range-ordering during delithiation of the \(\text{LiMn}_2\text{O}_4\) cathode material
    H. Björk, T. Gustafsson, J.O. Thomas, V. Petřiček and S. Lidin
    *Submitted to J. Mater. Chem.*

V. Cooperativity in lithium ordering across the series \(\text{Li}_x\text{V}_6\text{O}_{13}, x = 0, 2/3, 1, 2\)
   and 3
   H. Björk, T. Gustafsson and J.O. Thomas
   *In manuscript*

Papers not included in this thesis:

VI. Direct XRD observation of oxidation-state changes on Li-ion insertion into transition-metal oxide hosts
    Ö. Bergström, H. Björk, T. Gustafsson and J.O. Thomas
    *Journal of Power Sources*, **81-82** (1999) 685

VII. Direct observation of XRD redox processes in TMO’s
    H. Björk, T. Gustafsson and J.O. Thomas

VIII. High pressure structural studies of two vanadium oxides \(\text{V}_2\text{O}_5\) and \(\text{V}_6\text{O}_{13}\)
    Y. Xu, H. Björk and R. Norrestam
    *Submitted to J. Sol. State Chem.*
Specification of my contribution to the included papers:

I. Data collection; refinement; writing the manuscript

II. All experimental work except single-crystal XRD on the Li_{2/3}V_{6}O_{13} phase; refinements; writing the manuscript

III. Single-crystal synthesis; all electrochemical work; single-crystal XRD; data evaluation; writing the manuscript

IV. Single-crystal synthesis; all electrochemical work; refinement and evaluation of data together with S. Lidin; writing the manuscript

V. All experimental work on the Li_{2/3}V_{6}O_{13} and LiV_{6}O_{13} structures; deformation refinement of LiV_{6}O_{13}; internal difference deformation refinement; writing the manuscript
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1.1 The history of batteries
Electricity has fascinated the human race ever since our ancestors first witnessed lightning. In Ancient Greece, Thales observed that rubbing amber, for which the Greek word is electron, could generate an electric charge. The first evidence of batteries comes from archaeological digs in Baghdad, Iraq and is dated to around 250 B.C. The battery (Fig. 1) was probably used in simple operations to electroplate objects with a thin layer of metal. Batteries were rediscovered in the late 18th century by Luigi Galvani, who observed that when connected pieces of iron and brass were applied to frog’s legs, they caused them to twitch. Galvani thought that this effect was due to the leg tissue; what he did not realize was that he had pioneered “voltaic” electricity. The development of batteries has proceeded ever since, and some of the highlights are listed below:

Figure 1. The Baghdad battery.

- In 1799, the Italian inventor Alessandro Volta presented the first device for generating a continuous flow of electricity. Volta’s discovery of how to convert chemical energy into electrical energy has formed the basis for all modern batteries.
- The French physicist Gaston Planté invented the lead-acid storage battery in 1859.
Based on his work in France between 1867 and 1877, Georges Leclanché developed the World's first widely used battery, the dry-cell battery, also known as the zinc-carbon battery.

In 1890, Thomas Edison invented the first rechargeable nickel-iron cell.

The common nickel-cadmium (Ni-Cd) cell was invented by the Swede, Waldemar Jungner in 1899.

During the interwar years, battery performance was greatly enhanced. This was achieved through better selection of materials and methods of manufacture. Batteries are now an essential part of everyday life. They are the power source for millions of consumer, business, medical, military and industrial appliances worldwide with a continuously growing demand.

The rapidly expanding market for portable electronics has created a big demand for lightweight, high-performance, energy-storage solutions. Many of the battery concepts mentioned above contain heavy metals that are harmful for the environment, are not rechargeable, and do not provide sufficient capacity. The NiCd and NiMH batteries also have the drawback of the memory effect, which is a loss of capacity due to shallow or partial discharge. Not all active material present is cycled, which causes changes of the physical properties as well as an increase in resistance. An alternative concept is the lithium based rechargeable battery, first proposed by Armand in 1978.

Lithium ion batteries have become very popular due to the fact that they have a high capacity, are lightweight, and have reasonably high voltages (~3.7 volts (Tab. 1)). This means that less cells are needed to power today's highly demanding electronics. The main commercial usage is in consumer electronics typified by the “3C’s”; cellular phones, camcorders and portable computers.

Table 1. Comparison of different battery types and their properties.

<table>
<thead>
<tr>
<th>Battery type</th>
<th>Operating voltage (V)</th>
<th>Specific energy density (Wh/kg)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-acid</td>
<td>1.9</td>
<td>30</td>
<td>Car battery, heavy with low energy density</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>1.2</td>
<td>40</td>
<td>Environmental pollution, memory effect, lower energy density than Li-ion</td>
</tr>
<tr>
<td>Ni-MH</td>
<td>1.3</td>
<td>50</td>
<td>Memory effect, lower energy density than Li-ion</td>
</tr>
<tr>
<td>Rechargeable alkaline</td>
<td>1.4</td>
<td>80</td>
<td>No memory effect, high capacity for low-power devices</td>
</tr>
<tr>
<td>Li-ion</td>
<td>3.7</td>
<td>130-150</td>
<td>Thin, light, no memory effect, high capacity, good charge retention, expensive</td>
</tr>
</tbody>
</table>
1.2 Elementary battery concepts

A battery is an electrochemical cell that converts chemical energy into electrical energy through a reduction-oxidation (redox) reaction. There are two different types of battery: primary batteries, where the battery reaction is not reversible and hence the battery is not rechargeable; and secondary batteries, where the electrode reactions are reversible, resulting in a rechargeable battery. In the electrochemical cell reactions, the electrodes are a positive cathode and a negative anode. At the cathode, a reduction reaction occurs as the electrode accepts electrons from the outer circuit when the cell is discharged. The anode releases electrons to the outer circuit and an oxidation reaction takes place. The electrodes are separated by an electronically insulating and ionically conducting electrolyte, which serves as a transport medium for ions to travel from one electrode to the other; it also acts as a physical barrier between the electrodes to prevent short-circuiting in the cell.

The standard potential, $E_0$, of the cell is dependent on the active materials used (anode and cathode) and can be calculated from tabulated standard electrode reduction potentials as in the example below. The cell reactions can be written:

Anode: \(-Zn^{2+} + 2e^- \rightarrow Zn\) \(-0.76\) V \(1\)

Cathode: \(Cl_2 + 2e^- \rightarrow 2Cl^-\) \(1.36\) V \(2\)

Total: \(Zn + Cl_2 \rightarrow ZnCl_2\) \(2.12\) V \(3\)

The cell voltage is also dependent on other factors such as concentration and temperature. The voltage $E$ is then given by Nernst equation:

$$E = E_0 - \frac{RT}{nF} \ln \frac{[ZnCl_2]}{[Zn][Cl_2]} \quad (4)$$

Where $[X]$ denotes the chemical activity of species $X$, which is proportional to the concentration and for solid species can be approximated to 1, $R$ is the gas constant, $F$ is Faraday’s constant, $n$ the number of electrons involved in the electrode process and $T$ the absolute temperature.

The capacity of a battery is a measure of the total charge involved in the electrochemical reaction and a theoretical capacity can readily be calculated for known compounds. The capacity is given in coulombs (C), or in ampere-hours (Ah). The specific capacity is given in Ah/kg and the volumetric capacity in Ah/l. The energy density is expressed as the specific capacity $\times$ midpoint voltage, giving the unit Wh/kg. The power density is given in W/kg.
Chapter 2

THE LITHIUM-ION BATTERY

2.1 The lithium-ion battery

The lithium-ion battery concept consists of an anode and a cathode separated from one another by a non-aqueous liquid electrolyte (Fig. 2). The cathode consists of an active lithium-ion insertion/extraction compound, usually a transition-metal oxide (TMO), which acts both as an ionic and electronic conductor with a reasonably high electrode potential vs. Li/Li⁺. The anode is an active lithium-ion insertion/extraction compound either in the form of graphite, a metal alloy such as Cu₆Sn₅ or InSb or a transition metal oxide such as LiTiO₂, which all have low electrode potentials vs. Li/Li⁺. The electrolyte used is an aprotic organic electrolyte which is a good ionic conductor and electronically non-conductive. Ethylene carbonate (EC) or dimethyl carbonate (DMC), are commonly used. In the case of liquid electrolytes, a separator is used as physical barrier to prevent the cell from short-circuiting. Another option is to use a solid polymer electrolyte (SPE), e.g., a modified polyethylene oxide (PEO). A lithium salt, typically LiBF₄ or LiPF₆, is dissolved into the electrolyte to serve as charge carrier.

Figure 2. A schematic representation of the charge/discharge process in a lithium-ion battery.
When graphite is used as anode, a solid electrolyte interphase (SEI)\textsuperscript{13} is formed during the first charge. This layer is formed by a variety of solvent and salt reduction products and is necessary for the graphite anode to function properly, although it results in a capacity loss of up to \(\sim 20\\%\). Pure lithium metal has a very high theoretical capacity (3860 mAh/g) compared to 370 mAh/g for graphite and may also be used as anode. The use of metallic lithium as anode is not as commercially practical as graphite since its high reactivity with air and water implies a safety hazard. Lithium metal also has a tendency to form dendrites as lithium is re-plated during charge; this can short-circuit the cell and lead to an explosion. Dendrite formation can be prevented using a SPE. This concept is used in a lithium polymer battery.

2.2 Design considerations
The most important properties in designing a battery are energy- and power-density. As described above, a combination of materials with suitable voltages vs. Li/Li\textsuperscript{+} and high specific capacity facilitate the design of high energy-density cells with a high working potential. Other properties to consider are cyclability, shelf-life, safety, economy and environmental acceptability. In this light, research currently addresses the following specific problems:

- Reduced life-time under deep discharge.
- Irreversible capacity-loss under extreme conditions.
- Narrow operating-temperature range, \(e.g.,\) dramatic capacity drop below 0°C.
- Sensitivity to overcharge; a series-connected cell can be damaged if it reaches full charge and is then overcharged while other cells are still charging.

Electrolyte decomposition/oxidation, lithium deposition, dissolution of active material, slow kinetics, phase transformations in the active material and structural breakdown all contribute to these problems.

2.3 The scope of this thesis
Understanding lithium insertion/extraction mechanisms in battery materials is of critical importance in developing new materials with better cycling abilities. These are rather difficult to probe experimentally since they require techniques with high atomic resolution.

Much effort has been focused on structural studies of electrode materials in order to understand insertion/extraction processes on electrochemical cycling. Powder X-ray and neutron diffraction are techniques commonly used in these investigations. Since lithium is a poor X-ray scatterer, powder X-ray diffraction (XRD) often cannot give sufficiently accurate information about the lithium ions. Even neutron powder diffraction can prove inadequate in revealing subtleties in the structure;
some elements are also inaccessible to neutron diffraction studies, e.g., vanadium barely scatters neutrons at all.

Lithium-ion insertion/extraction mechanisms are studied in this thesis work for two different cathode materials for lithium-ion batteries on the basis of structural studies made by the combination of electrochemistry and single-crystal X-ray diffraction. The materials investigated are V₆O₁₃ and the cubic LiMn₂O₄ spinel. Different types of cathode material and their properties are discussed in Chapter 3.

One of the most challenging tasks in this thesis is to grow good quality single crystals of these two materials. The synthesis of V₆O₁₃ single crystals has previously been carried out successfully at our laboratory; the method is described in Chapter 4. The synthesis technique of LiMn₂O₄ single crystals has been developed in collaboration with McMaster University, Brockhouse Institute for Materials Research, Toronto, Canada and is discussed in Chapter 4 and in paper I.

Single-crystal XRD is a most powerful tool in determining the exact lithium content of different phases. As seen in papers II-IV, it can also reveal superlattice formation. Furthermore, deformation electron density refinement can give unique information about changes occurring in the oxidation state of the TMO’s during electrochemical cycling. It is thereby possible to reveal the electronic rearrangement in the structure during solid-state redox reactions, which is critically valuable information in understanding lithium-ion insertion/extraction processes. This method has been applied in paper V, and is described in detail in Chapter 4.

A compound which exhibits a wide compositional range is commonly known to form modulated structures; this is the case for LiMn₂O₄. A technique for refining incommensurate crystal structures in (3+n)-dimensional space has been used in paper IV the method is also described in Chapter 4.
Chapter 3

CATHODE MATERIALS

3.1 General structural aspects
A typical lithium-insertion material has reasonably good electronic conductivity and provides a network of pathways for the lithium ions to diffuse in and out of the structure. When discharging a Li-ion battery, lithium ions are inserted into the cathode material, whereupon the transition-metal ions are reduced. On charging, lithium ions are extracted and the transition-metal ions are reoxidised. The transition-metal provides a high redox potential vs. Li/Li$^+\), thus making it a suitable cathode material. The layered TiS$_2$ was the first cathode material used for this purpose.15 Many TMO’s have since been investigated as insertion electrodes for lithium batteries, particularly the oxides of the first-row transition-metal elements Ti, V, Mn, Fe, Co and Ni.16-18 Most of the structures have closed-packed oxygen arrays, which consist of a network of oxygen tetrahedra and octahedra. The TMO’s have either a cubic-close-packed (ccp) oxygen arrangement, where the octahedra share edges, or a hexagonal-close-packed (hcp) oxygen arrangement, where the octahedra share both faces and edges. In general, ccp arrangements are more stable since, on insertion, the lithium ions usually occupy octahedral sites, rather far from adjacent transition-metal ions thanks to the edge-sharing octahedra. In hcp structures, the lithium ions are closer due to the face-sharing octahedra which results in electrostatic interactions with the transition-metal ions, and in a shearing towards ccp packing.

3.2 Comparison of different structure types
There are two types of host structure commonly used as cathode material: a two-dimensional layered structure or a three-dimensional framework structure (Fig. 3). Both structures types generally have a 3d transition-metal in a six-fold MO$_6$ octahedron. LiNiO$_2$ and LiCoO$_2$ are two interesting cathode materials with the layered rock-salt structure.19,20 Because of its simple synthesis route and high capacity, LiCoO$_2$ is the most common cathode material used in the lithium-ion battery industry today, usually with a high degree of Ni-doping. LiNiO$_2$ is cheaper and has a higher capacity, but is less stable and therefore more difficult to synthesise. A drawback with these structures, however, is that the different cations, alkaline metal and transition-metal occupy alternate oxygen layers. Removal of lithium on charging causes an increased electro-repulsive force between the oxygen layers, causing a large expansion of the structure in the $c$-direction. This also leads to an irreversible migration of the transition-metal ion into the former lithium site. In the fully charged state, all lithium ions are removed and the strong electro-repulsive force between the adjacent oxygen layers convert the structure irreversibly
into a CdCl₂ structure. Moreover, Co⁴⁺ and Ni⁴⁺ cations in fully charged CoO₂ or NiO₂ are chemically unstable.

Figure 3. The most common host structures for lithium insertion. a) The two-dimensional layered structure LiCoO₂. b) The three-dimensional cubic spinel structure LiMn₂O₄.

The three-dimensional framework oxides commonly have both lithium and transition-metal ions occupying the same layer, implying that, in a fully charged state, transition-metal ions always interleave each oxygen layer, giving an effective shielding against electro-repulsion between oxygens. These three-dimensional structures usually expand isotropically, in contrast to the anisotropic expansion occurring in the two-dimensional layered structures.

Two different types of framework oxide are commonly studied as possible cathode materials. One is the lithium-free transition-metal oxide such as V₆O₁₃, V₂O₅, and MnO₂. A drawback with these materials, however, is that they are best used in combination with a lithium-metal source and thus only suitable for Li-polymer batteries. The other type of framework oxide carries its own source of lithium, e.g., LiMn₂O₄, LiV₄O₁₁,²¹⁻²³ and LiMPO₄ (M=Fe, Mn and Co),²⁴⁻²⁶ which may be used in Li-ion battery concepts.

3.3 V₆O₁₃ - structural aspects in a battery context

There are a wide variety of vanadium oxide materials, all with open framework structures. The differences between the structures lie in the arrangement of coordination polyhedra.²⁷ Due to the variety of vanadium oxidation-states and
their redox properties, these materials have attracted much interest as possible cathode materials for secondary lithium batteries; V$_2$O$_5$, LiV$_3$O$_8$ and V$_6$O$_{13}$ are the most commonly studied for this purpose. Other vanadium oxides are interesting for their role in oxidative catalysis.

In 1979, Murphy et al. first suggested the use of V$_6$O$_{13}$ as a possible cathode material. The structure can be described in terms of two alternating layers of VO$_6$ octahedra, one single-layer at z=0 and one double-layer at z=0.5. The two layers are connected by corner-sharing oxygens (Fig. 4). The structure is charge-ordered and contains three unique vanadium atoms: the V1 atom has oxidation state 4+ and is located in the single-layer; the V2 (5+) and V3 (4+) atoms are situated within the double-layer. The space-group is C2/m.

Figure 4. The crystal structure of V$_6$O$_{13}$ viewed along the b-axis.

The discharge curve for a V$_6$O$_{13}$-based cathode vs. Li/Li$^+$ shows several quasi-vertical sections (Fig. 5), each corresponding to a discrete lithiated phase, Li$_x$V$_6$O$_{13}$. Between these regions, plateau-like sections occur which correspond to two-phase regions. The voltage for a V$_6$O$_{13}$ electrode vs. Li/Li$^+$ is 2.85 V. The theoretical capacity is 860 Wh/kg, based on eight lithium ions being inserted into the cathode; the practical capacity is ~70 % of this value. There are still doubts concerning the maximum amount of lithium inserted; suggestions range from x=6 to 8.
3.4 LiMn$_2$O$_4$ - structural aspects in a battery context

The wide range of possible oxidation states of Mn (II-VII) provides the possibility of forming an immense number of Li-Mn-O phases (Fig. 6). The phases of interest for the use as cathode materials in batteries comprise the Mn$^{4+}$/Mn$^{3+}$ redox couple. These phases are located within the triangle of the Li$_x$Mn$_{2x}$O$_3$-LiMn$_2$O$_4$-MnO$_2$ tie-lines. Compounds within this region have long been investigated as possible cathode materials for Li-ion batteries.

LiMn$_2$O$_4$ is one of the most interesting; it has a spinel structure and is both a cheap and environmentally friendly material. The structure is cubic (Fd-3m) with a
cubic-close-packed oxygen array. Mn ions occupy the octahedral (16d) sites and Li ions the tetrahedral (8a) sites (Fig. 7). Together these atoms form intermixed layers, connecting the oxygen layers, which are perpendicular to the <111> direction.

Figure 7. Stereo-view of the cubic spinel structure LiMn$_2$O$_4$.

The MnO$_6$ octahedra are edge-shared and form a continuous three-dimensional array, which is very stable. Of the possible vacant positions the Li (8a) site is furthest away from the (16d) site, which also accounts for the stability of the spinel. Lithium ions diffuse in and out of the structure via the open framework of linked tetrahedral (8a) sites and octahedral (16c) sites. The average manganese oxidation-state is 3.5+, i.e. there are equal numbers of Mn$^{3+}$ and Mn$^{4+}$ ions, although the structure would not seem to be charge-ordered at room temperature. The charge/discharge range extends from the fully charged $\text{O}^-$-MnO$_2$ phase, in which the composition is $\sim$Li$_{0.6}$Mn$_2$O$_4$, to the Li$_x$Mn$_2$O$_4$ phase, which has a rock-salt structure. The range used in battery applications is the two-plateau region corresponding to the composition 0.27$<x<$1 in Li$_x$Mn$_2$O$_4$ at $\sim$3.9-4.2 V (Fig. 8).

Figure 8. The discharge curve for a $\text{Li} \mid \text{Li}^{+}$ cell.
The two plateaus are separated by 100-150 mV at a composition \( \text{Li}_0.5\text{Mn}_2\text{O}_4 \). The reason for this potential step has been studied extensively.\(^{43-45}\) Ohzuku et al. were the first to speculate about long-range lithium ordering.\(^{46}\) Synchrotron XRD studies have shown evidence for a discrete phase in the material occurring at the voltage step at 4.1 V \( \text{vs.} \) Li/Li\(^+\).\(^{47}\) Recent \(^6\)Li and \(^7\)Li NMR studies show results that confirm lithium environments related to charge-ordering in the material during charge.\(^{48}\) The first evidence for superlattice formation can be found in paper III.

Additional features have been observed below room temperature. Cubic \( \text{LiMn}_2\text{O}_4 \) transforms to a distorted orthorhombic phase at 290 K.\(^{49,50}\) At 230 K, the structure acquires an orthorhombic \( 3 \times 3 \times 1 \) superstructure with five independent Mn sites, in which two sites are well-defined Mn\(^{4+}\) ions and the other three Mn sites are mixed valence Mn\(^{3+}/\text{Mn}^{4+}\) sites.\(^{51}\)

In the lower voltage region, a Jahn-Teller (J-T) distortion occurs when lithium is inserted into the spinel \( \text{LiMn}_2\text{O}_4 \) to form \( \text{Li}_2\text{Mn}_2\text{O}_4 \). The average manganese oxidation-state decreases, \( i.e. \) the fraction of Mn\(^{3+}\) ions increases. These ions have a \( \text{d}^4 \) electron configuration, which stabilises the J-T distortion. The \( e_g \) (\( \text{d}^{\uparrow\uparrow} \)) and \( e_g \) (\( \text{d}^{\downarrow\downarrow} \)) orbitals have the same energy and are orbitally degenerate, \( i.e. \) the single electron in the \( e_g \) state may occupy either one. The complex will then distort to remove the degeneracy and achieve a lower energy. Most commonly the electron occupies the \( e_g \) (\( \text{d}^{\uparrow\downarrow} \)) orbital, resulting in an elongation of two axial bonds and the compression of the four bonds in a plane (Fig. 9).

**Figure 9.** Jahn-Teller distortion of the \( \text{d}^4 \) electron configuration for \( \text{LiMn}_2\text{O}_4 \).
The Li$_2$Mn$_2$O$_4$ crystal structure becomes tetragonal with a $c/a$ ratio of 1.16. This $c/a$ ratio is commonly used as a measure of the magnitude of the J-T distortion, which is, in turn, directly coupled to the average manganese oxidation state. This large difference in cell axes results in a great deal of strain in the material, which has a negative effect on the cycling capacity.

Another disadvantage of the material is the fact that the manganese slowly dissolves into the electrolyte through the disproportion reaction:

$$2 \text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$$ (5)

The extent of spinel dissolution is dependent on the acidity of the electrolyte, and the choice of solvent and salt. Doping of the spinel structure with various transition metals or with excess lithium Li$_{1-x}$Mn$_{2-x}$O$_4$, $0<x<0.33$ has shown to decrease Mn dissolution.

Substitutions of Mn$^{2+}$ ions into the tetrahedral (8a) site occur during synthesis of LiMn$_2$O$_4$, if the temperature is too high. The ideal synthesis temperature for LiMn$_2$O$_4$ powder samples has been found to be slightly above 800 °C. At higher temperatures, a number of different phases may be obtained with varying degrees of Mn$^{2+}$ substitution into the (8a) site. The Mn$^{2+}$ ions on the tetrahedral site lower the manganese oxidation state in the octahedral site to (3+), causing a J-T distortion. Substitution of all of the lithium ions in LiMn$_2$O$_4$ by Mn$^{2+}$ ions results in hausmannite Mn$_3$O$_4$ with $c/a=1.16$. 
Chapter 4

METHODS

4.1 Synthesis of single-crystal V$_6$O$_{13}$
Synthesis of V$_6$O$_{13}$ single-crystal was performed by chemical vapor transport (CVT), using a mixture of phase pure V$_6$O$_{13}$ powder and TeCl$_4$ (Merck, as received), which acts as transport agent, in a mass ratio 20:1. The mixture was placed in one end of a silica tube, which was sealed under vacuum. The tube was placed in a furnace in a temperature zone of 670-650 °C, creating a gradient of 20 °C; crystals were obtained in the low-temperature end of the tube after ca. three weeks. The crystals so obtained were black, needle-shaped and of approximate size 0.1 × 0.1 × 0.4 mm.

4.2 Synthesis of single-crystal LiMn$_2$O$_4$
Crystals of LiMn$_2$O$_4$ were synthesized by a flux method, using a 1:10 mixture of LiCl (BDH, 99%) and LiBO$_2$ (Alfa, 99%), where the LiBO$_2$ provides a seal against the atmosphere. A mixture of MnO (Aesar, 99.5%) and MnO$_2$ (Baker, 99.5%) was used to maintain the average manganese oxidation-state at 3.5+. The mixture was heated to 880 °C in a Pt-crucible, for 4 h and then slowly cooled at 0.7 °C/h to 850 °C, where the crystals were separated by a hot-pouring process. The crystals were black and had an octahedral shape measuring ca. 0.2 × 0.2 × 0.2 mm.

4.2.1 Synthesis optimization
The synthesis of LiMn$_2$O$_4$ spinel single crystals involved optimization of following parameters:

- Ratio of start materials
- Temperature
- Cooling rate

Various ratios of Mn$^{2+}$: Mn$^{4+}$ materials were tried and a 1:3 molar ratio, giving the average Mn oxidation state +3.5 was found to be a good starting point. Syntheses using pure LiMn$_2$O$_4$ powder as start material also gave satisfying results.

The temperature showed to have greatest influence on the result. Crystals synthesized in the range 910-980 °C all showed some amount of J-T distortion due to the substitution of Mn$^{2+}$ ions into the tetrahedral 8a site. One of these compounds synthesized at 980 °C is described in paper I. Syntheses performed at 880 °C showed satisfying result, but this seems to be the lowest useable
temperature. Below 880 °C no crystals were obtained. The cooling rate affects the size of the crystals and a rate of 0.7 deg/h gave nicely grown crystals with a size of \( \sim 0.2 \times 0.2 \times 0.2 \) mm. The single-crystals were black and octahedral shaped and can be seen in Fig. 10.

![Image 10](image)

Figure 10. Scanning electron microscope picture of a LiMn\(_2\)O\(_4\) single crystal.

These single crystals were of the composition LiMn\(_2\)O\(_4\) according to the refinements of single crystal XRD data described in paper IV. One drawback with the crystals is that most of them are twinned and must be cut before use.

4.3 Electrochemical lithiation/delithiation of single-crystals

The single crystals were examined by single-crystal XRD to assure their quality, and then incorporated into the composite cathode of a \(<\text{Li} \mid \text{liq. electrolyte} \mid \text{TMO}\>\) “coffee-bag” type cell in which the TMO had the same composition as the single crystal. Electrochemical lithiation/delithiation of the single crystals was achieved by the selection of a suitable voltage and careful charge/discharge, controlled by a MacPile II\® potentiostat. The potential was changed in steps of ±10mV when the current density had fallen to \( \sim 1 \) \( \mu \)A/cm\(^2\). Using this method, known as electrochemical voltage spectroscopy (EVS), the cell is maintained close to electrochemical equilibrium during the entire discharge.\(^{65}\) The cells were mainly maintained at a slightly elevated temperature (ca. 35 °C) in order to enhance reaction kinetics and lithium-ion diffusion during electrochemical cycling. The resulting single crystals were recovered from the cathode and mounted on an X-ray goniometer.
4.4 Single-crystal X-ray diffraction

X-rays interact with the electrons of the atoms of a crystal during the diffraction process. Constructive interference occurs in a material as Bragg’s law is fulfilled according to:

\[ 2d \sin \theta = n\lambda \]  
\[ (6) \]

A general expression for the measured intensity for reflection H is:

\[ I_H = k I_0 \ LPTE \ |F_H|^2 \]  
\[ (7) \]

Where \( I_0 \) is the intensity of the incident beam, \( k \) is a constant, \( L \) is the Lorentz factor, \( P \) the polarization factor, \( T \) the transmission factor, and \( E \) the extinction coefficient. \( |F_H| \) is the structure factor for reflection H (=h, k, l).

Since no physical lens can focus the X-rays, a mathematical lens in the form of a Fourier synthesis is used to obtain the electron density. The electron density at any point in the cell \( \rho(x, y, z) \) is then given by the Fourier summation:

\[ \rho(x,y,z) = \frac{1}{V_c} \sum_{h+k+l=0} F_{hkl} \exp[-2\pi i(hx + ky + lz)] \]  
\[ (8) \]

\( V_c \) is the volume of the unit-cell and \( F_{hkl} \) is the structure factor for the (h, k, l) reflection. Only the modulus of the structure factor \( |F_{hkl}| \) can be obtained from the diffraction intensities. The phase information is lost in the diffraction process. Hence, no information can be obtained about the atomic positions. This is generally referred to as the crystallographic phase problem. There are several methods for obtaining the associated phase angle, e.g., direct methods, the Patterson method, and the heavy-atom method. If the structure to be solved closely resembles an already known structure, its coordinates can be used as a start model. Once a reliable model has been found, differences between the observed and the calculated structure factors can be minimized in a least-squares refinement procedure. In each refinement cycle a residual (R) is calculated, as a measure of the fit:

\[ R = \frac{\sum |F_{obs}| - |F_{calc}|}{\sum |F_{obs}|} \]  
\[ (9) \]

In this thesis, all structures solved were closely related to existing known structures. Refinements were performed using either the program DUPALS or JANA2000.
4.4.1 Deformation electron density refinement
Accurate determination of the electron density distribution is of importance in several scientific areas, e.g., for the study of electronic structures of metals and alloys, metal-ligand interactions and variations of solid-state properties with temperature. Calculation of structure factors normally involves the use of spherically symmetric terms. This neglects any non-spherical electron distribution, and the error incurred is absorbed into the structural parameters, mainly the thermal displacement factors but also the atomic coordinates. To treat this problem in a more satisfactory way, Hirshfeld introduced a non-spherical electron distribution description into the refinement procedure, where the adjustable parameters describe departures from a spherical atomic charge distribution. The atom charge density may then be described as:

\[ \rho_{\text{atom}}(r) = \rho_{\text{core}}(r) + \rho_{\text{valence}}(r) + \rho_{\text{def}}(r) \]  

(10)

Where \( \rho_{\text{core}} \) and \( \rho_{\text{valence}} \) are the spherically symmetric terms, and \( \rho_{\text{def}} \) is the non-spherical distortion resulting from bond formation. The deformation density term is described by a linear combination of functions centered on the nuclei, such that the charge deformation is expanded in terms of a fixed basis of density functions whose coefficients are the variable parameters. The linear combination can be expressed as:

\[ \rho_{\text{def}}(r) = \sum_i c_i \rho_i \]  

(11)

Where \( c_i \) are the coefficients to be determined and \( \rho_i \) are the smoothly varying electron deformation functions. These functions are related to spherical harmonics and consist of a radial and an angular function. The angular functions have the general form \( \cos^n \theta \) where \( n = 0, 1, 2, 3, \ldots \), and \( \theta \) is defined in relation to a set of \( (n+1)(n+2)/2 \) polar axes. The radial functions have the form:

\[ R_n(r) = r^n e^{-JR} \]  

(12)

where \( r \) is the distance from the atom centre and \( \gamma \) is a constant. The deformation density can then be expressed as:

\[ \rho_{\text{def}}(r) = \sum_{n,k} c_{n,k} R_n(r) \cos^n \theta_k \]  

(13)

where \( \rho_{n,k}(r) = N_n r^n e^{-Jr} \cos^n \theta_k \) and \( N_n \) is a normalization factor.

The deformation refinements made in these studies involve \( n = 0, 1 \) and \( 2 \) for all atoms, which corresponds to spherical, linear and quadratic deformation terms.
METHODS

Local coordinate systems for the deformation functions are defined individually for each atom. The radial charge distribution parameter, \( \gamma \), for each atom has previously been optimized empirically to 4.0.

4.4.2 Refinement of modulated structures
Structure refinement are normally based on a set of Bragg reflections \((h, k, l)\) where \(h, k\) and \(l\) are integers. This is based on the assumption that the structure possesses a strictly 3-dimensional periodicity. The presence of periodic distortions (modulations) is revealed by the occurrence of superlattice reflections, which are regularly distributed within the diffraction pattern. If these reflections can be labelled by rational indices in terms of the original reciprocal basic lattice, the structure is commensurate and creates a superstructure of the basic cell. If the superlattice reflections correspond to non-rational indices, this implies that the periodic distortions are incommensurate with the translation periods of the basic structure.

Modulated structures consist of two parts: the underlying average structure and a modulation thereof. The nature of the modulation can be positional, occupational or mixed positional and occupational in character, and can be described by one or more linearly independent primary modulation wave-vectors \( \mathbf{q}_1, \mathbf{q}_2, \ldots, \) etc. Depending on the number of wave-vectors needed, a modulated 3-dimensional structure can be described in \((3+n)\) dimensions, where \(n = 1, 2\) or 3. A schematic representation of two types of a modulated 1-dimensional structure can be seen in Fig. 11.

In this work, various compounds of the \( \text{Li}_x\text{Mn}_2\text{O}_4 \) structure are found to be modulated, and the modulation can be described by adding a single modulation vector \( \mathbf{q} \). The 3-dimensional material can then be described using four indices \(hklm\), forming a \((3+1)\)-dimensional superspace. A \((3+1)\)-dimensional reciprocal lattice is obtained which is related to the physical structure. To illustrate a modulated structure, the information obtained from higher-dimensional reciprocal space must be transformed back into 3-dimensional real space. Fourier maps are thus defined by a combination of one physical axis \((x, y\) or \(z))\) and the internal axis, \(t\), which describes the modulation.
4.5 Bond valence calculations
The bond valence of an atom in a compound can be calculated using the experimentally obtained bond lengths. Comparing tabulated empirical values of bond distances with measured bond distances for a certain pair of atoms yields a valence distribution for that particular bond. The valence contributions are added to give the approximate oxidation state of the central atom.\(^{72}\)

The technique can thus be used to determine oxidation states and partial occupancies of atomic sites. The method is applicable to all substances that show some degree of ionic bonding, but not to metallic solids or organic molecules. A realistic condition on using the method is that the experimentally measured bond length should have accuracy better than 0.05 Å. In this work, bond valence calculations were performed using the software VaList\(^{73}\) to show possible charge-ordering in the TMO structures.
LITHIUM INSERTION MECHANISM IN V$_6$O$_{13}$

Several different lithium insertion processes into V$_6$O$_{13}$ can be imagined. One possibility is a continuous insertion of lithium ions creating a disordered Li$_x$V$_6$O$_{13}$ material. This would result in a homogeneity region from $x=0$ to $x=6$ or 8. However, the step-wise shape of the discharge curve does not support this idea as it consists of several quasi-vertical sections corresponding to discrete lithiated phases as discussed previously (Fig. 5). The form of the discharge curve would rather indicate that the lithium insertion process involves the formation of discrete, ordered Li$_x$V$_6$O$_{13}$ phases with phase boundaries moving through the particles during lithium insertion. If we consider the structural arrangement of the unlithiated material with space group C2/m and $Z=2$, insertion of lithium ions into a general position would create the composition Li$_4$V$_6$O$_{13}$. Insertion of lithium ions into a 4-fold special site creates the Li$_2$V$_6$O$_{13}$ structure as has been shown in previous studies. As seen in the discharge curve, discrete phases exist with lower lithium content. Several different ways of forming these phases can be envisaged. If lithium ions occupied a 2-fold special site (which corresponds to positions within the V-O layers), this would lead to the composition LiV$_6$O$_{13}$. Another way would be for the structure to lose symmetry by going, for example, to the space group P2/m, C2 etc. A third possibility would be to create a larger unit-cell. If the unit-cell dimensions were, e.g., doubled in the $a$ or $c$-direction and the space group maintained, then the 2-fold symmetry element would occur more seldom in space and the structure would acquire more formula units in its cell. If we consider a doubling of the unit-cell (to give $Z=4$), lithium occupation at a 4-fold site then would give the composition LiV$_6$O$_{13}$. The way these new phases are formed is addressed in this chapter.

5.1 Superstructure formation

The structures of Li$_{2/3}$V$_6$O$_{13}$ and LiV$_6$O$_{13}$ obtained from single-crystal X-ray diffraction data of electrochemically lithiated samples (paper I) both reveal superlattice formation. The structure of Li$_{2/3}$V$_6$O$_{13}$ has a tripled unit-cell volume compared to the original V$_6$O$_{13}$, and the LiV$_6$O$_{13}$ structure corresponds to a unit-cell doubling, the cell parameters can be seen in Tab. 2.
Table 2. Cell parameters for the $x = 0$, 2/3 and 1 structures of $\text{Li}_x\text{V}_6\text{O}_{13}$.

<table>
<thead>
<tr>
<th>$x$ in $\text{Li}_x\text{V}<em>6\text{O}</em>{13}$</th>
<th>$a$ /Å</th>
<th>$b$ /Å</th>
<th>$c$ /Å</th>
<th>$\beta$ °</th>
<th>$V$ /Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.920 (1)</td>
<td>3.6786 (4)</td>
<td>10.140 (1)</td>
<td>100.88 (1)</td>
<td>436.63 (6)</td>
</tr>
<tr>
<td>2/3</td>
<td>21.848 (2)</td>
<td>3.6904 (3)</td>
<td>17.245 (2)</td>
<td>105.01 (1)</td>
<td>1343.0 (2)</td>
</tr>
<tr>
<td>1</td>
<td>21.955 (10)</td>
<td>3.686 (2)</td>
<td>11.850 (6)</td>
<td>110.66 (1)</td>
<td>897.3 (8)</td>
</tr>
</tbody>
</table>

The $\text{V}_6\text{O}_{13}$ structural host remains virtually intact in both structures with its alternating single- and double-layers of $\text{VO}_6$ (Fig. 12). The formation of the superstructures requires three times and twice as many atoms in their respective unit-cells compared to the original $\text{V}_6\text{O}_{13}$ structure. All these atoms can be related to atoms in the original $\text{V}_6\text{O}_{13}$ cell (except for the lithium ions). Hence, in the $\text{Li}_{2/3}\text{V}_6\text{O}_{13}$ structure, there are three vanadium atoms (labelled $\text{V}_{11}$, $\text{V}_{12}$ and $\text{V}_{13}$) related to the atom labelled $\text{V}_1$ in $\text{V}_6\text{O}_{13}$, three related to $\text{V}_2$ etc. In the $\text{LiV}_6\text{O}_{13}$ structure, two atoms occur of each type, labelled in an analogous way. Both structures have the monoclinic space-group $\text{C2/m}$, although the directions of the $a$- and $c$-axes differ. The lithium ions coordinate to oxygens in the single-layer and to the corner sharing oxygens in the single- and double- layers. The lithium ions distribute regularly throughout the structure in fully occupied, chemically equivalent sites, with five-fold oxygen coordination in tetragonal pyramids; Li-O distances lie in the range 1.95-2.35 Å for $x=2/3$, and 1.97-2.35 Å for $x=1$.

Figure 12. The structures of a) $\text{Li}_{2/3}\text{V}_6\text{O}_{13}$ and b) $\text{LiV}_6\text{O}_{13}$. The double V-O layers are shaded in grey.
The V2 coordination in the original V$_6$O$_{13}$ structure includes one short V-O bond at 1.65 Å.$^{13}$ This bond is typical for V$^{5+}$-O coordination but also exists for the V$^{4+}$ coordination and is described as a vanadyl bond, usually considered as a double bond.$^{13}$ As previously seen by difference deformation density studies of the Li$_x$V$_6$O$_{13}$ structure, the V2 atom undergoes a reduction from 5$^+$ to 4$^+$ as lithium ions are inserted.$^{14}$ This reduction can also be seen in the elongation of the previously short vanadyl V2-O5. For each of the new structures, corresponding V2X-O5X bond in one of the V2-O octahedra is significantly elongated compared to the original V$_6$O$_{13}$ structure. This is indicative of a reduction from V$^{5+}$ to V$^{4+}$ for the V23 atom in the x=2/3 structure, and for the V21 atom in the x=1 structure. Bond lengths for all V2X atoms can be seen in Tab. 3, where the V2X-O5X bonds are marked with bold text.

Table 3. Bond lengths for the V2X-O coordination octahedra for x=0, 2/3 and 1 in Li$_x$V$_6$O$_{13}$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length V$<em>6$O$</em>{13}$ (Å)</th>
<th>Bond</th>
<th>Bond length Li$_{2/3}$V$<em>6$O$</em>{13}$ (Å)</th>
<th>Bond</th>
<th>Bond length Li$_x$V$<em>6$O$</em>{13}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V2-O5</td>
<td>1.6489(5)</td>
<td>V21-O52</td>
<td>1.666(3)</td>
<td>V21-O51</td>
<td>2.030(1)</td>
</tr>
<tr>
<td>V2-O7</td>
<td>1.7581(5)</td>
<td>V21-O72</td>
<td>1.770(4)</td>
<td>V21-O72</td>
<td>1.842(1)</td>
</tr>
<tr>
<td>V2-O2</td>
<td>1.9014(2)</td>
<td>V21-O23</td>
<td>1.899(1)</td>
<td>V21-O22</td>
<td>1.879(1)</td>
</tr>
<tr>
<td>(x2)</td>
<td></td>
<td>(x2)</td>
<td></td>
<td>(x2)</td>
<td></td>
</tr>
<tr>
<td>V2-O3</td>
<td>2.0856(5)</td>
<td>V21-O32</td>
<td>2.044(4)</td>
<td>V21-O31</td>
<td>2.055(1)</td>
</tr>
<tr>
<td>V2-O7</td>
<td>2.2811(5)</td>
<td>V21-O71</td>
<td>2.396(6)</td>
<td>V21-O71</td>
<td>1.897(1)</td>
</tr>
<tr>
<td>V22-O51</td>
<td></td>
<td>V22-O52</td>
<td>1.652(3)</td>
<td>V22-O52</td>
<td>1.662(1)</td>
</tr>
<tr>
<td>V22-O71</td>
<td>1.754(5)</td>
<td>V22-O21</td>
<td>1.904(1)</td>
<td>V22-O21</td>
<td>1.894(1)</td>
</tr>
<tr>
<td>(x2)</td>
<td></td>
<td>(x2)</td>
<td></td>
<td>(x2)</td>
<td></td>
</tr>
<tr>
<td>V22-O31</td>
<td>2.096(4)</td>
<td>V22-O32</td>
<td>2.036(1)</td>
<td>V22-O32</td>
<td>2.036(1)</td>
</tr>
<tr>
<td>V22-O72</td>
<td>2.284(5)</td>
<td>V22-O72</td>
<td>2.323(4)</td>
<td>V22-O72</td>
<td>2.323(4)</td>
</tr>
<tr>
<td>V23-O21</td>
<td>1.882(9)</td>
<td>V23-O33</td>
<td>2.069(4)</td>
<td>V23-O33</td>
<td>2.069(4)</td>
</tr>
<tr>
<td>(x2)</td>
<td></td>
<td>(x2)</td>
<td></td>
<td>(x2)</td>
<td></td>
</tr>
</tbody>
</table>

Bond valence calculations for the V2 atoms in the structures confirm the reduction of these atoms. The coordination polyhedra for all V2 atoms in the x=2/3 structure can be seen in Fig. 13. The V21 and V22 polyhedra for the x=1 structure show similar coordination.
Figure 13. VO₆ octahedra in the Li₂/₃V₆O₁₃ structure for a) the V21 atom b) the reduced V23 atom, and c) the V22 atom.

O5 is the corner-sharing oxygen between the V1 and V2 octahedra. The elongation of the V2-O5 bond causes a contraction of the V1-O5 bond, which forms a vanadyl bond instead; V13-O53=1.624(4) Å for x=2/3 and V11-O51=1.619(1) Å for x=1, compared to 1.972(1) Å in the original V₆O₁₃ structure. At the same time, the V13-O42 bond is elongated from 1.764(1) Å in V₆O₁₃ to 1.955(3) Å in x=2/3, corresponding behavior can be seen for x=1. To compensate for the short vanadyl bond the coordination changes from octahedral to square pyramidal (Fig. 14), with V13-O62 distance 2.775(4).

Figure 14. Coordination polyhedra for a) V1 in V₆O₁₃ and b) V13 in Li₂/₃V₆O₁₃.

The relaxation of the vanadyl bonds in the reduced vanadium coordination polyhedra causes the reduced vanadium atoms to approach one another and form a metal-metal bond with bond lengths 2.542(1) Å and 2.546(1) Å for the x=2/3 and...
x=1 structures, respectively. By applying the unit-cell transformation described in paper V, the orientation corresponding to the original V₆O₁₃ cell can be obtained (Tab. 4).

Table 4. Cell parameters for the x=0, 2/3 and 1 structures of LiₓV₆O₁₃ transformed to correspond to the V₆O₁₃ orientation.

<table>
<thead>
<tr>
<th>x in LiₓV₆O₁₃</th>
<th>a /Å</th>
<th>b /Å</th>
<th>c /Å</th>
<th>β°</th>
<th>V /Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0*</td>
<td>11.920(1)</td>
<td>3.6786(4)</td>
<td>10.140(1)</td>
<td>100.88(1)</td>
<td>436.63(6)</td>
</tr>
<tr>
<td>2/3</td>
<td>35.729 (2)</td>
<td>3.6904 (3)</td>
<td>31.143 (3)</td>
<td>101.14 (1)</td>
<td>4029.0 (6)</td>
</tr>
<tr>
<td>1</td>
<td>11.850 (6)</td>
<td>3.686 (2)</td>
<td>20.950 (10)</td>
<td>101.30 (1)</td>
<td>897.3 (8)</td>
</tr>
</tbody>
</table>

*Cell parameters from ref 14.

After dividing these transformed c-axes by three and two, respectively, a smooth expansion can be seen in the c-axis for the x=0, 2/3, 1 and 2 structures followed by a sharp decrease for x=3 (Fig. 15). This smooth expansion can well explain the good cyclability of V₆O₁₃; the small stepwise expansion of the cell axes reduces the strain during cycling.

Figure 15. The length of the c-axis in LiₓV₆O₁₃ for x=0, 2/3, 1, 2 and 3.
5.2 Deformation density for LiV$_6$O$_{13}$

The deformation electron densities for all six independent vanadium atoms in the LiV$_6$O$_{13}$ structure all have the similar dumb-bell shaped appearance, with regions of electron deficiency extending in the $<10\bar{1}>$ direction (Fig. 16).

Figure 16. Deformation electron density map for LiV$_6$O$_{13}$ at $y=0$ in the $ac$-plane. Contour intervals at 0.05 $e/\AA^3$; negatively charged regions are drawn as solid lines; positive regions are dashed.

The oxygen atoms generally show electron excess in the $c$-direction, except for the O5X and O6X atoms, which show electron excess in the direction of the bonds between the layers i.e. perpendicular to the V-O layers. The O12 exhibits some dipolar character. The effective ionic charges on the atoms are given in Tab. 5.

The pairs of independent atoms associated with one atom in the V$_6$O$_{13}$ structure are separated into two groups: one group relates to the unliitted V$_6$O$_{13}$ structure (group 2), while the other is influenced by lithium insertion (group 1).
Table 5. Ionic charges associated with the refined internal charge deformation model in LiV₆O₁₃.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge (group 1) /e</th>
<th>Charge (group 2) /e</th>
<th>Charge “group 1-group2” /e</th>
</tr>
</thead>
<tbody>
<tr>
<td>V11, V12</td>
<td>0.68</td>
<td>0.68</td>
<td>0.0</td>
</tr>
<tr>
<td>V21, V22</td>
<td>0.55</td>
<td>0.66</td>
<td>-0.11</td>
</tr>
<tr>
<td>V31, V32</td>
<td>0.70</td>
<td>0.66</td>
<td>+0.04</td>
</tr>
<tr>
<td>O11, O12</td>
<td>-0.30</td>
<td>-0.22</td>
<td>-0.08</td>
</tr>
<tr>
<td>O21, O22</td>
<td>-0.58</td>
<td>-0.49</td>
<td>-0.09</td>
</tr>
<tr>
<td>O31, O32</td>
<td>-0.32</td>
<td>-0.20</td>
<td>-0.12</td>
</tr>
<tr>
<td>O4</td>
<td>-0.32</td>
<td>-0.32</td>
<td>0.0</td>
</tr>
<tr>
<td>O51, O52</td>
<td>-0.32</td>
<td>-0.25</td>
<td>-0.07</td>
</tr>
<tr>
<td>O61, O62</td>
<td>-0.27</td>
<td>-0.27</td>
<td>0.0</td>
</tr>
<tr>
<td>O71, O72</td>
<td>-0.24</td>
<td>-0.45</td>
<td>+0.21</td>
</tr>
<tr>
<td>Li</td>
<td>0.17</td>
<td>-</td>
<td>0.17</td>
</tr>
</tbody>
</table>

5.2.1 Difference deformation density for LiV₆O₁₃

Since the LiV₆O₁₃ structure is described in terms of two independent atoms for each original V₆O₁₃ atom, it is possible to compare the electron distribution between pairs of atoms, which are equivalent in the V₆O₁₃ structure. The electron redistribution resulting from lithium insertion into V₆O₁₃ is given by the “difference” deformation electron density, where the refined coefficients, cₙ,k, for the two independent atom-pairs in the LiV₆O₁₃ structure are subtracted from one another term-by-term.

The difference deformation electron density map in Fig. 17 shows a redistribution of electron density around V11; Electron deficiency occurs close to the V11 nucleus and instead there is an accumulation of electron density in the direction of the vanadyl bond formed with O51 and also towards O62, which coordinates to the lithium atom. V31 shows a slight excess of electron density compared to V32, which is reasonable since V32 coordinate to a lithium coordinated oxygen atom.
V21 exhibits the largest electron density difference of all the vanadium atoms; there is an increase in electron density in the directions of the V-O bonds, implying that V21 undergoes the largest change in oxidation state. This is formally from 5+ to 4+ on the basis of the bond valence calculations, although such large effective changes in formal charge are never found experimentally, since charge is shared with the neighbouring oxygens. It can be seen from this difference deformation refinement that the transferred charge also accumulates on the oxygen atoms, although the largest change is for the O71 atom, which exhibits an electron deficiency compared to the other oxygen atoms, which either have slight electron excess or remain unchanged. These results resemble earlier difference deformation refinements between Li$_2$V$_6$O$_{13}$-V$_6$O$_{13}$, although it should be noted that we here compare differences within the LiV$_6$O$_{13}$ structure and not between lithiated and un lithiated structures. Theoretical studies on lithiated V$_6$O$_{13}$ have shown that the vanadium atoms take up the majority of the electrons transferred during lithium insertion, and that a small amount of electron excess is found on the oxygen atoms.}\]
5.3 Lithium insertion mechanism in $V_6O_{13}$
As can be seen in the $Li_{2/3}V_6O_{13}$ structure, the inserted lithium ions are periodically distributed in the $V_6O_{13}$ host structure. The lithium ions occupy chemically equivalent sites and tend to form pairs in the structure. The reduced V23 atom is situated between the lithium ions, and this leads to the formation of electrochemically active sheets with a separation of ca. 21 Å (Fig. 18).

Figure 18. $Li_{2/3}V_6O_{13}$ presented as a 3×1×3 expansion of the basic $V_6O_{13}$ lattice. The grey regions mark the electrochemically active sheets, containing pairs of lithium ions and the reduced V23 atoms (marked with rectangles). The original unit-cell is indicated.

In the $x=1$ structure, the lithium ions occupy chemically equivalent sites, as in the $x=2/3$ structure, and the electrochemically active sheets remain, but with a smaller separation of ca. 11 Å (Fig. 19).
LITHIUM INSERTION MECHANISM IN V$_2$O$_3$

Figure 19. LiV$_{2/3}$O$_{13}$ presented as a 3×1×3 expansion of the basic V$_2$O$_3$ lattice. The grey regions mark the electrochemically active sheets, containing pairs of lithium ions and the reduced V21 atoms (marked with rectangles). The original unit-cell is indicated.

Apart from the addition of new lithium ions, the phase transformation from Li$_{2/3}$V$_2$O$_{13}$ to LiV$_{2/3}$O$_{13}$ also requires a rearrangement of the lithium ions already present, which is likely to occur within the V-O layers.

Although the lithium ions are rearranged, the reduced V2 atoms remain between the pairs of lithium ions, i.e., the rearrangement in the lithium ions is followed by a rearrangement in the electron distribution. For the x=2 case, the electrochemically active sheets now occupy the whole structure (Fig. 20) and some new insertion mechanism must occur on further lithium insertion. In the x=3 structure, lithium ions insert within the V-O layers$^{7}$ which can explain the sharp drop in the c-axis cell parameter (Fig. 15).
Figure 20. Li$_2$V$_6$O$_{13}$ presented as a 3×1×3 expansion of the original cell. The grey regions mark the electrochemically active sheets containing pairs of lithium ions and the reduced V2 atoms (marked with squares). The sheets now occupy the entire structure.
Chapter 6

LITHIUM EXTRACTION PROCESS FOR LiMn$_2$O$_4$

The LiMn$_2$O$_4$ structure has space group Fd-3m with Z=8 and lithium lying in an 8-fold special position. If extraction of lithium from this site were to create a random arrangement of lithium ions in the structure, this would result in a homogeneity range during the whole charge process, which would be consistent with the observed continuous decrease in cell parameters from 8.24 Å in the fully lithiated material to 8.03 Å in the ca. Li$_{0.27}$Mn$_2$O$_4$. On the other hand, this model cannot explain the voltage step occurring at 4.1 V vs. Li/Li$^+$ in the <Li| liq. electrolyte |LiMn$_2$O$_4$> system (Fig. 8). Analogous to the quasi-vertical sections in the discharge curve for V$_6$O$_{13}$, this voltage step is likely to correspond to some kind of single-phase region as a result of structural ordering. The composition here would appear to be Li$_{0.5}$Mn$_2$O$_4$; convincing evidence for the existence of this phase was first found by synchrotron powder XRD as discussed in section 3.4. Since lithium already occupies the highest symmetry site in the space group, the alternatives for creating this phase are: a lowering of the symmetry, or some form of superlattice formation, as discussed for V$_6$O$_{13}$. This delithiation processes will be discussed in the following chapter.

6.1 Superlattice formation

Single crystals of composition LiMn$_2$O$_4$ were delithiated electrochemically at four different voltages: 4.06, 4.08, 4.10 and 4.25 V vs. Li/Li$^+$. This delithiation causes a continuous rearrangement of the lithium atoms in the structure, leading to the formation of several modulated structures, which can be recognized by superlattice reflections occurring at the fraction $\gamma$ between the main reflections, where $\gamma$ is equal to the length of the modulation vector $q$ in reciprocal space.

A 3-fold superlattice is obtained at 4.10 V, and a 7-fold superlattice at 4.25 V. This is described in paper III. Very poor crystal quality has meant that these 3-fold and 7-fold structures could not be solved. Single crystals were equilibrated at 4.06 V and 4.08 V vs. Li/Li$^+$ for several weeks longer than for the 3- and 7-fold structures and proved to be of better quality for single-crystal XRD. This prolonged equilibration time may well affect the amount of lithium extracted, so the precise voltages at which the phases were identified may not be consistent with the lithium content found. The crystal at 4.06 V vs. Li/Li$^+$ was multi-phased and showed superlattice reflections which could be related to three different phases; the 3-fold superstructure, and two incommensurate structures with $\gamma$=0.75 and $\gamma$=0.57. The phase with $\gamma$=0.75 was dominant and hence these reflections were integrated, ignoring the contribution from the other phases. This modulation
LITHIUM EXTRACTION PROCESS FOR
LiMn₂O₄

closely but not exactly corresponds to a commensurate phase, which would be
expressed as a 4-fold supercell.

The inflection point region of the discharge curve would seem to correspond to
several phase transitions, since the cell parameters for these three phases are very
similar, implying that they are likely to have similar lithium content. That a
multi-phase crystal is formed implies that all phases are more or less equally
favourable kinetically; no one phase is thermodynamically more stable than
another.

Crystals at both 4.06 and 4.08 V vs. Li/Li⁺ showed twinning effects, with all main
reflections overlapping. As discussed in paper IV, delithiation causes this twinning,
with the original cubic crystal loosing symmetry to acquire the space group R-3m,
which is a subgroup of Fd-3m, in which the 4-fold axis is lost. The rhombohedral
unit-cell has its unique c-axis along the body diagonal of the original cubic cell, and
its a- and b-axes along the cubic face diagonals. In each twin domain, the
rhombohedral c-axes are thus oriented along one of the four <111>, directions. A
high diffuse-scattering background for the 4.08 V vs. Li/Li⁺ structure made it
impossible to resolve the satellite reflections, and hence terminated any further
work on this structure. The cell parameters obtained for the average structures of
all above-mentioned phases are in agreement with neutron powder diffraction
studies (Tab. 6).

Table 6. Cell parameters obtained for single crystals of LiMn₂O₄ delithiated at
different voltages.

<table>
<thead>
<tr>
<th>Voltage (V) vs. Li/Li⁺</th>
<th>Axis in cubic 1×1×1 cell (Å)</th>
<th>Modulated phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.80</td>
<td>8.244(4)</td>
<td></td>
</tr>
<tr>
<td>4.08</td>
<td>8.142(1)</td>
<td>Incommensurate, γ=0.57</td>
</tr>
<tr>
<td>4.10</td>
<td>8.14 (1)</td>
<td>3-fold</td>
</tr>
<tr>
<td>4.06</td>
<td>8.142(4)</td>
<td>Incommensurate, γ=0.75</td>
</tr>
<tr>
<td>4.25</td>
<td>8.061(4)</td>
<td>7-fold</td>
</tr>
</tbody>
</table>
6.2 The structure at 4.06 V vs. Li/Li⁺

The average structure of the 4.06 V vs. Li/Li⁺ phase was refined using only the main reflections; these all contain contributions from the four twin domains. The four components were refined simultaneously; refinement parameters are given in Tab. 7, and the resulting refined structure parameters in Tab. 8.

Table 7. Crystal data for the Li₁₋ₓMn₂O₄ phase delithiated to 4.06 V vs. Li/Li⁺.

<table>
<thead>
<tr>
<th>Unit-cell parameters</th>
<th>a= 5.762(1) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>c= 14.080(4) Å</td>
</tr>
<tr>
<td></td>
<td>γ= 120°</td>
</tr>
<tr>
<td></td>
<td>V= 404.8 (1) Å³</td>
</tr>
<tr>
<td>No. of measured reflections</td>
<td>2981</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>675</td>
</tr>
<tr>
<td>R_m</td>
<td>10.25 %</td>
</tr>
<tr>
<td>wR(F)_all</td>
<td>14.97 %</td>
</tr>
</tbody>
</table>

The structure is closely related to the original LiMn₂O₄ structure but the coordination polyhedra for the different Mn atom differ slightly. Bond valence calculations for the average structure show that the Mn1 atom has more Mn³⁺ character, with an average Mn1-O distance of 2.22(2) Å. The Mn2 coordination is more contracted, with an average Mn2-O distance of 1.85(2) Å, indicative of Mn⁴⁺ character.

The average 4.06 V vs. Li/Li⁺ structure can be seen in Fig. 21. The structure showed superlattice reflections along the <001> direction, with modulation vector q=0.75c*. The reflexion pattern for the 4.06 V vs. Li/Li⁺ structure again contained much diffuse scattering, which could not be handled satisfactorily. Thus, the structure obtained does not give a complete picture of the material.

Table 8. Refined atomic parameters and isotropic displacement parameters for the average structure model of Li₁₋ₓMn₂O₄.

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U_iso (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1</td>
<td>3b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.026(2)</td>
</tr>
<tr>
<td>Mn2</td>
<td>9e</td>
<td>-1/8</td>
<td>-1/3</td>
<td>-1/3</td>
<td>0.013(1)</td>
</tr>
<tr>
<td>O3</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>-0.2654(9)</td>
<td>0.022(5)</td>
</tr>
<tr>
<td>O4</td>
<td>18h</td>
<td>-0.1593(12)</td>
<td>-0.319(2)</td>
<td>-0.6266(10)</td>
<td>0.026(3)</td>
</tr>
<tr>
<td>Li</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>-0.1163(2)</td>
<td>0.021(4)</td>
</tr>
</tbody>
</table>
Figure 21. The average structure of the Li$_{1-x}$Mn$_2$O$_4$ phase obtained at 4.06 V vs. Li/Li$^+$; the lithium site is partially occupied.

The modulated structure was refined in (3+1) dimensions using the four indices $hklm$ and only first-order satellites. Positional modulation waves were introduced for the Mn and O atoms, and modelled by sinusoidal functions. The occupational modulation for lithium was modelled by a square-wave function with an optimized occupation of 50%, as could be expected for a structure obtained at this voltage. The Mn atoms, and O3 atom, are found to be quite close to the ideal positions, with maximum shifts of ~0.1 Å, as can be seen in Fig. 22, where the displacive modulation of the electron density along the internal axis $t$ is plotted as a function of the physical $z$-axis.
LITHIUM EXTRACTION PROCESS FOR LiMn$_2$O$_4$

Figure 22. Sections through the electron density map of Li$_{1-x}$Mn$_2$O$_4$ showing the modulation of a) Li, O3 and Mn1 and b) O4 and Mn2 as a function of the z-axis for the 4.06 V structure.

The t axis describes the modulation along the q-vector from a fixed origin in the direct cell. The period of the modulation extends over 0 < t < 1; the modulation repeats every 0.75c$^*$ in reciprocal space.

The Mn sites show evidence of random occupation, but this occupancy value is difficult to refine due to the poor quality of the data. In fact, some dissolution of Mn from the spinel is known to occur during lengthy storage of a <Li| liq. electrolyte |LiMn$_2$O$_4$> cell at elevated temperatures. The O4 atom shows occupational modulation, indicative of oxygen deficiency. Two different scale factors were used in the refinements, one for the main reflections and one for the satellite reflections. These differed significantly, implying that the modulated structure refined described only a part of the true modulation. This is reasonable since only $\gamma$=0.75 satellites were integrated, and we know that the crystal consisted of several phases which also gave a large amount of diffuse scattering, which was not analyzed.

6.2.1 The 4-fold supercell

The length of the reciprocal modulation vector is very close to $\gamma$=¾ of c*, corresponding to a modulation vector of 4/3c in direct space, implying that the structure can be approximated to a 4-fold supercell expanded along <001>, with cell parameters a=5.771(1) Å and c=56.321(4) Å. This results in a model comprising five unique Mn atoms: Mn1-1 and Mn1-2 originating from Mn1 in the modulated structure and Mn2-1, Mn2-2 and Mn2-3 originating from Mn2. This structure also contains eight independent O atoms and two Li atoms (Tab. 8). Since the structure is not exactly an 4-fold expansion, this supercell cannot be refined. The parameters are thus given in Tab. 8 without standard deviations.

The coordination polyhedra for the Mn1 atoms have significantly longer Mn-O distances than in the original structure, which can in turn be related to be reduced Mn$^{3+}$ ions. The Mn2 atoms have contracted coordination polyhedra and are ascribed to oxidised Mn$^{4+}$ ions (Tab. 9), although bond valence calculations imply an even stronger charge-ordering as seen in paper IV. This Mn$^{3+}$/Mn$^{4+}$ charge-ordering gives the average Mn oxidation state +3.75, which corresponds to the composition Li$_{0.5}$Mn$_2$O$_4$, provided that all sites are fully occupied.

The structure of the supercell (Fig. 23) shows that the delithiation occurs in a sheet-like manner between the cubic close-packed oxygen layers; this, in combination with the charge-ordered Mn ions, results in the superlattice formation. A driving force for this mechanism could be that the removal of one lithium ion from an
intermixed layer causes a local distortion in the surrounding atoms, which then energetically favours the further removal of lithium ions from this same layer.

Table 9. Atomic parameters, isotropic displacement parameters and average Mn-O bond lengths for the 4-fold supercell of Li$_{x}$Mn$_2$O$_4$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{iso}$ (Å$^2$)</th>
<th>Average Mn-O distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1-1</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.1264</td>
<td>0.0231</td>
<td>2.328</td>
</tr>
<tr>
<td>Mn1-2</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.3764</td>
<td>0.0231</td>
<td>2.270</td>
</tr>
<tr>
<td>Mn2-1</td>
<td>18b</td>
<td>-0.1676</td>
<td>-0.3353</td>
<td>-0.0855</td>
<td>0.0158</td>
<td>1.825</td>
</tr>
<tr>
<td>Mn2-2</td>
<td>9d</td>
<td>-1/6</td>
<td>-1/3</td>
<td>1/6</td>
<td>0.0158</td>
<td>1.817</td>
</tr>
<tr>
<td>Mn2-3</td>
<td>9e</td>
<td>-1/6</td>
<td>-1/3</td>
<td>2/3</td>
<td>0.0158</td>
<td>1.815</td>
</tr>
<tr>
<td>O3-1</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.0659</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>O3-2</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.3168</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>O3-3</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.5667</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>O3-4</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.8158</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>O4-1</td>
<td>18b</td>
<td>-0.1568</td>
<td>-0.3136</td>
<td>-0.1544</td>
<td>0.0133</td>
<td></td>
</tr>
<tr>
<td>O4-2</td>
<td>18b</td>
<td>-0.1582</td>
<td>-0.3165</td>
<td>0.0935</td>
<td>0.0133</td>
<td></td>
</tr>
<tr>
<td>O4-3</td>
<td>18b</td>
<td>-0.1608</td>
<td>-0.3216</td>
<td>0.3454</td>
<td>0.0133</td>
<td></td>
</tr>
<tr>
<td>O4-4</td>
<td>18b</td>
<td>-0.1593</td>
<td>-0.3187</td>
<td>0.5975</td>
<td>0.0133</td>
<td></td>
</tr>
<tr>
<td>Li-1</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.0304</td>
<td>0.0259</td>
<td></td>
</tr>
<tr>
<td>Li-2</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.2804</td>
<td>0.0259</td>
<td></td>
</tr>
</tbody>
</table>
6.3 The lithium extraction process

The lithium extraction process for LiMn$_2$O$_4$ would appear to be rather complex. As mentioned earlier, structures formed at 4.10 V vs. Li/Li$^+$, showed a 3-fold expansion and at 4.25 V vs. Li/Li$^+$ a 7-fold expansion occurs.

The nearly 4-fold superlattice structure, with superlattice reflections at $\gamma=3/4$, was shown to consist of charge-ordered Mn$^{3+}$/Mn$^{4+}$ ions in a 1:3 ratio, giving the average Mn oxidation state $+3.75$, consistent with the composition Li$_{0.5}$Mn$_2$O$_4$. This superlattice results from a long-range charge-ordering of Mn and Li ions. This same general model can be applied to all the structures found, assuming they all involve charge-ordered Mn ions. The incommensurate structure, with modulation vector...
close to 4/7 ($\gamma \approx 0.57$) can then correspond to an average Mn oxidation state $+3.57$, which is equivalent to an $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio of 3:4; long-range-ordering of the manganese and lithium atoms can thus be achieved, resulting in the composition $\text{Li}_{0.86}\text{Mn}_2\text{O}_4$. Similarly, the modulation of the 3-fold superstructure can involve a charge-ordering of one Mn$^{3+}$ and two Mn$^{4+}$ together with long-range lithium ordering. This would result in a structure similar to the 4-fold superstructure, with the difference that every third “lithium layer” is missing, to give a composition $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$. These different superlattices and proposed charge-ordering schemes are given in Tab. 10. A schematic model for the lithium ordering in the different phases is seen in Fig. 24. Evidence of superlattice formation at 3.91 V vs. Li/Li$^+$ has been found previously, suggesting that a whole series of modulated phases occurs in the compositional range $\text{Li}_{x}\text{Mn}_2\text{O}_4$ for $0 < x < 0.73$.

Table 10. Superlattices obtained for different compositions and the possible charge-ordering of manganese ions.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Average Mn oxidation state</th>
<th>Mn $^{3+}/\text{Mn}^{4+}$ ions in unit-cell</th>
<th>Superlattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LiMn}_2\text{O}_4$</td>
<td>$+3.5$</td>
<td>$3$</td>
<td>none</td>
</tr>
<tr>
<td>$\text{Li}_{0.86}\text{Mn}_2\text{O}_4$</td>
<td>$+3/7$</td>
<td>$333$</td>
<td>Incommensurate $\gamma \approx 0.57$</td>
</tr>
<tr>
<td>$\text{Li}_{2/3}\text{Mn}_2\text{O}_4$</td>
<td>$+3/3$</td>
<td>$3$</td>
<td>3-fold</td>
</tr>
<tr>
<td>$\text{Li}_{5/4}\text{Mn}_2\text{O}_4$</td>
<td>$+3/4$</td>
<td>$3$</td>
<td>$\gamma \approx 0.75$</td>
</tr>
<tr>
<td>$\text{Li}_{3/4}\text{Mn}_2\text{O}_4$</td>
<td>$+3/8$</td>
<td>$3$</td>
<td>7-fold</td>
</tr>
</tbody>
</table>

Figure 24. Suggested lithium ordering in a) $\text{Li}_{0.86}\text{Mn}_2\text{O}_4$ b) $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$ c) $\text{Li}_{5/4}\text{Mn}_2\text{O}_4$ and d) $\text{Li}_{3/4}\text{Mn}_2\text{O}_4$. The grey layers consist of Mn-O octahedra.
Charging a cell at a very slow charge rate (< C/500) reveals a number of extra plateaus in the discharge curve in the region of the potential step at ~4.1 V vs. Li/Li’ (Fig. 24). Under faster charging, this appears as only one quasi-vertical region (Fig. 8). Cyclic voltammetry studies using a C/50 charge rate reveal similar behaviour. The potential step occurs in two sections in the range 4.03-4.19 V vs. Li/Li’; three sections appear with inflection points at ca. 4.08 and 4.16 V vs. Li/Li’. Considering the amount of charge passed, these inflection points correspond well with the earlier discussed compositions. Suggestions for the phases obtained during delithiation are given in Fig. 25.

Figure 25. Discharge curve for a <Li|liq. electrolyte|LiMn_2O_4> cell at C/1700 including proposals for the modulated structures obtained.
Chapter 7

CONCLUDING REMARKS

This thesis has introduced new insights into lithium-ion insertion processes in transition-metal oxides. Much effort has been made to understand the very finest and subtle detail of the chemistry of the mechanisms involved. The use of single-crystal XRD has been shown to be a powerful tool for following lithiation processes at the atomic level.

Studies of the V$_6$O$_{13}$ system have exposed a level of complexity in its lithium insertion mechanism, which previously never been observed in any cathode material. However, in the light of the fact that nature is more symmetrical and well-ordered than we often imagine, this result is perhaps not so surprising. The V$_6$O$_{13}$ host structure maintains its rather robust V-O network as lithium is inserted to form electrochemically active sheets, consisting of lithium and reduced vanadium ions. As more lithium is inserted the sheets approach one another, necessitating the rearrangement of lithium and the reduction of vanadium atoms. It is reasonable to suppose that there are, in principle, numerous lithiated phases of lower composition than Li$_{2/3}$V$_6$O$_{13}$.

The successful synthesis of single crystals of LiMn$_2$O$_4$ was a crucial breakthrough in studies of the spinel system, although the crystals obtained are not of the best quality and further improvements in the synthesis technique are needed. The Li$_{1-x}$Mn$_2$O$_4$ system was shown to involve long-range-ordering effects, which lead to the formation of modulated structures over the entire compositional range 0< x <0.73. The lithium extraction process stimulates the formation of a continuous sequence of long-range-ordered phases involving sheet-like lithium ordering in combination with charge-ordering of the Mn ions.

In general terms, all systems strive to achieve their lowest energy. In the context of lithium-ion insertion/extraction processes in transition-metal oxides, this would seem to be achieved through an ordered arrangement of lithium ions, extending throughout the structure. The lithium ions and the host structure rearrange cooperatively to form superlattices through lithium and transition-metal ion charge-ordering. A picture begins to emerge of a universal two-dimensional lithium ion insertion/extraction mechanism, analogous to the familiar staging sequence in graphite.
Chapter 8

FUTURE WORK

There have long been doubts as to the maximum amount of lithium that can be incorporated into the Li\textsubscript{1-x}V\textsubscript{x}O\textsubscript{13} system; suggestions have earlier been in the range x=6-14 but tend now to be in the region x=6-8. Powder XRD has been insufficient to prove a clear answer. Single-crystal studies at 1.8 V \textit{vs.} Li/Li\textsuperscript{+} would be most desirable and could give a final answer to the maximum amount. Such studies have so far proved highly problematical.

The single-crystal studies of the LiMn\textsubscript{2}O\textsubscript{4} system leave much to be desired. The single crystals obtained so far have been of poor quality. Optimizations of the synthesis technique could include heat treatment, both to relieve stress in the individual crystals and homogenize the composition within a batch. Much effort is still needed to completely solve the delithiation process in LiMn\textsubscript{2}O\textsubscript{4}, which would seem to be highly complex, involving both long- and short-range-ordering effects. These could perhaps be probed by Reverse Monte Carlo simulation. Transmission electron microscopy could also be an interesting technique to clarify twinning and domain-formation issues.

As is often the case, this thesis would seem to have raised more new questions than it has answered on the subject of lithium ordering in transition-metal oxides. The vanadium and manganese systems examined here behave in a similar way in as much as both exhibit “two-dimensional” long-range-ordering of lithium ions coupled to charge-ordering of the transition metal ions on lithium insertion/extraction. However, much more work is needed if we are to discover the precise delithiation process in LiMn\textsubscript{2}O\textsubscript{4}. Other transition-metal oxide systems must also be examined to probe further the notion of some universal lithium insertion process associated with oxidation-state ordering.

Computer simulation and band-structure calculations based on the superlattices formed would also be valuable for better understanding underlying mechanisms. Earlier calculations have always assumed the original unlithiated or lithiated unit-cell; the superlattices found here have so far never been used in any calculations.

The development of a “single-crystal battery”, its use for \textit{in situ} electrochemical cycling/XRD studies would be a very precise technique for studying insertion mechanisms. It would make it possible to follow lithium diffusion at every stage in the discharge curve, and to couple directly voltage to the phase obtained. Work is already underway in this area, but it is proving a challenge to find a working design.
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As I have been gazing my years through the microscope in the search for suitable crystals, I have reflected over issues of decisive importance; the faces may be beautiful, but what is important is the inside; without mosaicity constructive interference would not arise. Good quality crystals are difficult to find. More thorough examinations of apparently good species often reveal unpleasing properties, so if you manage to find one, treat it gently; it easily breaks or even disappears. Crystals might age with time, change some properties and form new phases and patterns; hopefully the new properties still gratify your inquisitiveness forever on. Thanks Örjan for your patience and beautiful mind!

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Helen Björk
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