Novel Lithium-ion Host Materials for Electrode Applications

Christopher Lyness, M.Chem.

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ABSTRACT

Two novel lithium host materials were investigated using structural and electrochemical analysis; the cathode material Li$_2$CoSiO$_4$ and the LiMO$_2$ class of anodes (where $M$ is a transition metal ion).

Li$_2$CoSiO$_4$ materials were produced utilising a combination of solid state and hydrothermal synthesis conditions. Three Li$_2$CoSiO$_4$ polymorphs were synthesised; $\beta_{\text{I}}$, $\beta_{\text{II}}$ and $\gamma_0$. The Li$_2$CoSiO$_4$ polymorphs formed structures based around a distorted Li$_3$PO$_4$ structure. The $\beta_{\text{II}}$ material was indexed to a $Pmn2_1$ space group, the $\beta_{\text{I}}$ polymorph to $Pbn2_1$ and the $\gamma_0$ material was indexed to the $P2_1/n$ space group. A varying degree of cation mixing between lithium and cobalt sites was observed across the polymorphs.

The $\beta_{\text{II}}$ polymorph produced 210mAh/g of capacity on first charge, with a first discharge capacity of 67mAh/g. It was found that the $\beta_{\text{I}}$ material converted to the $\beta_{\text{II}}$ polymorph during first charge. The $\gamma_0$ polymorph showed almost negligible electrochemical performance. Capacity retention of all polymorphs was poor, diminishing significantly by the tenth cycle. The effect of mechanical milling and carbon coating upon $\beta_{\text{II}}$, $\beta_{\text{I}}$ and $\gamma_0$ materials was also investigated.

Various Li$_{1+x}$V$_{1-x}$O$_2$ materials (where 0≤$X$≤0.2) were produced through solid state synthesis. LiVO$_2$ was found to convert to Li$_2$VO$_2$ on discharge, this process was found to be strongly dependent on the amount of excess lithium in the system. The Li$_{1.08}$V$_{0.92}$O$_2$ material had the highest first discharge capacity at 310mAh/g. It was found that the initial discharge consisted of several distinct electrochemical processes, connected by a complicated relationship, with significant irreversible capacity on first discharge.
Several other LiMO₂ systems were investigated for their ability to convert to layered Li₂MO₂ structures on low voltage discharge. While LiCoO₂ failed to convert to a Li₂CoO₂ structure, LiMn₀.₅Ni₀.₅O₂ underwent an addition type reaction to form Li₂Mn₀.₅Ni₀.₅O₂. A previously unknown Li₂NiₓCo₁₋ₓO₂ structure was observed, identified during the discharge of LiNi₀.₃₃Co₀.₆₆O₂.
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Chapter 1: Introduction
1.1. Thesis Introduction

The ability to store electrical energy has become a fundamental necessity for modern society, from the small scale, powering our portable technology, to the large scale, as a crucial component of our burgeoning renewable energy infra-structure. We are now able to store more energy at greater density with more efficiency than ever before. Our understanding of the techniques and mechanisms for storing energy and converting it into useful power is ever expanding, constantly providing innovative and elegant means to produce electricity as and when we need it.

The ability to store energy chemically and convert it, when needed, to electrical power has been known in modern times since the Italian physicist Alessandro Volta first described the electrochemical storage device the ‘Volta pile’ in 1800\(^1\). Since then several battery systems have been developed and intensely researched, each improving on an aspect of battery function (be it safety, energy density or any of the many factors affecting battery performance). Today much attention is focussed on the ubiquitous Li-ion battery, first theorised by Whittingham in the late 70’s\(^2\); its high energy density and convenient discharge voltage have allowed it to dominate in an ever expanding number of applications.

While the concept of lithium ions moving between host electrodes has remained relatively unchanged for twenty years since the rechargeable Li-ion battery was first commercialised\(^3\), the individual components have undergone a constant evolution. Today, the once widespread LiCoO\(_2\) cathode is being replaced by the cheaper and safer LiFePO\(_4\), first proposed by Goodenough et al.\(^4\). However the amount of chemical energy that the battery can store has not grown significantly over the two
decades, with the storage ability of the cathode still lagging significantly behind the anode. As the fledgling field of partially and fully electric vehicles makes ever increasing demands on battery lifetime and cell kinetics, the search for new cathode materials is intensifying. Graphite still maintains its dominance of anode materials but its low volumetric capacity and near-lithium intercalation voltage are less than ideal and the search into replacement anode materials is gaining momentum.

Li-ion batteries span the fields of electrochemistry and solid state chemistry and as such, the investigation of any new battery materials relies on analytical techniques from both disciplines. Utilising structural characterisation and electrochemical analysis, this work comprises an investigation into a promising cathode material and a novel class of anodes. The aim of this research is to understand the mechanisms and processes occurring within these electrode materials in order to further inform our understanding of lithium ion host materials.
1.2. References

Chapter 2. Current Battery Technology
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Chapter 2: Current battery Technology

2.1. Battery Overview

2.1.1. Basic Theory

At its heart, the lithium intercalation battery system is a simple thermodynamic pump. Within the battery are two, thermodynamically distinct, reservoirs of charge; the cathode and the anode. On discharge the charge carriers are forced from anode to the cathode due to the electrode’s thermodynamic difference. The charge is drawn by the lower Gibbs free energy position of the cathode. Upon charging an external force has to be applied to drive the charge carriers back to the higher Gibbs energy position of the anode. The thermodynamic difference between the anode and cathode free energy gives the cell voltage, one of the fundamental properties of the cell, highlighted in the schematic in Figure 2.1.1

Figure 2.1.1. Schematic of the thermodynamic properties of a lithium intercalation galvanic cell (generic example voltages given, not to scale).

From an electrochemical perspective a lithium intercalation battery revolves around a reversible ion/electron reaction at each electrode. The anode, traditionally, consists of a material (such as graphite) which can intercalate Li\(^+\) ions at a voltage near to the lithium equilibrium potential. The cathode reaction also involves insertion of
lithium into a host material with a transition metal redox couple allowing for charge compensation on insertion and removal of lithium. A typical half equation is given in equation 1.

\[ x\text{Li}^+ + xe^- + [\text{H}] \longrightarrow \text{Li}_x[\text{H}]^{x^-} \]

\([\text{H}]\) is the host material, \(x\) is the intercalation fraction (i.e. the number of lithium ions intercalated per unit cell).

An intercalation battery consists of 3 parts, the cathode, electrolyte and the anode. Upon charging, lithium ions are removed from the cathode, migrate through the electrolyte and are inserted within the graphite layers of the anode. Meanwhile the electrons travel through the external circuit from the cathode to the anode. Whilst discharging the lithium ions travel in the reverse direction from anode to cathode, as do the electrons through the external circuit. A schematic of this process is shown in Figure 2.1.2.

**Figure 2.1.2.** Schematic representation of a lithium intercalation battery operation.
2.1.2. Battery Components

Fundamentally the Li-ion battery consists of 3 components:

The anode: Traditionally graphite, this incorporates lithium ions within its layered structure and has a similar Li$^+$ ion deintercalation potential to lithium metal. Graphite is most widely used because it exhibits good cycling stability, good volumetric capacity whilst also being low cost. Other cathode materials have been suggested, mainly lithium metal alloys Li$_x$M (M= Al, Sn, Si, Sb etc.)$^{1-5}$. Though these materials generally display large volumetric capacities they have problems with large volume expansion/contractions upon cycling that can cause poor structural stability over large numbers of cycles.

The electrolyte: This conducts lithium ions between the two electrodes and comprises of a lithium salt (LiPF$_6$ and lithium bis (trifluoromethane sulfonyl) imide are some of the more ubiquitous salts) usually dissolved within a liquid organic carbonate (common commercial electrolytes use, both on their own and as binary mixtures, ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) amongst others). The electrolyte must have high stability within the electrochemical ‘window’ between anode and cathode potentials and have low volatility whilst still ensuring good ion migration between the electrodes.

The cathode: This provides the source of the lithium ions and usually is based on either a transition metal dichalcogenide or a transition metal oxide (such as LiMO$_2$ (M=Co, Ni, Mn$^{6-8}$) or spinel LiMnO$_2$)$^9). More recently LiFePO$_4$$^{10}$ has been implemented in some applications. Intercalation is driven by a charge transfer (see Figure 2.1.1) from the intercalant to the host in what can be thought of as charge transfer on a discrete
atomic level, on the molecular level of a polyatomic moiety or as part of the material conduction band, depending on the nature of the process.
2.2. Intercalation materials

2.2.1. Cathode

Cathode materials form an integral part of the Li-ion battery and currently stand as the limiting factor for the amount of charge that can be stored in a battery (graphite can host one lithium per six carbons giving a capacity of 370 mAh/g). Often the stability of the cathode can determine the lifetime of the cell as a whole.

A desirable cathode material would have a relatively flat open circuit voltage over a range of lithium content, ensuring a constant voltage is supplied upon discharge. A critical property for lithium intercalation is the potential at which lithium can be extracted and inserted. If the potential is too high then side reactions such as electrolyte oxidation may occur, if the potential is too low it risks diminishing the gravimetric and volume energy density of the material. The optimum cathode would have an extraction/insertion potential residing within the voltage range of 2.5 - 4.0V vs. Li$^+/ Li$ (Voltages in excess of 4.5V generally are not used because of limits imposed by commercial electrolyte stability windows) though with the introduction of more exotic electrolytes, such as those based on dry polymers or ionic liquids, this voltage ‘ceiling’ may be increased\(^{11}\). The material should also be inexpensive, easy to fabricate, environmentally benign as well as being electrochemically and mechanically stable.

Reversible intercalation has been achieved by a number of different compounds, namely transition metal dichalcogenides and transition metal oxides, the latter being far more widely implemented in commercial applications. The metal
oxides generally have a layered structure in which lithium ions sit between the layers, the most widely used compound being LiMO$_2$ ($M=$Co, Ni or solid solutions of the two).

LiCoO$_2$ is utilised in many commercial batteries as it does not suffer from the same instabilities as its nickel counterpart. The voltage for complete lithium intercalation/ deintercalation is around 4.7 V vs. Li$^+/\text{Li}^6$ ensuring the material has a suitably high gravimetric energy density. Unfortunately LiCoO$_2$ is unable to facilitate complete lithium extraction at such high voltages without suffering structural changes (this probably occurs via an exothermic reaction between the cobalt rich phase and the electrolyte). Thus for commercial applications only 0.5 Li is removed at a cut off voltage of 4.2V vs. Li$^+/\text{Li}$ giving a maximum practical capacity of 130 mAh/g$^{12}$. 

Both cobalt and cobalt nickel solid solution cathode materials have inherent safety issues. In the delithiated state both are strong oxidisers which is problematic when in contact with an organic electrolyte. There are also some long-term stability problems with the commercially available oxides, for example durability when exposed to extremes of temperature, such as the fully charged phase of Li$_{1-x}$CoO$_2$ which loses oxygen at elevated temperatures (>180°C)$^{13}$. 

These factors in conjunction with the rarity and expense of pure cobalt mean the usage of such materials in large battery applications, such as transportation, is questionable and other more stable options have to be explored; one of the more promising materials is LiFePO$_4$. 


2.2.1.1. **LiFePO$_4$**

Iron based cathodes offer an excellent alternative to the aforementioned metal oxides as the iron compounds are generally cheap, the starting materials prolific and compounds tend to be both environmentally and physiologically benign. Unfortunately iron oxides in the form of LiFeO$_2$ are ill suited to cathode applications as the Fe$^{4+}$/Fe$^{3+}$ redox couple lies too far below the Li anode Fermi level and the Fe$^{3+}$/Fe$^{2+}$ redox level is too close to be exploited. To avoid this problem polyanions, such as (SO$_4$)$_2^-$, (PO$_4$)$_3^-$ and (AsO$_4$)$_3^-$ amongst others$^{14}$, can be employed to lower the Fe$^{3+}$/Fe$^{2+}$ redox energy to a point far enough below the lithium Fermi level to provide a useful voltage.

Phosphate based intercalation compounds were first described in the research of Delmas et al. into the NASICON based phase of NaTi$_2$(PO$_4$)$_3$-which upon intercalation gives Na$_3$Ti$_2$(PO$_4$)$_3$. At the same time lithium intercalation of NASICON type materials was also researched, e.g. Li$_3$Fe(PO$_4$)$_3$ (with LiFePO$_4$ being described as an impurity!).

LiMPO$_4$ ($M$=Fe, Mn, Co and Ni. known as phospho-olivines) as a lithium intercalation material was first described by Goodenough et al.$^{10}$. Attempts to delithiate LiNiPO$_4$, LiMnPO$_4$ and LiCoPO$_4$ all failed$^{17}$ and so research centred on LiFePO$_4$. It was found that the Fe$^{3+}$/Fe$^{2+}$ redox level is around 3.5eV below the Li Fermi level in Li$_{1-x}$Fe(PO$_4$)$_3$ which compares favourably with Li$_{3+x}$Fe(PO$_4$)$_3$ (2.8eV)$^{12,13}$ and surpassed other polyanions such as Li$_2$FeTi(PO$_4$)$_3$ (2.75 eV)$^{15}$.

The nature of the LiFePO$_4$ structure involves a Fe-O-P linkage. The oxygen becoming electron deficient by its proximity to the electrophilic phosphorus ion. In turn the Fe ion feels an inductive effect from the electron deficient oxygen, removing electron density from a 3d antibonding orbital (Fe HOMO). This decreases the Fermi
level of the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) couple, which, in turn, causes an increased cell voltage (via increasing the gap between the cathode and anode redox levels). Its counterpart oxide \( \text{LiFeO}_2 \) has no such polarised oxygen.

\[ \text{Equation 2.} \quad \text{LiFePO}_4 \rightarrow \text{FePO}_4 + \text{Li}^+ + e^- \]

The reaction scheme in equation 2 displays the intercalation behaviour of \( \text{LiFePO}_4 \) which has a theoretical capacity of around 170 mAh/g. Upon cycling the compound shows a voltage plateau at 3.45V vs. \( \text{Li}^+/\text{Li} \). Though initially the intercalation process was assumed to be a two phase process it now appears more complicated, involving multiple phases, the type of which depends on the lithium content\(^{17}\). The morphology and stoichiometry of the pristine materials also plays a crucial role of the phase behaviour during cycling\(^{18}\) with evidence that single phase behaviour is possible with delicate control of the particle size.

A major drawback to the large-scale implementation of this material has been its inherent poor electronic conductivity (\( 10^{-9} \text{ S/cm at room temperature} \))\(^{19}\). Because of the low electronic conductivity of the compound various mechanical and synthetic processes have been proposed to improve electrochemical performance. It would seem the best performance is offered from two simple processes, by reducing the length of the lithium transport paths, via producing nano-sized or highly porous particles\(^{20,21}\) and coating the particles in a thin layer of conducting material (usually graphite\(^{21-23}\)). Heating the mixture of active material and carbon precursor coats the material in the carbon, at the same time sp\(^2\) linkages within the carbon material itself are increased. When both processes are used in conjunction, near theoretical capacities have been reported\(^{24}\) (though it has been suggested that the limiting factor
is primarily the ionic conductivity$^{25}$. Another optimisation approach is to partially replace the iron with a similar transition metal. Studies have shown that when low levels of Co are introduced to the LiFePO$_4$ system (such as in LiCo$_{0.2}$Fe$_{0.8}$PO$_4$) an increase in capacity compared to the iron only olivine is observed$^{26}$. Pure LiCoPO$_4$ shows irreversible cycling behaviour, possibly caused by the high Co$^{2+}$/Co$^{3+}$ redox level (4.8V vs. Li$^+$/Li) and subsequent electrolyte-salt decomposition$^{21}$ (though limited progress has been made recently$^{27,28}$).

2.2.1.2. Li$_2$MSiO$_4$

A logical extension of research into the phospho-olivine type materials is the similar silicate polyanion family which has the generic formula of Li$_2$MSiO$_4$. This material displays similar structural properties to Li$_3$MPO$_4$$^{29}$. The silicates again exploit the $M^{3+}$/M$^{2+}$ transition during lithium extraction/insertion but with the added possibility of more than one lithium extraction, through utilisation of the $M^{4+}$/M$^{3+}$ couple of the transition metals to extract two lithiums per formula weight. For example the complete oxidation of Li$_2$CoSiO$_4$ would probably result in a two step process with two corresponding voltage plateaus (seen in equation 3 and 4).

$$\text{Equation 3. } \text{Li}_2\text{CoSiO}_4 \rightarrow \text{LiCoSiO}_4 + \text{Li}^+ + e^-$$

$$\text{Equation 4. } \text{LiCoSiO}_4 \rightarrow \text{CoSiO}_4 + \text{Li}^+ + e^-$$

The specific capacity of Li$_2$CoSiO$_4$, and the related Fe and Mn analogues, is a contentious issue as it depends whether the capacity is defined with respect to one or two lithium ion extractions per unit cell. While some of the literature suggests that more than one lithium extraction is possible$^{30}$ it has never been shown that $>$1 Li$^+$
capacity exists past the first cycle and thus spurious side reactions can’t be ruled out as a cause of these high initial capacities. In light of this, the more conservative estimate of one lithium extraction per unit cell is adopted for Li$_2$CoSiO$_4$, giving a specific capacity of 162 mAh/g (rather than 325 mAh/g).

2.2.1.2.1. Structural considerations

The Li$_2$MXO$_4$ group can be thought of as a slightly distorted form of oxide hexagonal close packing. Half the tetrahedral sites are occupied by cations such that face sharing between the pairs of tetrahedral sites is avoided$^{31}$. The structures show polymorphism and can be divided into 2 families $\beta$ and $\gamma$ (seen in Figure 2.2.1.), which are based on the Li$_3$PO$_4$ nomenclature$^{32}$. Within the $\beta$ form all the tetrahedra point in the same direction, perpendicular to the close packed oxygen plane, and share only corners with each other.

The $\gamma$ polymorphs contain tetrahedra arranged in groups of 3 with the central tetrahedra pointing in the opposite direction to the outer 2, with which it shares edges$^{33}$. At low temperatures $\beta$ is stable and at high temperature $\gamma$ is the equilibrium phase. Cooling the $\gamma$ form at high temperatures causes a sluggish conversion to the $\beta$ phase, thus $\gamma$ can be conserved at low temperatures by rapid cooling suppressing the transition of phases and producing a material that is kinetically stable but only meta-stable thermodynamically. During polymorph transition the oxide layer remains unmoved, with migration between sites only thought to occur amongst the transition metal cations$^{32}$.
Several variants of both $\beta$ and $\gamma$ exist involving either ordering or distortions of the parent structures, they are denoted $\beta_{\nu}, \gamma_{\nu}, \gamma_{\mu}$ etc. It has been suggested previously that transition to the sub-polymorphs would not involve a cation migration, instead requiring a minor step that only distorts the lattice of the patriarch phase perhaps through rotation of $\text{MO}_4$ tetrahedra$^{34}$, though this has yet to be experimentally observed. Previous work on $\text{Li}_2\text{MSiO}_4$ has been limited, with the majority occurring in the early 70’s on $\text{Li}_2\text{CoSiO}_4$ and latterly around $\text{Li}_2\text{FeSiO}_4$ as an intercalation material.

Two crystallographic distinct cation sites exist, M1 and M2, these introduce selectivity into the structure which becomes an important feature when more than one transition metal ion is present, such as in solid solutions. The M2 site is always larger than the M1 site in olivines$^{35}$. This implies that larger cations are favoured for this site. It has also been suggested that another predominant factor is the electronegativity of the ions. It is thought that the M2 sites in olivine structures are more ionic than the M1 site$^{36}$ suggesting that less electronegative ions prefer the M1 site. Though it has been shown that neither ionic radii nor electronegativity has a systematic effect on the choice of cation site, when both are combined a more

Figure 2.2.1. Schematic representations of the $\text{Li}_3\text{PO}_4$ structure. A) The $\beta$ type structure, B) The $\gamma$ type structure.
consistent picture emerges. This may not affect the site selectivity in Li$_2$MSiO$_4$ because of the radii and electronegativity disparity between Li$^+$ and $M$ but may become a deciding factor if considering Li$_2$M$'$MSiO$_4$ selectivity for solid solutions.

Like LiFePO$_4$, the silicates have a structure that contains a Si-O-$M$ system, where $M$=Fe, Co or Mn. The Si-O acts in a similar manner to the P-O bond component in LiFePO$_4$, causing an electronic polarisation towards the silicon atom. The lower electrophilicity of silicon vs. phosphorus should reduce the inductive effect of the oxygen in the $M$-O bond and in turn reduce the voltage difference between the $M^{3+}/M^{2+}$ couple and the graphite lithium intercalation level. This may be useful for the transition metal ions with higher redox levels-like Co. Again a silicate battery material would have the safety and cost benefits of the phospho-olivine.

2.2.2. Current Research

2.2.2.1. Li$_2$MSiO$_4$

By fine-tuning the $M$-O-X linkage the redox level (and thus the lithium intercalation voltage) can be affected. This notion has been further examined by computation, the study$^{37}$ looked at different compositions of Li$_2$MXO$_4$ (where $M$=Fe, Co and Mn and X=P, Si, Ge, As and Se) and centred around the ion-covalent character of the $M$-O bond. The nature of this bond is known to be influenced through the inductive effect, felt from the polarising X atom (in the $M$-O-X bond) thus by careful selection of X, the transition-metal redox level can be systematically altered.

In all cases the insertion voltage increased with the electronegativity of the X counter ion. This relationship displayed almost linear dependence, the explanation
being that by increasing the polarisation of the X-O bond (and hence the inductive effect felt by the transition-metal ion) less electron density remained upon the transition-metal ion, this in turn increased the voltage of insertion. To fully optimise the potential of lithium intercalation it was suggested that the redox level could be more intimately tuned by introducing a second polyanion metal to give the material formula \( \text{Li}_2\text{MSi}_{1.3}\text{X}_1\text{O}_4 \)

Though in theory it is possible to remove two lithiums through utilisation of both \( M^{3+}/M^{2+} \) and \( M^{4+}/M^{3+} \), 3d metal couples, several problems may arise with the extraction of a second lithium.

It is unlikely that in \( \text{Li}_2\text{FeSiO}_4 \) extraction above 1 Li ion is useful because of the highly stable \( \text{Fe}^{3+} \) oxidation state occurring when one lithium is removed and a high energy barrier exists for further oxidising it. A second lithium extraction from \( \text{Li}_2\text{CoSiO}_4 \) is thought to be possible but this would occur at a voltage outside of commercial electrolyte windows. \( \text{Li}_2\text{MnSiO}_4 \) has the lowest theoretical second lithium extraction potential (4.4V vs. \( \text{Li}^+/\text{Li} \)) but poor conductivity may make even extraction of the first lithium difficult and thus preclude a second lithium extraction.

2.2.2.2. \( \text{Li}_2\text{FeSiO}_4 \)

Initial attempts to synthesise \( \text{LiFe(III)SiO}_4 \) resulted in mixed phase products (primarily spodumene \( \text{LiFeSi}_2\text{O}_6 \)) and it wasn’t until 2003 when \( \text{Li}_2\text{FeSiO}_4 \) was produced as the sole product of a reaction\(^{38} \). The material \( \text{Li}_2\text{FeSiO}_4 \) is by far the most developed of the polyanion silicates because of the benign nature of iron compared to other first row transition metals (and its favourable electrochemistry) making it a particularly attractive cathode material.
Two crystal structures have been proposed for Li$_2$FeSiO$_4$; Nyten et al.$^{39,40}$ suggest (in agreement with Tarte and Cahay$^{29}$) that the structure takes the form of a Pmn2$_1$ space group with lattice parameters of a=6.266(5)Å b=5.3295(5) Å and c=5.0148(4) Å and is isostructural with Li$_3$PO$_4$. The differences between the structures is discussed by Nishimura et al.$^{41}$.

Studies of the electrochemistry of the compound have been ambiguous, Nyten et al. reported a shift in the Li$_2$FeSiO$_4$ voltage plateau from 3.1 to 2.8V vs. Li$^+$/Li after the first cycle; this was attributed to a possible transition to a more stable Li$_2$FeSiO$_4$ phase. Other work where the purity of Li$_2$FeSiO$_4$ was confirmed by magnetic measurements$^{14}$ disagreed with previous studies and found an absence of the 3.1V oxidation plateau reported in the Nyten papers (though this does go against the grain of most reports). It was suggested that the high quality of the material is responsible for the lack of change in the plateau voltage when cycling the material. Stable charging capacities of around 140 mAh/g and discharge capacities of around 130 mAh/g have been reported for Li$_2$FeSiO$_4$.$^{38,40,42,43}$

2.2.2.3. Li$_2$MnSiO$_4$

Work on Li$_2$MnSiO$_4$ has thus far shown Mn based materials to be an inferior cathode material to Li$_2$FeSiO$_4$, Dominko et al. achieved a first charge removal of 0.6 Li which subsequently dropped to 0.3 Li by the 5$^{th}$ cycle.$^{42}$ This is thought to be due to the relatively poor electronic conductivity compared to Li$_2$FeSiO$_4$, as theorised by Arroyo-de Dampablo et al.$^{37}$ Structural studies have concluded that Li$_2$MnSiO$_4$ crystallises isostructurally to Li$_2$FeSiO$_4$.$^{42}$
2.2.2.4. \textbf{Li}_2\text{CoSiO}_4

The first work on Li$_2$CoSiO$_4$ was carried out by West and Glasser in the early 1970s$^{32}$ (though not motivated by interest in intercalation compounds). The polymorphs (of which four were found, denoted $\beta_1$, $\beta_{II}$ or $\gamma_0$, $\gamma_{II}$) and their transition temperatures were identified. Access to the four polymorphs was achieved by exploiting the slow rates of inversions of the high temperature $\gamma$ polymorphs to the low temperature $\beta$ structures, rapid quenching was employed to overcome such temperature dependencies. The $\beta_{II}$ phase was researched most intensively (mainly because of the ability to isolate single crystals of the polymorph$^{44}$). It was found that $\beta_{II}$ exhibited disorder in Co$^{2+}$ and Li$^+$ positions$^{45}$ that were absent in the other polymorphs.

2.2.3. \textbf{Anode}

The anode for the lithium ion battery serves as the counter-electrode to the cathode, traditionally intercalating ions close to the lithium equilibrium potential, the anode acts as a store of lithium ions which, upon discharge, are released to intercalate into the cathode.

Historically it was the introduction of the carbon anode$^{46,47}$ that freed the lithium ion battery from many of its inherent safety issues (such as dendritic growth upon cycling) and allowed its wide-spread commercialisation.

Many properties required of anode materials are similar to those for the cathode (such as high theoretical capacity, and mechanical and chemical stability on multiple cycles). A significant number of these demands are met in the layered carbon
material graphite, it being cheap, ubiquitous, benign and having a high specific
capacity (~370mAh/g) (the drawbacks of low volumetric capacity and safety concerns
forcing lower rate capability on cycling being outweighed by the benefits).

It was found that graphite could accommodate Li$^+$ ions in-between the layers of
sp$^2$ carbon ring systems to a stoichiometry of LiC$_6$. It does so at a voltage of ~0.1 V
versus the lithium couple making it an ideal lithium metal replacement. While graphite
provides a convenient anode material it is not without its faults. A low volumetric
power density (800 Ah/l) combined with its inability to handle the higher rate
capabilities needed to satisfy future applications (i.e. electric vehicles) have caused
alternatives to be sought.

The success of the graphite anode has meant that anodes have received less
attention than their cathode counterpart due to the cathode contributing the limiting
capacity to the battery system and the convenience of the graphite anode which
diminished the need for an alternative. Recent advances in cathode design have
instigated a search for more versatile anode materials which are able to offer greater
volumetric stability on cycling or present alternative intercalation voltages to match
the high voltage spinel cathodes or avoid any lithium metal plating issues during, for
example, a fast recharge.

Much research has focused upon lithium metal alloys, most popularly tin
alloys$^{1-3,50-52}$. Some of the alloys show packing Li densities similar or above Li metal
itself, obviously an advantage compared to graphite. The primary problem with alloys
is they show up to 4-fold volume change between lithiated and delithiated forms, this
can cause large mechanical stresses through the alloy material and battery as a whole
causing cracking and crumbling of the alloy anode; subsequently the conductivity of the electrode is reduced and the internal resistance of the cell increases. Thus far a serious commercially viable alloy anode hasn’t been developed (Fuji’s STALION battery being the only serious contender, though development is in progress, utilising recent advancement in high surface area silicon anodes, by companies such as Nexeon) but interest continues due to the impressive volumetric and gravimetric capacities, with research now focusing on materials utilising two different active phases which operate at different voltages\textsuperscript{53}, each material being used to stabilise the other while electrochemically inactive (so called buffer matrices).

A recently developed class of anodes is the ‘zero strain’ series of materials which show no volume change upon lithiation and de-lithiation\textsuperscript{54-59}, the most prominent being Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}. Lithium titanates have high cycling stability due, in part, to their negligible crystallographic volume change during cycling, a flat voltage response at 1.5V and excellent lithium diffusivity, but they suffer from low gravimetric capacity and so far have only been applied to specialist applications which utilise a high voltage cathode (to maintain power density).

After the work of Fuji Co. on metal vanadates which found the materials to be low potential/large capacity compounds\textsuperscript{60}, various layered Li-metal oxide systems were investigated\textsuperscript{61}. It was determined that at low potentials these systems behaved in a different manner to the classic intercalation process, instead of inserting lithium into the host structure an electrochemical formation of metal nanoparticles is believed to occur during first discharge and is accompanied by production of Li\textsubscript{2}O\textsuperscript{62-64}. Various layered oxide systems have been explored\textsuperscript{65-70} a typical example is the CoO system
which revolves around the reaction in equation 5. This is thought to have a capacity > 1000mAh/g (compared to the 370mAh/g capacity offered by graphite).

**Equation 5.**

\[ 2\text{Li} + \text{CoO} \rightarrow \text{Li}_2\text{O} + \text{Co} \]

On charging to 3V the lithia is reduced via the catalytic activity of the nanoscale metal which then regenerates the metal oxide.

Recently Thackeray et al.\textsuperscript{71-75} have explored a different type of anodic reaction involving layered oxides. It was found for certain oxides (i.e. LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}) with the classic \( \alpha\text{-NaFeO}_2 \) \( R\bar{3}m \) structure, an alternative reaction took place at low voltages. Instead of the so called dissociation reaction (eq. 5) an addition of lithium to the LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} system was seen to cause a phase change to Li\textsubscript{2}Mn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} \( P\bar{3}m\bar{1} \) rhombohedral structure, as per eq. 6 (both structures can be seen in Figure 2.3.1.)

**Equation 6.**

\[ \text{Li} + \text{LiMO}_2 \rightarrow \text{Li}_2\text{MO}_2 \]

Similar to the \( \alpha\text{-NaFeO}_2 \) structure, the transition metal layer has all the octahedral holes filled but the lithium ions occupy all of the tetrahedral holes in the lithium layer. This structure had been chemically synthesised in Li\textsubscript{2}NiO\textsubscript{2}\textsuperscript{76,77} and Li\textsubscript{2}MnO\textsubscript{2}\textsuperscript{78} but never seen as a consequence of electrochemical lithiation until the work of Thackeray et al.
Both LiCoO$_2$ and LiNiO$_2$ materials have also been tested to determine their low voltage behaviour, but unlike LiMn$_{0.5}$Ni$_{0.5}$O$_2$ it was found that they are predisposed to the dissociation type reactions\textsuperscript{73}. It was concluded that the reaction path of anodic insertion of LiMO$_2$ depends on kinetic factors such as the lithium diffusion and the cell current rates in addition to the thermodynamic factors and thus the true reaction path is difficult to predict easily. Work by Thackeray \textit{et al}.\textsuperscript{75,73} suggested that three types of reaction can occur; (1) the addition reaction to form Li$_2$MO$_2$ (2) the decomposition reaction in which the metal oxide and Li$_2$O are formed and (3) the displacement reaction in which the metal and Li$_2$O are formed (probably a sequential reaction involving both 2 and 3 reaction pathways). In work on layered oxide anodes (both MO and LiMO$_2$ type materials) it has been noted that there is a considerable irreversible capacity on first discharge, this has been ascribed to significant SEI formation by Tarascon\textsuperscript{62,79} due to displacement of metallic transition metal ions during the first discharge. This theory has yet to be explored fully, due in part to the amorphous and possibly nano-scopic nature of the products of this process.
Lithium vanadate is a relatively neglected material with the majority of studies of layered LiVO$_2$ focussing upon the novel thermal behaviour of the V-V distance and unusual orbital degeneracy formed by the V$^{3+}$ triangular lattice in LiVO$_2$$^{80-84}$. Some cathodic studies have been carried out, with the material characterised in various delithiated phases$^{82,85-87}$ where it was found to undergo a spinel transformation at low lithium concentrations. It was found that just as there is a ‘high temperature’ and ‘low temperature’ structure for LiCoO$_2$$^{88}$ there also exist two structurally similar LiVO$_2$ phases which have different electrochemical properties$^{89}$. It was not until very recently that LiVO$_2$ was seen as a viable anode$^{90-92}$. Samsung initially established the ability of LiVO$_2$ to intercalate one lithium and form Li$_2$VO$_2$, but little is currently known about the processes which occur within the electrode as lithium is inserted and a phase change occurs. LiVO$_2$ exhibits rather poor capacity retention on cycling, the cause of this is yet to be explored, but it may have some correlation with the unexplained large irreversible capacity seen on the first cycle.

Currently there are more questions than answers with the layered oxide anode systems, given the ambiguous preference for dissociation vs. addition reactions especially in materials where both LiMO$_2$ and Li$_2$MO$_2$ phases are known to exist but (presumably due to kinetic factors) do not undergo this transformation. To improve matters more systems must be identified which can form Li$_2$MO$_2$ phases under low voltage cycling and further investigation is needed into the structural changes that occur throughout cycling to better understand the nature of reaction pathway selection.
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3.1. **Chemicals**

3.1.1. **Li$_2$CoSiO$_4$**

3.1.1.1. **Solid State Preparation**

Lithium acetate (0.02M, Aldrich) was dispersed with cobalt acetate (0.01M, Aldrich) and tetraethylorthosilicate (TEOS)(0.01M, Aldrich) in a 50:50 mixture of distilled water and ethanol. The solution was stirred for two days and the resulting solid filtered and dried overnight at 60$^\circ$C. The solid was then calcinated at 350$^\circ$C for 4hrs before being pressed into a pellet for two seconds at a pressure of 13x10$^3$ KN/m$^2$ (2 ton/inch$^2$) and heated to 700$^\circ$C for 3 hours in a reducing gas flow (Ar:H$_2$ 95:5 V:V, BOC Gas) to suppress any oxidation of the transition metal that may occur.

3.1.1.2. **Hydrothermal Preparation.**

LiOH.H$_2$O (0.05moles, Aldrich) was added to fumed SiO$_2$ powder (0.0125M, Aldrich) in 20ml of distilled water and the mixture was stirred till homogeneous. At the same time CoCl$_2$ (0.0125M, Aldrich) was added to 10ml of ethylene glycol and stirred under gentle heat until it was seen to dissolve. The two solutions were then mixed and further stirred till homogeneous. This slurry was decanted to a 40ml Teflon lined autoclave and the remaining volume topped up with de-oxygenated distilled water. The autoclave was sealed and placed in an oven for 72 hours at 150$^\circ$C. The resulting material was filtered and placed in an oven at 60$^\circ$C overnight to dry.

Not all polymorphs could be achieved directly. To realise the $\beta_i$ phase the hydrothermally produced $\beta_{II}$ polymorph was placed in an oven (in air) and quickly heated, at a rate of 300$^\circ$C/h to 700$^\circ$C for two hours and allowed to cool with the oven.
To form the $\gamma$$_{O}$ phase the hydrothermal material was quickly heated at a rate of
300°C/h in an oven to 1100°C for two hours. The oven was cooled to 850°C where the
material was removed and allowed to cool to room temperature (the heating regimes
were based on the work of West and Glasser$^1$).

3.1.1.3. **Mechanical (ball) Milling**

The active material was sealed inside a tungsten carbide milling vessel with
two tungsten carbide (Ø 10mm) ball bearings. The whole container was then
mechanically shaken (SPEX Centri-Prep 8000 M mixer/mill) for 30 minutes and the
milled material was recovered.

3.1.1.4. **Carbon coating**

The as-prepared material was ground with the carbon xerogel precursor (0-20% wt.) in a pestle and mortar in acetone for 10 minutes. The acetone was allowed to
evaporate, then the material was placed in a furnace under flowing argon and heated
from 500-1000°C for 8-24hrs and allowed to cool with the oven.

To make the Xerogel; resorcinol, C$_6$H$_4$(OH)$_2$ (Aldrich) and formaldehyde, CH$_2$O
(35% wt. aq.) (Aldrich) were mixed in a molar ratio of 1:2. sodium carbonate, Na$_2$CO$_3$
(Aldrich) was added as a catalyst at a molar ratio of 50:1 resorcinol: Na$_2$CO$_3$. The pH of
the solution was initially set at 6 by addition of dilute nitric acid, HNO$_3$ (1M, Aldrich).
The solution was sealed in a Teflon$^{TM}$ (Dupont) lined autoclave and stirred magnetically
for thirty minutes. The mixture was then cured for one week in an oven at 85°C. The
resulting gel was washed with acetone for three days, fresh solvent was added daily
after vacuum filtration. The washed gel was heated under nitrogen gas in a tube
furnace at 65°C for 5hrs, where upon the temperature was increased to 110°C and
held for a further 5hrs. The pyrolysis stage of the dried gel occurred at a chosen temperature (700°C - 1000°C, depending on desired properties for the gel) for three hours under nitrogen.

3.1.2. LiMO₂ Anode materials

3.1.2.1. LiVO₂

Li₅ₓVₓO₂ was synthesised from lithium carbonate and vanadium oxide using a solid state method. Appropriate ratios of dried V₂O₅ (Aldrich, 99%) and Li₂CO₃ (Aldrich, 99+%) powders were mixed together in an argon atmosphere, placed in a gas-tight container and subsequently ball-milled for sixty minutes (SPEX Centri-Prep 8000 M mixer/mill). The mixture was then placed in an alumina crucible, covered with a lid (to reduce lithia vaporisation) and heated at 800°C for ten hours under flowing argon. The compound was allowed to cool to room temperature then heated to 850°C for twelve hours under a flowing gas mixture of 95% argon/5% hydrogen (to suppress the conversion of V³⁺ to V⁴⁺).

3.1.2.2. LiMO₂ (M=Co,Ni,Mn or a combination thereof)

Layered transition metal compounds LiCoO₂ (Aldrich), LiNi₀.₅Mn₀.₅O₂ (Fluka), and LiMnO₂ (made in house²) were checked for purity by X-ray diffraction and used as received from the supplier. LiMn₀.₃₃Ni₀.₃₃Co₀.₃₃O₂, LiNiₓCo₁₋ₓO₂ (where x=0.33,0.5 & 0.66) & LiMn₀.₅Co₀.₅O₂ were synthesised by the resorcinol/formaldehyde gelation method³. Resorcinol (0.1 mol, Fluka; 99%), formaldehyde (0.15 mol, Fluka; 36.5 % in aq.) and lithium carbonate (0.5 mmol, Aldrich) were added to a given amount of
distilled water and the mixture was stirred until the resorcinol was seen to dissolve. Stoichiometric quantities of the lithium and transition metal acetates were added to the stirring mixture until all had dissolved. The resulting solution was then heated in a sealed moist atmosphere for 10hrs at 90°C. The resultant mixture was placed in an alumina crucible and calcined in a furnace at 900°C for 12hrs in air.
3.2. Electrochemical Techniques

Electrochemical analysis is a broad subject, encompassing many useful techniques, the procedures and theory discussed below represent just a fraction of the many different methods that exist that can be used to inform and illuminate the inner processes occurring inside batteries. For a more in-depth discussion surrounding electrochemistry and the techniques that can be used, a good starting point for general electrochemistry is; Electrochemical Methods: fundamentals and applications\(^4\), more specific to ionic host materials is Solid State Electrochemistry\(^5\) amongst others\(^6,7\) as well as useful review articles\(^8\). For AC impedance, Impedance Spectroscopy\(^9\) by Barsoukov and Macdonald and Electrochemical Impedance Spectroscopy\(^10\) are useful references.

3.2.1. Composite Electrode

To make a composite electrode for testing, the active material is mixed with a high surface-area carbon to improve conductivity (a binder is also used to improve electrode homogeneity and texture).

The active-material is ground (either in a pestle and mortar or through mechanical milling) with Super P carbon (TIMCAL Graphite and Carbon). A polymer binder (Kynar Flex™ 2801 binder) is then mixed with the material resulting in a composite material with a final composition of active material: carbon: kynar at a ratio of 80:10:10 respectively (this composition is dependent on the conductivity of the active material, better conductivity = less carbon etc.). All capacities are calculated with this in mind and are quoted for the active material only.
3.2.2. Coin Cells

Coin cells offer a convenient method to prepare and test laboratory battery systems. Unlike their commercial counterparts, coin cells pack a very low density of materials (compared to the rolled cylindrical or prismatic cells for example) but because of their convenient preparation and durable nature make for an excellent and accessible way to characterise battery systems.

![Figure 3.2.1. Schematic of the CR2025 battery coin cell system.](image)

The CR2025 coin cell comprises several individual bespoke components that fit together to form a gas tight seal. Inside the coin cell an electrolyte soaked fibreglass disc separates the cathode from the lithium foil anode. The two electrodes are in turn contacted to a sprung steel current collector, thus ensuring a good contact with the coin cell can. The exterior cell can is made of high quality stainless steel (electrochemically inert in the voltage region under investigation) with a top cap and a bottom cap that fit together utilising a plastic washer/gromit to ensure the internal atmosphere is maintained. When the cell is assembled it is compressed using a pneumatic press to ensure a good gastight seal and contact between various components (as seen in Figure 3.2.1). All cells were constructed and handled in an Ar
3.2.3. **Galvanostatic cycling**

The most widely used battery testing technique is galvanostatic cycling. By the application of a constant current to a cell, the change in voltage as a function of time can be measured. By forcing charge into, or removing charge from a cell the cathode and/or anode undergo reactions to accept or extrude the electrons (and charge carriers). Each reaction has a distinct thermodynamic free energy which corresponds to the voltage observed at the electrode. The length of time a certain voltage is maintained corresponds to the length of time the system is receiving or extruding charge at that voltage. Thus, the amount of charge at a known rate for a given length of time can be used to determine the capacity for each voltage step.

The capacity generated by each voltage step (and the reaction associated with it) can then be calculated by the charge passed multiplied by time (t) and is normally quoted as mA.h (milli-amps (mA) multiplied by hours(h)). More commonly used is the gravimetric capacity, which is calculated from the total amount of charge passed per unit mass of the active electrode material (g) for a complete charge (or discharge) given by the equation below.

**Equation 1**

\[
\text{Gravimetric capacity} = \frac{Q \cdot t}{m}
\]

*Where Q is the constant charge applied (mA) t is the time passed (h) and m is the mass (g)*
If we assume all (or nearly all) of the capacity generated from a galvanostatic cycle is generated from the intercalation process, then by dividing the gravimetric capacity by the theoretical gravimetric capacity (given in equation 2) we can match each voltage step to a different composition of lithium in the compound (so after 50mAh/g of capacity passing in a material of the formula LiMO$_2$ which has a theoretical capacity of 100mAh/g we can say 0.5 Li have been removed, or the material’s composition is now Li$_{0.5}$MO$_2$)

**Equation 2**

For the half reaction; $\text{Li}_n\text{A} \rightarrow n\text{Li}^+ + n\text{e}^- + \text{A}$

Theoretical capacity (mAh/g) = $\frac{[(1/m) \times nF]}{3.6}$

Where $m$ is the molar mass of $\text{A}$, $n$ is the moles of $\text{Li}^+$ ions exchanged, $F$ is the Faraday constant (3.6 is the conversion factor encompassing the change from seconds into hours and amps to milli-amps).

This allows us to plot how the voltage changes with lithium composition, which is similar to an 'equation of state'. If the electrode undergoes reversible changes from cycle to cycle then the plot should not change between cycles, and hence the plot must not change as a function of cycle number.

![Figure 3.2.2 Schematic of a galvanostatic charge and discharge profile.](image-url)
Figure 3.2.2 shows a typical galvanostatic profile of a cathode material with a lithium counter electrode. The initial steep voltage increase on charging suggests no electrochemical activity at those voltages due to the minimal capacity generated. The voltage plateau is the first hint of a sustained electrochemical process. The existence of a flat plateau is due to a two phase transformation process caused by the co-existence of two phases, a Li$^+$ dilute and a lithium concentrated phase with a distinctive voltage associated with the transformation from one to the other. The movement of lithium ions is dominated by a phase boundary movement rather than Li diffusion through particles (characterised by a sloping galvanostatic profile). After the charging section of the cycle has reached the designated voltage cut off the current is reversed and discharge begins. Discharge is characterised by an inflow of current to the cathode, in Figure 3.2.2 this is displayed as reduction of capacity. In a fully reversible system the charge and discharge sections of the galvanostatic profile should be almost equal-ideally with similar length plateaus (the profile in Figure 3.2.2 generates more capacity on charging than discharging).

An extension of this technique is the incremental capacity plot (or differential capacity plot) where the differential product of the galvanostatic plot is plotted against voltage (E vs. dQ/dE). This is calculated from adjacent points in the voltage time data using the known value for the current I and the active electrode mass m. The resulting plot is roughly analogous to the potential sweep voltammetry technique with some important differences. The plot shows the rate of change of capacity versus the voltage, thus plateaus are equivalent to a constant rate of change and peaks equate to a local maxima or minima (i.e. a plateau in the galvanostatic plot). Unlike with potential sweep techniques, there is little or no sweep rate dependence.
and hence the exact voltage position of the peaks is less likely to be masked by overcharge issues. This technique has the advantage of easily identifying individual processes within the electrochemical cycle because each peak represents a plateau from the galvanostatic load curve, with the voltage of the peak representing the mid-plateau voltage. Thus even minor galvanostatic plateaus can be identified by the peaks in an incremental capacity plot. By integration of the area under the peak we are also able to calculate the exact capacity of each peak (and hence the capacity of the associated electrochemical process).

A special case of galvanostatic cycling is Galvanostatic Intermittent Titration (GITT). It is a method to establish the equilibrium (or near equilibrium) voltage of the material, versus lithium composition of an electrode. To achieve this, a pulse of current is applied to a cell for a discrete time period (thus inserting or removing a known amount of lithium and hence causing a voltage response from the electrode). The cell is then allowed to relax to an open circuit voltage which can be linked with the current lithium composition of the cell. The time taken to reach open circuit voltage upon relaxation can provide information on the kinetics of electrode processes.

3.2.4. **Potentiostatic cycling**

Potentiostatic cycling (including voltammetry and cyclic voltammetry) utilises a different method to galvanostatic cycling. Instead of current being applied and the voltage measured, a uniformly changing voltage is used to generate a current, which is then measured and thus, the relative amount of current generated at a certain voltage can be plotted. Since the thermodynamic free energy of an electrochemical reaction
can be linked to the voltage, the amount of charge developed at a voltage is indicative of the amount of charge developed by a reaction linked with that voltage (once the number of electrons involved with the reaction are known, the amount of current generated can be used to inform on matters such as kinetics of the reaction).

Due to the constantly changing nature of the voltage, the amount of current generated is dependent on internal and external kinetics of the material and the system at large (e.g. if the sweep rate is on a considerably faster kinetic scale to lithium diffusion through the particle, only a small amount of generated current will be observed at the voltage usually associated with lithium removal/insertion, i.e. equilibrium voltage). So by altering the speed at which the voltage changes (the so called ‘sweep rate’) various kinetic parameters of the system can be determined and the various rate dependencies of electrochemically distinct processes can be determined.

A key factor in voltammetry is the over-potential, at high sweep rates or when the reaction is kinetically hindered the potential at which charge is developed may be different from the equilibrium potential for the reaction; this must be taken into account when looking at the absolute voltage. The over-potential is governed by the relationship described in the Nernst equation (given as for the reduction half reaction in equation 3)

\[ \varepsilon = \varepsilon^0 - \frac{RT}{nF}\ln\left(\frac{C_{\text{oxidised}}}{C_{\text{reduced}}}\right) \]

Equation 3. Nernst equation. \( \varepsilon \) is the observed reduction potential, \( \varepsilon^0 \) equilibrium potential, \( R \) is the universal gas constant, \( T \) is the temperature, \( n \) is the number of electrons being transferred, \( F \) is the Faraday constant, \( C_{\text{oxidised}} \) is the concentration of oxidised species present and \( C_{\text{reduced}} \) is the concentration of reduced species present- to convert the equation for the oxidised half reaction invert the concentration term
A cyclic voltammetry plot is shown in Figure 3.2.1 for the common electrolyte LP30. The profile shows very little current generated across the 1-5V region selected (note for slower scan rates more current would be expected as the system is less kinetically hindered) the rise at the end of oxidation near 5V is the electrolyte disassociating suggesting that above ~4.6V the electrolyte may become unstable and side reactions may become prevalent. On reduction, near 1V we see a slight increase in current suggesting the start of an electrochemical process and may define the low voltage stability of the electrolyte. It can be observed that this reaction is seemingly a reversible process (at least in the non-technical sense of the word) due to the presence of a corresponding peak at 1.5V with oxidation (slightly offset due to over-potential effects) and, alternatively, may represent impurities in the sample.

From a battery electrode point of view when testing with cyclic voltammetry, mildly offset, symmetric peaks in both oxidation and reduction sections which do not change with repeated cycling show a stable lithium insertion and removal process.
Figure 3.2.3. Cyclic voltammetry plot for the electrolyte LP30 (1:1 by weight mixture of dimethyl carbonate(DMC) and ethylene carbonate(EC) with 1M LiPF$_6$ as the conductive salt) at a (slow) scan rate of 0.05mV/s at 30°C.

Potentiostatic measurements were carried out on a Biologic VMP3 multichannel potentiostat, using the ECLab program to record data.

3.2.5. **AC Impedance and DC Conductivity**

Much of electrochemistry is dominated by the interactions that occur at interfaces; various physical factors (electrical, morphological, crystallographic etc.) affect the conductivity of the system as a whole due to the inhomogeneous distribution of charge (polarisations) at the interface. Each interfacial interaction will have distinct polarisation behaviour when a potential difference or current is applied. The rate of change of polarisation when the potential (or charge) is applied or reversed will also be individual to the specific interface, allowing further characterisation of the interface.
Qualitatively the polarisation change is slow for chemical reactions and significantly faster across grain boundaries. Double layers and their capacitances, ubiquitous throughout many ‘wet’ electrochemical systems, can be determined by their (distribution of) relaxation times. While individual materials may produce a simple polarisation relaxation signature. The many interactions of individual components within an electrochemical system combine to form a cumulative signal which may contain overlapping contributions from various sources making determining individual contributions a distinctly non-trivial task.

Within the context of battery systems Impedance spectroscopy can be used to characterise the properties such as the dynamics of mobile charge carriers in the bulk or in boundary regions of materials, as well as the charge associated with electron transfer at the solid-electrolyte or solid-solid interface.

The basic impedance experiment consists of applying a known voltage or current and observing the resulting current or voltage response. The voltage (or current) is applied as an oscillating single frequency and the phase shift and amplitude (the real and imaginary parts, respectively) of the response of the current (or voltage) is recorded and analysed using Fast Fourier Transforms (FFT); this is normally repeated for frequencies in the range from mHz to MHz. The frequency signal can be described as a wave using \( v(t)=V_m \sin(\omega t) \) where \( v=\omega/2\pi \) (and \( \omega \) is the angular frequency), the resulting current response can be characterised by \( i(t)=I_m \sin(\omega t+\Theta) \) where \( \Theta \) describes the phase difference between the voltage and current (DC measurements are a special case of this, as there is no oscillation in the current there is no lag in the voltage response hence \( \Theta=0 \), and the simple ohmic relationship can be used).
Response from the capacitance and inductive elements can be divined from differential equations but the picture becomes increasingly complicated: a situation that is remedied through Fourier transforms. For simplicity, the frequency domain voltage/current relationship can then be expressed using the ohmic relationship of \( I(j\omega) = V(j\omega)/Z(j\omega) \) where the resistance has been replaced by the complex impedance \( Z(j\omega) \) (for capacitance \( Z(j\omega) = 1/C.j.\omega \) and for inductance \( Z(j\omega) = L.j.\omega \)) using the ohmic relationship a circuit with multiple elements can be modelled in a similar way to multiple resistors.

The real and imaginary elements of \( Z \) can be separated by expressing \( Z \) as a vector sum of the components \( a \) and \( b \) along the \( X \) and \( Y \) axis of a right hand orthogonal axis \((Z = a + jb \text{ with } j = \sqrt{-1} = \exp(j\pi/2))\) indicating (by counter clockwise rotation) that the real component, \( a \), is along the \( x \) axis and \( b \), the imaginary component, along the \( y \) axis hence the impedance \( Z(\omega) \) is equal to \( Z' + Z''j \) with \( Z' \) the real component and \( Z'' \) the imaginary (or expressed as rectangular coordinate \( Z' = |Z|\cos\Theta \) and \( Z'' = |Z|\sin\Theta \) respectively).

For real world systems (i.e. non ideal) impedance is normally constricted to the time or frequency domain and analytical techniques have grown up both empirically and theoretically, to support these functions. One of the most common ways of analysing impedance data is through a Nyquist plot. It involves a polar coordinate plot with the negative imaginary component \((-Z'')\) plotted against the real component \((Z')\), an example is shown in Figure 3.2.4.

One of the most prevalent techniques to analyse electrochemical Nyquist plots is equivalent circuit modelling. Equivalent circuit model attempts to replicate the
internal ‘wiring’ of the electrochemical systems using common electrical components, by pseudo-empirically producing a circuit model that is equivalent to the internal electrochemical behaviour. The model produces a theoretical Nyquist impedance spectrum and this is compared to the observed experimental spectrum using least squares fitting to determine the appropriate values of the circuitry components. How well the model fits (usually given a $\chi^2$ value) can then be used to analyse if the equivalent circuit model needs refinement. The ability of fitting an equivalent circuit is considerably easier with a greater number of elements. This is problematic as this may not represent the true nature of the processes occurring within the system, thus Occam’s razor dominates circuit selection, with the general rule that if a new element does not reduce the $\chi^2$ value by an order of magnitude then it can be ignored.

Figure 3.2.4 Example Nyquist plot.

To model the equivalent circuit a dipole couple of a capacitor and resistor in parallel is used. This is thought to model an individual time domain component, this describes the left hand, high frequency, semi circle. This is set in series with a constant
phase element and another resistor. The constant phase element accounts for the non-ideal nature of the capacitor (and hence, the semi-circle). Many explanations exist why some real-world systems do not display ideal capacitor behaviour, but it is generally thought that it is a consequence of inhomogeneous nature of the physical properties in the corresponding element in the real system\(^{10}\). The constant phase element is described by the equation below (eq. 4):

\[
Z_{\text{CPE}} = \frac{1}{Q_0 \omega^n} = \frac{1}{(Q_0 \omega^n) e^{-\pi/2}}
\]

Where \(Q_0 = 1/|Z|\) at \(\omega = 1\) rad/s, \(n\) then describes the ‘ideality’ of the CPE, \(n=1\) is an ideal capacitor, \(n=0\) is a pure resistor.

The equivalent circuit, shown adjacent to the Nyquist plot in Figure 3.2.4 displays a typical equivalent circuit that could be used to model the plot. It suggests that the plot was generated by a material (or system) with 2 different polarisation behaviours connected in series. This is typical of a polycrystalline material where the electrical interactions are dominated by bulk interactions (the high frequency semi-circle) and grain-boundary interactions (low frequency semi-circles), thus the individual capacity and resistance contributions from different physical regions in the material can be separated out and analysed individually (though care is needed to ensure only contributions from the active materials are present). Obviously, with more complex systems (such as a complete battery system) the picture becomes notably more complicated as more systems interact and overlap and care must be taken with analysis.

AC impedance and DC conductivity measurements were produced using Solatron Analytical Modulab equipment and the Modulab program, in conjunction with 2 stainless steel blocking electrodes. Equivalent circuit fitting was undertaken
using the ECLab Zfit program. All measurements were taken in a temperature controlled oven (Room temperature was set at 22°C).
3.3. **Structural Analysis**

3.3.1. **Transmission Electron Microscopy (TEM)**

Transmission electron microscopy (TEM) acts in a similar manner to other forms of microscopy in that a beam of light (or electrons) is incident on a material/substrate and the following scattering of the beam allows observation of physical properties of the material/substrate. In the case of TEM, electrons are the used as the incident beam. They are chosen specifically for their smaller de Broglie wavelength, allowing them to probe at a higher resolution and finer detail than visible light microscopy, this allows studying of materials on a micro (crystallite) to nano (molecular and even atomic) meter scale. Transmission electron microscopy uses a beam of electrons incident on a substrate, after passing through the substrate the scattered electron beam is incident upon a CCD detector and an image is developed. Under vacuum the TEM uses an electron gun to generate a beam of electrons which is focussed by a series of magnetic lenses, this is then incident on the sample and the transmitted electrons are picked up by the CCD detector.

All TEM images were taken by Mr Yu Ren, using a Jeol JEM-2011 HRTEM.
3.3.2. **X-ray Diffraction and Rietveld Refinement**

The following discussion is just a brief overview of the theory behind X-ray diffraction and structural refinement, more authoritative and definitive descriptions can be found in many textbooks, some good examples are the relevant chapters in Kittel’s solid state physics textbook\(^\text{12}\), similarly the textbook of Aschroft and Mermin\(^\text{13}\) and the work of Woolfson\(^\text{14}\).

3.3.2.1. **Diffraction theory**

When X-rays are incident upon electrons they are scattered, upon interacting with planes of electron density of similar scale to the X-ray wavelengths, constructive and destructive interference is set up within the scattered beams. This gives rise to the ‘peaks’ of a diffraction pattern, occurring where the scattered X-rays constructively interfere with so called ‘crystal planes’ and give areas of varying photon intensities on the detector. The angle from the incident beam can be used as a dimension to describe the position of photon intensity peaks within the scattered beam. The condition for interference of radiation scattered from crystalline materials was first described by Laue\(^\text{15-17}\) (for which he subsequently won the Nobel prize in physics) and later expanded by the Braggs\(^\text{18}\) (who were awarded the Nobel prize in physics the following year). By visualising a crystal as formed by infinite, uniformly spaced, parallel planes Bragg was able to theorise how X-rays would scatter from a crystal. Bragg the younger suggested that the angle of incident would be equal to the angle of reflection (\(\theta\)). Under this condition the radiation reflected from successive planes interfere constructively whenever their path difference is an integral multiple of the incident
wavelength (i.e. when the phase difference of the scattered wavelengths equals \( n2\pi \)) giving the famous Bragg condition.

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

*Equation 5.*

Where \( n \) is the integral, \( \lambda \) is the wavelengths of incident radiation, \( d \) is the distance between planes of uniform electron density, \( \theta \) is the angle between planes and the incident/reflected radiation.

Figure 3.3.1. Schematic of X-ray beam scattered from crystal planes.

For powder diffraction the samples consist of very small crystallites which are randomly orientated with respect to the incident beam. The random particle orientation will cause planes correctly orientated to the beam within the crystallites to scatter the beam constructively. As there is effectively an infinite number of crystallites within the powder (and hence an infinite number of orientations) all planes will be represented and hence all reflections can be observed.

A three dimensional repeating unit (unit cell) motif can be identified within the crystal structure which can be used to describe the atomic positioning throughout the entire crystal. The vast majority of materials have a unit cell that can be described by a Bravais lattice; these are a collection of 14 different crystal systems defined through
the ratio of the dimensions of the unit cell, the angles between the sides and the symmetry of the lattice.

To relate the Bravais lattice to the diffraction pattern we can use Miller indices. By labelling the sides of a unit cell h,k and l (along the X,Y, and Z axes, respectively) and equating the full length of the unit cell to one, we can then describe how a lattice plane intersects through a unit cell, by describing the point at which all three axis of the unit cell are intersected by a crystal plane (as a fraction of one). Each crystal plane that bisects the unit cell can be assigned an h,k,l value that corresponds to position of the intersecting crystal plane with respect to the unit cell. As each suitable crystal plane will generate its own constructive interference peak (i.e. peak in the diffraction pattern) these peaks can be assigned h,k,l values and be used to identify the unit cell from the diffraction pattern.

To determine the individual ionic or atomic positions in a unit cell (or crystal plane) a more intricate method has to be invoked. It helps if we look at the Laue approach in closer detail (Von Laue developed his work before the two Bragg’s work, and connects the scattering angles and the size and orientation of the unit-cell spacing in the crystal. Bragg built on this to produce the Bragg law which connects the observed scattering with reflections from evenly spaced crystal planes within the crystal).

Similarly to Bragg’s description, Von Laue considered a beam incident upon a lattice. Von Laue defined the conditions that two atoms/ions described by a vector would have to satisfy in order for there to be constructive interference. The scattered
rays will constructively interfere when the difference between the periods of the incident and scattered beam is an integer multiplied by $2\pi$.

In the case of a Bravais lattice, all atomic positions can be described by the vectors separating them i.e. the lattice is made up of an infinite set of points generated through discrete translation operations, so that the lattice can be expressed by a single term ($\mathbf{R}$) formed by the sum of vectors that span the lattice. The requirement for constructive interference then becomes that the difference between the incident and scattered beam wave vectors, after diffraction through atomic positions ($\mathbf{R}$), is equal to an integer multiple of $2\pi$. This is similar to saying any momentum transfer (i.e. change in wave vector) must have a periodicity of the Bravais lattice.

The set of wavevectors that are able to meet this condition are called the reciprocal lattice. As this is just an inverse of the ‘real space’ lattice, this is itself a Bravais lattice and can be described using the primitive vectors related to the real space lattice vectors by a geometric relationship. This reciprocal lattice vector ($\mathbf{G}$) can then be used to describe planes in the real lattice (as each crystal plane will have a reciprocal lattice vector that is normal to it) and so a plane with Miller indices of $h,k,l$, can be related to a reciprocal lattice vector.

It is then possible to relate the Von Laue conditions to the Bragg equation by stating if the difference in incident and scattered beam periodicity equals the reciprocal lattice vector ($\mathbf{G}$) the scattering must be elastic (i.e. the incident and scattered beams have the same magnitude) thus, the incident and scattering angle must be the same. By being able to describe the Miller indices of the real lattice in
terms of reciprocal space, Bragg was able to build on Von Laue’s work and develop his famous equation relating the spaces between crystal planes to the scattering angle of the incident beams.

From the Bragg equation (and Von Laue conditions) it can be seen that the diffraction peaks give the spacing between different crystal planes within the material, with each peak being assigned its own set of Miller indices to describe how it bisects the unit cell. These inter-planar distances can be used to assign the crystal to a crystal system and develop approximate values of the lattice parameters.

While it is possible to employ a computational method to search crystal systems for a reasonable d spacing match, a large number of peaks are required and the method is not fool-proof. In the vast majority of cases a prediction is made about the expected crystal system based on the materials and synthetic procedure used to form the materials, as well as any other methods of chemical analysis used in conjunction with the X-ray diffraction.

Bravais showed that there are only 14 types of space lattice when defined by their point symmetry, which is the symmetry taken from a central point in the lattice. This can define the repeating unit of the crystal without needing to directly reference the atoms/ions present. Finally an additional descriptor is added to fully describe the translational symmetry of the lattice. This involves describing spatial shifts in the symmetry in addition to point symmetry, when this is taken into account there are two hundred and thirty combinations which can describe any crystal symmetry, these are called the space groups.
After the lattice parameters of the unit cell have been determined and the reflection peaks have been assigned Miller indices, a study of the missing reflections can reveal the lattice type (face centred, body-cantered, primitive) and the transitional symmetry elements can be found. While the positions of the peaks are able to inform about the type of lattice, their relative intensities (peak height) can give information about the atomic arrangement inside the cell with reference to any lattice point.

Revisiting the conditions for constructive interference; if an incoming wave is scattered from two points \( r_i \) and \( r_j \) the path difference between the scattered rays will be differ by a factor of \( e^{i 2\pi \Delta K (r_i - r_j)} \) (where \( \Delta K \) is the difference between the incident and scattered wavevectors). Similarly the rays scattered from \( r_1 \rightarrow r_n \) will have phases in the ratio of \( e^{i 2\pi \Delta K (r_1)} \rightarrow e^{i 2\pi \Delta K (r_n)} \) and so, to describe rays from the entire cell the expression \( S_{\Delta K} = \sum_{j=1}^{n} e^{i \Delta K \cdot r_j} \) can be used.

The condition for constructive interference requires \( \Delta K \) be a reciprocal lattice vector (\( G \)), so the factor associated with a particular Bragg reflection can be expressed in terms of \( G \) as \( S_G = \sum_{j=1}^{n} e^{i G \cdot r_j} \). This is called the structure factor. The structure factor indicates to what extent a particular Bragg reflection is diminished by interference effects between identical ions. As the X-rays scatter from areas of electron density the total scattering from a distinct volume will be dependent on the concentration of electrons in that volume which can be expressed as a volume element \( dV \) which is proportional to the electron concentration. Expanding this idea to encompass atoms with different electron densities, a Fourier Transform can be applied to the structure.
factor for an electron density of \( n_j \) for each atom \( j \). This modulating factor is called the atomic scattering factor. The atomic scattering factor is an integral over all space associated with electron concentration of the \( j^{\text{th}} \) atom multiplied by the phase factor.

The phase factor depends on the position of the electron density with respect to the centre of the atom. If the corner of a unit cell is defined as \( r = 0 \) and \( \bar{r}_j \) is the centre of an atomic position then the atomic scattering factor can be written as:

\[
f_j = \int dV n_j (\bar{r} - \bar{r}_j) e^{i \mathbf{G} \cdot (\mathbf{r} - \mathbf{\bar{r}})}
\]

Adding this to the x-ray structure factor, this achieves:

\[
S_G = \sum_{j=1}^{n} e^{i \mathbf{G} \cdot \bar{r}_j} \int dV n_j (\bar{r} - \bar{r}_j) e^{i \mathbf{G} \cdot (\mathbf{r} - \mathbf{\bar{r}})} \quad \text{or} \quad S_G = \sum_{j=1}^{n} f_j e^{i \mathbf{G} \cdot \bar{r}_j}
\]

The structural factor, can of course, be written in terms of the miller indices:

\[
S_G = \sum_{j=1}^{n} f_j \exp[2\pi i (h\bar{x}_j + k\bar{y}_j + l\bar{z}_j)]
\]

Thus over a large enough number of reflections the structure factor can be used to calculate all the positions of the atoms in the cell.

One final addition to the structure factor is the effect of temperature on the atomic positions in the unit cell and hence the structure factor. Depending upon the temperature, the atoms/ions in the unit cell will deviate from their equilibrium positions through thermal motion (depending on factors such as how tightly bound in place they are etc.). With large deviations of atomic positions there is an effect of diminishing the amplitude of coherent scattering in the cell (by a factor of \( \exp(-2B_j \sin^2 \Theta/\lambda^2) \)) where \( B_j \) is the average displacement of an atom \( J \), and is called the
temperature factor in the intensity of the peaks). This temperature factor is called the Debye-Waller factor.

Resolving atomic positions using the structural factor is hampered by one of the most famous problems in powder diffraction structural refinement; the structure factor cannot be measured directly. This is due to the X-ray detector is only able to measure the intensity of the photons hitting the detector (i.e. the number of x-rays hitting the detector as a function of $2\Theta$) but the scattered x-rays not only have amplitude but phase information as well (vital for determining the structure factor). Due to this discrepancy, a method had to be evolved to solve the ‘phase problem’. This was done by assuming the structure factor is proportional to the amplitude of the scattered rays, and because the intensity is proportional to the square of the absolute value of the amplitude, the relative intensities of the Bragg peaks can, by proxy be used to determine information about the structure factor.

Thus the final structure factor can be written as:

$$S_G = \sum_{j=1}^{n} f_j \exp[2\pi i(hx_i + ky_i + lz_i)] \exp(-B_j \sin^2\Theta/\lambda^2)$$

The full structure factor is equivalent to the Fourier transform of the electronic charge distribution of an atom and depends upon the reciprocal lattice vector. It shows the relationship between a single electron acting as a single point in lieu of an atom and the amplitude of scattered coherent radiation.

3.3.2.2. Structural Refinement.

Structural refinement is a technique employed to model the structural nature of the unit cell. The Rietveld refinement method\(^{19}\), developed in 1969, introduced an
easy method of structural refinement from powder data. The method relies on a stepwise collection of data such that intensity is measured against a discrete finite $2\Theta$ scale. A calculated profile is then measured against the collected data. The calculated profile is built from the unit cell parameters, along with a zero point correction to determine the position of the Bragg peaks on the $2\Theta$ scale. The intensities of the peaks are then determined by atomic positions and displacement parameters (i.e. the calculated structure factor).

The individual peak profile is described by a peak function which is generally made up of a linear combination of Gaussian and Lorentzian terms, called the pseudo-Voight function and defined by $G_{ik} = \eta L + (1-\eta)G$ where $\eta$ is the mixing coefficient determining the size of contribution from the Lorentzian ($L$) and Gaussian ($G$) contribution. Generally an extra term is needed to fully describe a peak shape, accounting for any peak asymmetry due to instrumental and sample defects.

Another parameter that is commonly used considers the preferred orientation of the crystallites. If the powder particles have a common asymmetry to their shape (i.e. a cylinder where length $>>$ breadth) then it is likely that many of the crystallites will be lying in a similar way. This can cause a bias of certain crystal planes due to the unnatural prevalence of the crystal planes in the particles’ orientation. In this work preferred orientation has not been considered, as the particles are generally homogenous in dimensions, confirmed by TEM. Finally a background function is used to describe any non-peak intensity (i.e. background intensity).

The intensity of any calculated point $Y_i^{(calc)}$ is then compared to its observed counter-part $Y_i^{(obs)}$ across all $i$ steps of the pattern. This enables a refinement to take
place by comparing the calculated to the observed pattern and minimising the difference between them.

The so called ‘goodness’ of fit can be written as \( S = \sum W_i |Y_i(\text{calc}) - Y_i(\text{obs})|^2 \) where \( W_i \) is the weighted factor determined by the standard deviations of intensity of the \( i^{th} \) profile point.

Prior to starting refinement it is usual to have already established the nominal composition of the material (usually through knowledge of similar synthesis), the shape and approximate dimensions of the unit cell (from fitting of the d spacings or \textit{a priori} knowledge). It is usual that the most probable space group would have also been established (through previous knowledge and identifying any systematic absences in the diffraction pattern).

Structural refinement employs a computer program (in the case of this work GSAS\textsuperscript{20} was used) to perform least squares comparison of the calculated pattern to the observed diffraction pattern, attempting to minimise the difference between the experimental data and the model; this is expressed as the weighted R-factor, \( R_{wp} \). The \( R_{wp} \) represents the normalised weighted sum of the differences between the observed profile and the model and can be expressed as:

\[
R_{wp} = \sqrt{\frac{\sum W_i (Y_i(\text{obs}) - Y_i(\text{cal}))^2}{\sum W_i (Y_i(\text{obs}))^2}} \times 100
\]

Where the sums are taken over all the data points, \( Y_i(\text{obs}) \) and \( Y_i(\text{cal}) \) are the observed and calculated profile points, and \( w_i = (Y(\text{obs}))^{-1} \) is the weighting factor. The parameters, with respect to \( R_{wp} \) are minimised, include the scale factor, the fractional coordinates and the temperature factors of individual ions/atoms.
As well as $R_{wp}$ (and $R_p$, the unweighted R-factor) $\chi^2$ is also quoted. $\chi^2$ is a measure of the ‘goodness’ of fit. $\chi^2$ is derived from the formula $\chi^2 = S/(N-P)$ where $S$ is the term being minimised, $N$ is the number of profile points and $P$ is the number of parameters, generally the lower the $\chi^2$ value the better, though very low $\chi^2$ values can indicate the number of refinement parameters being employed possible exceeds the resolution of the profile.

The actual refinement involves the minimisation of $\chi^2$, through variation of the factors that contribute to the model pattern (atomic co-ordinates, displacement factors, peak profile parameters, background function, peak asymmetry, extinction coefficients and scale factors). The least squares process itself focuses on calculating the gradient of the $\chi^2$ function and trying to solve for the gradient equalling zero, i.e. a minima of $\chi^2$. There are several different methods which can be used (Newton-Raphson, Gauss-Newton etc.) but they all revolve around the above methodology.

Using these calculations, precise information about the crystal structure of novel and well established materials alike can be found. This in turn allows information about the bond length, bond angles and atomic coordination to be determined, which is of great importance when trying to establish the mechanisms and processes involved with cycling anodic and cathodic battery materials.

X-ray refinements were taken on several machines. The choice of machine was determined by the elements present in the materials and the radiation source offered by the machine in order to avoid fluorescence. Measurements of $\text{Li}_2\text{CoSiO}_4$, $\text{LiCoO}_2$ materials were undertaken on Stoe STADI-P powder diffractometer with $\text{Fe-K}\alpha1$ radiation, operating in flat plate (pristine materials) or silicon sealed 0.5mm Ø quartz
capillaries (ex situ materials) transmission mode. LiVO$_2$ and all other LiMO$_2$ material’s diffraction patterns were achieved on a Stoe STADI-P powder X-ray diffractometers with Cu K$\alpha$ radiation, again operating in flat plate (pristine materials) or silicon sealed 0.5mm Ø quartz capillaries (ex situ materials) transmission mode.

Rietveld refinements were undertaken using the GSAS program$^{20}$, utilising the EXPGUI graphical interface$^{21}$.

While this chapter seeks to provide basic explanations of the experimental techniques employed in this thesis, these are just brief overviews of the topics and only hint at the insights these analytical techniques offer. Far more authoritative descriptions exist to enable a more complete use of these powerful methods of analysis. There are also many other techniques which could be employed to provide a different perspective on the internal processes of lithium intercalation, not to mention the many novel analysis methods currently being developed which may provide useful insights in the future.
3.4. References

Chapter 4. \( \text{Li}_2\text{CoSiO}_4 \)
Chapter 4: Li$_2$CoSiO$_4$

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4.1. **Introduction**

This chapter explores the structural and electrochemical properties of Li$_2$CoSiO$_4$ and three of its polymorphs. *(A summary of some of the results presented in this chapter can be found in two published papers, attached as appendix i and ii).*

While silicate polyanion materials are a well understood class of minerals and have been investigated for a considerable time, their properties as cathode material have only recently been explored. The investigation of the silicate three dimensional polyanion class of compounds is a logical extension of the recent research, and the subsequent commercialisation of LiFePO$_4$\textsuperscript{1-3}. While the Li$_2$MSiO$_4$ materials typically offer slightly lower specific capacities than their LiMFePO$_4$ cousins (Li$_2$CoSiO$_4$ = 162.5 mAh/g, LiCoPO$_4$ = 166.6 mAh/g) olivine type silicates may offer a cheaper and potentially, more readily available alternative to LiMPO$_4$ materials. The subtleties in the different chemistries contained within the structures of Li$_2$MSiO$_4$ (M= Fe, Co, Mn...) potentially enables a great degree of engineering available on the molecular scale compared to the LiMPO$_4$ counter-parts.

While the low toxicity and potentially low price of Li$_2$FeSiO$_4$ and Li$_2$MnSiO$_4$ make these particularly attractive battery materials, it has been suggested that inherent conductivity problems may arise in the manganese and iron analogues which would not be present in the cobalt Li$_2$MSiO$_4$ system\textsuperscript{4}, making Li$_2$CoSiO$_4$ an obvious material to investigate. Furthermore in Li$_2$CoSiO$_4$ the cobalt ion is positioned in a three dimensional oxide lattice negating many of the safety problems associated with Co$^{3+/4+}$electrolyte reactions seen in LiCoO$_2$\textsuperscript{5}. Li$_2$CoSiO$_4$ also may provide important
insight into the mechanism of lithium insertion and removal of the Li$_3$PO$_4$ type materials.

The first work on Li$_2$CoSiO$_4$ was carried out by West and Glasser$^{6,7}$ in the early 1970s. Several polymorphic structures (derivatives of the Li$_3$PO$_4$ structure) were investigated and rudimentary phase diagrams were established. It was found that the Li$_2$MSiO$_4$ group may be thought of as based around a slightly distorted oxide hexagonal close packing with half the tetrahedral sites occupied by cations such that face sharing between the pairs of tetrahedral sites is avoided$^1$. It was found that the structures show polymorphism and can be divided into 2 families, β and γ. Within the β form all the MO$_4$ (M= Li, Si, Co) tetrahedra point in the same direction, perpendicular to the close packed oxygen plane, sharing only corners with each other. The γ polymorphs contain tetrahedra arranged in groups of 3 with the central tetrahedra pointing in the opposite direction to the outer 2, with which it shares edges, examples of the β and γ polymorphs are shown in figure 4.1.1.

Variants of both β and γ polymorph exist, involving distortions of the parent structures; they are denoted β$_\nu$, β$_\mu$, γ$_0$ and γ$_\mu$. At low temperatures β is the stable structure and at high temperature γ is the stable equilibrium phase. Cooling the γ form at high temperatures causes a sluggish conversion to the β phase, thus γ can be conserved at low temperatures by rapid cooling. This fast ‘quench’ suppresses the transition of phases and produces a material that is kinetically stable but only meta-stable thermodynamically. During polymorph transition the oxide layer remains unmoved, with migration between sites only thought to occur amongst the transition metal cations$^6$. It is suspected that transition to the sub-polymorphs doesn’t involve a
cation migration, instead involving a minor step that only distorts the lattice of the patriarch phase, perhaps through rotation of $MO_4$ tetrahedra. By re-visiting the polymorphic structures of Li$_2$CoSiO$_4$ materials with modern techniques it should be possible to elucidate a more thorough picture of the differences between the polymorphs and how these structural differences affect the electrochemical behaviour of the polymorphs.

Previous work upon the Li$_2$MSiO$_4$ structures has been brief and focussed on structural determination, with Glasser et al. establishing some basic structures of various Li$_2$MO$_4$ and Li$_2$MXO$_4$ compounds and investigating the phase boundaries of many of the polymorphs contained within these systems. Subsequent work on Li$_2$MSiO$_4$ solved the full structure for some of the polymorphs. The Bruce group has recently published two papers covering the preliminary investigation of Li$_2$CoSiO$_4$ materials which has sparked some interest in the topic.

From recent first principle work it has been established that insertion voltage (and band gaps) of Li$_2$MSiO$_4$ materials roughly correlate to the electronegativity of their late 3rd period metal, e.g. silicon. This behaviour revolves around the $M$-O-Si
relationship, which is ubiquitous throughout the $\text{Li}_2\text{MSiO}_4$ structure. This can be seen in Figure 4.1.1. as the corrugated layers of $\text{Li}_2\text{CoSiO}_4$ where a SiO$_4$ tetrahedra shares all 4 of the corner oxygen atoms with 4 different CoO$_4$ tetrahedra and so on through the 3D mosaic. It has been established in LiMO$_2$ systems that the lithium insertion voltage can be linked to the $M^{n+1/n}$ redox level$^2$. It has been suggested that this theory can be extended to the $\text{Li}_2\text{MSiO}_4$ system with the addition of the $M$-O-Si relationship exhibiting a strong influence upon the $M^{n+1/n}$ redox level.

In $\text{Li}_y\text{MXO}_4$ materials the precise nature of the transition metal redox level (or bonding to anti-bonding orbital band gap of the $M$ ion) is thought to be intricately linked to the P-block ion (for example, silicon) through the inductive effect across the $M$-O-X triplet (where $M$ is the transition metal, O is the oxygen and X is the P-block ion, in this case silicon). The inductive effect is manifested by the polarisation of the metal-oxygen bond due to the adjacent Si-O bond. This effect is thought to control the ionic-covalent nature of the $M$-O bond, and subsequently the redox level of the transition metal ion.

First principles investigations into the factors that affect the transition metal redox level have suggested that, given the nature of the $M$-O-X group a weak correlation between the electronegativity of the P-block element and the redox level of the transition metal exists$^4$. The reasons for this have yet to be experimentally investigated but it has been suggested that by lowering the electronegativity of the X ion in the $M$-O-X couple, the polarisation of the O-X bond is decreased and the $M$-O bond subsequently shortens. By shortening the $M$-O bond the electron density on the transition metal ion is increased and hence affects the $M^{n+1/n}$ redox couple and the
lithium insertion voltage. From an atomic orbital perspective, by shortening the $M$-O bond length, the orbital overlap between the $O_2p$ and $M_{3d}$ orbital is increased. This pushes ‘bonding’ $O_p$ orbitals lower and the anti-bonding d-orbitals of the transition metal ion higher, increasing the band gap (the electron that is introduced with $Li^+$ insertion fills the transition metal anti-bonding d-orbital).

![A schematic representation of the Cobalt(green) to Oxygen(red) to Silicon(blue) connectivity in the $\beta_I$ polymorph.](image)

One of the more promising aspects of $Li_2MSiO_4$ as a battery material is the possibility to insert/remove 2 lithia per formula weight. Recent studies on $Li_2MnSiO_4$ and $Li_2FeSiO_4$ materials have given mixed results as to their ability to remove more than one electron. The manganese based cathode has been shown to have the ability to remove more than 1 $Li^+$ ion per cycle$^{4,3}$. This performance has yet to be well established and attempts to extract more than one lithium from the iron silicate have so far been unsuccessful$^{17}$. It is thought the poor conductivity of the manganese sample in its native (un-doped) state and the iron silicate upon removal of 1 $Li^+$ may be the cause of the lithium extraction limit. By using crystal field theory a consistent picture emerges which explains why the conductivity may have an important role to play in the removal of lithium from the structure.
The nature of the band-gap and orbital into which the electron is inserted dictates the ability of the material to accept or expel an electron during lithium removal or insertion. In the case of silicate materials this orbital is thought to be the LUMO of the transition metal. For example both Mn$^{2+}$ (the reduced state) and Fe$^{3+}$ have half filled orbital states ($d^5$) according to crystal field theory. When the metals occupy these oxidation states they are particularly stable (or in crystal field terms, the tetrahedral geometry causes a large (hence stable) gap between the filled e to unfilled $t_2$ level giving transitions between the two a lower probability). This infers a reluctance to accept or lose an electron (the effect will, of course, vary with differing orbital states, degeneracy and bonding/anti-bonding interactions).

The ability of cobalt silicate material to insert or remove more than one lithium is currently unknown, if the crystal field theory is consistent then neither of the cobalt oxidation states should yield a $d^5$ state and thus should not meet the conductivity problem when removing or inserting more than one lithium. As the electronic conductivity is also intimately linked to the ability of the material to accept or impart electrons, resistivity measurements in conjunction with the galvanostatic performance will be used to assess the affect the transition metal state has upon the lithium insertion process.

There are several structural factors that could affect the lithium insertion/removal efficiency of Li$_2$CoSiO$_4$ materials, and with close analysis of the physical and electrochemical properties of the materials it is hoped that a clear picture of the Li$_2$CoSiO$_4$ lithium insertion and removal mechanisms can be elucidated.
4.2. **Results and Discussion**

4.2.1. **Structural Studies of Lithium Cobalt Silicates**

Both solid state and hydrothermal production methods were investigated to determine the most convenient method of Li$_2$CoSiO$_4$ synthesis. Due to the energetic nature of the hydrothermal conditions, the synthesis was expected to produce one of the more thermodynamically stable phases (i.e. closer to equilibrium). If, as suggested in previous work, the Li$_2$CoSiO$_4$ structure is analogous to Li$_3$PO$_4$ and its associated β and γ polymorphs$^7$, it is most likely that the low temperature Li$_3$PO$_4$ variant (β) would be the most thermodynamically stable (given the room temperature existence of γ Li$_3$PO$_4$ phase is dependent upon its very slow kinetic transformation to the β phase) and so one of the β Li$_2$CoSiO$_4$ polymorphs would be expected to be produced. According to the work of West and Glasser$^6$ the solid state preparation should produce the β$_1$ phase due to the heating regime involved in the final phase of the preparation method.
4.2.1.1. Li$_2$CoSiO$_4$ $\beta_{II}$ polymorph

The hydrothermal synthesis method natively produced the phase identified by West et al. as $\beta_{II}$ and the X-ray diffraction pattern (and subsequent Rietveld fitting) can be observed in Figure 4.3.1. The Rietveld fit was made using the $Pmn2_1$ space group and gave a reasonable fit of $R_{wp}=8\%$. With suitably similar lattice parameters to those reported previously$^5$ (this was further confirmed through subsequent neutron diffraction work carried out by Dr A. Armstrong within the Bruce group, which has since been published$^{11,12}$)

![Figure 4.3.1 X-ray diffraction pattern and Rietveld refinement fit of $\beta_{II}$ of Li$_2$CoSiO$_4$: (1) X diffraction data, - Rietveld fit; (2) Peak marks generated from the $Pmn2_1$ space group; (3) data and fit difference](image)

The material was assumed to be phase pure and free of other impurities. As is shown in Table 4.3.1 the material deviates slightly from an ideal $\beta_{II}$ model as it contains both lithium and cobalt within the 4b site at approximately equal ratios. This leaves
the 2a site exclusively for lithium occupation, giving the material an overall composition of Li$_{2.06}$Co$_{0.94}$SiO$_4$. (This disorder was also confirmed by a $^7$Li NMR study$^{11}$)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Symbol</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>B$_{iso}$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>2a</td>
<td>0.0000</td>
<td>0.178(1)</td>
<td>0.760(2)</td>
<td>0.1(7)</td>
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</tr>
<tr>
<td>Si1</td>
<td>2a</td>
<td>0.5000</td>
<td>0.180(2)</td>
<td>0.842(2)</td>
<td>0.10(2)</td>
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</tr>
<tr>
<td>Li2/Co1</td>
<td>4b</td>
<td>0.2529(9)</td>
<td>0.337(2)</td>
<td>0.339(2)</td>
<td>0.13(5)</td>
<td>0.53/0.47(1)</td>
</tr>
<tr>
<td>O1</td>
<td>4b</td>
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<td>0.328(2)</td>
<td>0.761(1)</td>
<td>0.02(2)</td>
<td>1</td>
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<tr>
<td>O2</td>
<td>2a</td>
<td>0.0000</td>
<td>0.146(2)</td>
<td>0.247(3)</td>
<td>0.010(1)</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>2a</td>
<td>0.5000</td>
<td>0.181(2)</td>
<td>0.339(2)</td>
<td>0.015(4)</td>
<td>1</td>
</tr>
</tbody>
</table>

$a = 6.2606(7)$  $b = 5.3264(6)$  $c = 4.9401(6)$  
Space Group: Pmn2$_1$

Cell Volume = 164.74(5) Å$^3$, $R_p=6.22\%$, $R_{wp}=8.03\%$, $\chi^2=1.654$

Table 4.3.1 Refined parameters Li$_2$CoSiO$_4$ β$_{II}$ polymorph from the hydrothermal preparation

<table>
<thead>
<tr>
<th>Average Bond Length Å</th>
<th>Li1-O</th>
<th>Li2-O</th>
<th>Co1-O</th>
<th>Si1-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>2.037(8)</td>
<td>2.189(7)</td>
<td>2.189(1)</td>
<td>1.625(9)</td>
</tr>
<tr>
<td>O1</td>
<td>2.037(8)</td>
<td>1.940(8)</td>
<td>1.94(1)</td>
<td>1.644(9)</td>
</tr>
<tr>
<td>O2</td>
<td>1.93(1)</td>
<td>1.940(6)</td>
<td>1.94(1)</td>
<td>1.67(1)</td>
</tr>
<tr>
<td>O3</td>
<td>2.020(6)</td>
<td>1.893(7)</td>
<td>1.893(8)</td>
<td>1.754(4)</td>
</tr>
</tbody>
</table>

Table 4.3.2 Selected polyhedra bond lengths and volumes for β$_{II}$ Li$_2$CoSiO$_4$ material.

The disorder amongst the cation sites could be due to the hydrothermal synthesis method, where the possibility exists for the nucleation of small crystallites to occur under fairly energetic atomic/ionic movement allowing for significant cation mixing.$^{18,19}$
Table 4.3.2 displays selected bond distances of the metal tetrahedra within the material and may hint towards some of the electrochemical behaviour of the material. It can be expected that, as the $\beta_{II}$ phase displays 2 structurally distinct Li$^+$ sites, removal/insertion of lithium will favour one over the other. There is a chance that the lithium-only 2a site (Li1-O) will be chosen, given that the 4b lithium site shares occupancies with cobalt, possibly occluding the free lithium movement (the 2a lithium site also has the larger of the 2 LiO$_4$ polyhedra volumes, reducing the thermodynamic burden of lithium movement$^{20,21}$).

Figure 4.3.2. Schematic representations of $\beta_{II}$ Li$_2$CoSiO$_4$ structures, obtained from Rietveld refinement. Blue Polyhedra LiO$_4$, Grey polyhedra SiO$_4$, Green Polyhedra (Co/Li)O$_4$, Red spheres Oxygen atoms.
Figure 4.3.2. displays structural projections of the $\beta_{III}$ phase. All polyhedra within $\beta_{III}$ are arranged so that the vertices of the corner sharing tetrahedra point along the $c$ axis, with the disordered lithium/cobalt tetrahedra translating along the $a$ axis and alternating chains of LiO$_4$ and SiO$_4$ tetrahedra running in parallel.

Figure 4.3.3. Schematic representation of a potential lithium insertion/removal pathway in $\beta_{III}$ Li$_2$CoSiO$_4$; Grey polyhedra SiO$_4$, Green polyhedra (Co/Li)O$_4$, Blue spheres lithium (in 2a site), Red spheres Oxygen).

Figure 4.3.3 shows one of the potential lithium removal/insertion pathways present within the $\beta_{III}$ phase. The 2a lithium sites are aligned in a linear arrangement along the $b$ axis. Though not placed ideally within this ‘tunnel’ the lithium ions could easily propagate along the channel, possibly improving the favourability of removing lithium from this site (compared to the 4b shared site, shown as green polyhedra).
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The hydrothermal synthesis presents several advantages over the solid state method, such as cost (especially with respect to up-scaling) and exploitation of ‘wet’ chemistry environment to manipulate chemical conditions of production. These factors make accessing the polymorphs from the natively produced β₃" phase a very attractive proposition. To this end (as suggested by the work of West⁶) the synthesis of the β₁, γ₁, and γ₀ phases was pursued through reheating the hydrothermal product and using an appropriate temperature/cooling regime to access the other polymorphs.

4.2.1.2. **Li₂CoSiO₄ β₁ polymorph (hydrothermal)**

It was found that the β₁ phase could be easily achieved by heating the hydrothermally produced β₃" material to 700°C for 2hrs, in air, and allowing the material to cool with the oven (at a rate of approximately 1.6°C/min).

![X-ray diffraction pattern and Rietveld refinement fit of β₁ of Li₂CoSiO₄.](image)

*Figure 4.3.4. X-ray diffraction pattern and Rietveld refinement fit of β₁ of Li₂CoSiO₄.*
The Rietveld fit of $\beta_i$ was based on the data obtained from a single crystal refinement by Yamaguchi\textsuperscript{10} of Li\textsubscript{2}ZnSiO\textsubscript{4}, who indexed the structure to an orthorhombic $Pbn2_1$ space group (Yamaguchi reports this material as $\beta_{II}$ using different notation to West). The $\beta_i$ (hydrothermal) material gave a fit of $R_{wp}=17.67\%$, which is not ideal though the low $\chi^2(1.157)$ suggests this could be improved by improved diffraction statistics. (The nature of the $\beta_i$ structure and its structural parameters have subsequently been confirmed through neutron diffraction and the nature of the lithium environments in the structure corroborated with $^7$Li NMR\textsuperscript{11}). The $\beta_i$ material has lower symmetry than its parent $\beta_{II}$ phase, indicated by the approximate doubling of the unit cell along the $b$ axis. From Table 4.3.3 we can see that cation mixing occurs within both the cobalt site (0.93% Co/ 0.07% Li) and one of the lithium sites (0.95% Li/ 0.05% Co) giving the material an overall stoichiometry of Li\textsubscript{2.02}Co\textsubscript{0.98}SiO\textsubscript{4}. The disorder did not vary greatly when different heating (or grinding and reheating) times were employed and thus, may be a consequence of the disorder in the $\beta_{II}$ starting material and subsequent formation.
Chapter 4: Li$_2$CoSiO$_4$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Symbol</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>B$_{iso}$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1</td>
<td>4a</td>
<td>0.498(2)</td>
<td>0.1647(7)</td>
<td>0.273(1)</td>
<td>0.054(3)</td>
<td>Co 0.930/Li 0.070(7)</td>
</tr>
<tr>
<td>Si1</td>
<td>4a</td>
<td>0.248(3)</td>
<td>0.413(1)</td>
<td>0.265(9)</td>
<td>0.079(6)</td>
<td>1</td>
</tr>
<tr>
<td>Li1</td>
<td>4a</td>
<td>0.02(1)</td>
<td>0.160(8)</td>
<td>0.22(2)</td>
<td>0.18(2)</td>
<td>Li 0.95(1)/Co 0.05(1)</td>
</tr>
<tr>
<td>Li2</td>
<td>4a</td>
<td>0.69(3)</td>
<td>0.41(1)</td>
<td>0.23(2)</td>
<td>0.12(7)</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4a</td>
<td>0.033(3)</td>
<td>0.344(2)</td>
<td>0.159(5)</td>
<td>0.01(1)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>4a</td>
<td>0.240(3)</td>
<td>0.560(2)</td>
<td>0.165(5)</td>
<td>0.017(4)</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>4a</td>
<td>0.251(4)</td>
<td>0.409(2)</td>
<td>0.605(4)</td>
<td>0.009(3)</td>
<td>1</td>
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<tr>
<td>O4</td>
<td>4a</td>
<td>0.475(4)</td>
<td>0.332(2)</td>
<td>0.156(5)</td>
<td>0.012(6)</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ \begin{align*}
    a &= 6.2826(4) \\
    b &= 10.7029(7) \\
    c &= 4.93465(3) \\
    \text{Space Group: } &Pbn2_1 \\
    \text{Cell Volume} &= 331.017(2) \text{ Å}^3, \\
    R_p &= 13.02\% \\
    R_{wp} &= 17.69\% \\
    \chi^2 &= 1.157
\end{align*} \]

Table 4.3.3. Refined parameters for β$_1$ polymorph obtained via reheating hydrothermal product to 700°C for 2hr.

<table>
<thead>
<tr>
<th></th>
<th>Li1-O</th>
<th>Li2-O</th>
<th>Co1-O</th>
<th>Si1-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>1.99(1)</td>
<td>2.29(1)</td>
<td>1.919(8)</td>
<td>1.622(9)</td>
</tr>
<tr>
<td>O2</td>
<td>1.843(8)</td>
<td>2.194(6)</td>
<td>1.94(2)</td>
<td>1.64(1)</td>
</tr>
<tr>
<td>O3</td>
<td>1.956(5)</td>
<td>1.971(7)</td>
<td>1.962(7)</td>
<td>1.678(1)</td>
</tr>
<tr>
<td>O4</td>
<td>2.152(7)</td>
<td>1.69(1)</td>
<td>1.89(1)</td>
<td>1.754(9)</td>
</tr>
</tbody>
</table>

Average Bond Length Å

|        | 1.9852 | 2.0363 | 1.9277 | 1.6735 |

Tetrahedra volume Å$^3$

|        | 5.166(7) | 5.599(7) | 4.6(3) | 2.62(2) |

Table 4.3.4 Selected polyhedra bond lengths and volumes for β$_1$ Li$_2$CoSiO$_4$ material.

Table 4.3.4 indicates that there is considerable difference within the MO$_4$ polyhedra environments present in β$_1$ material compared to the β$_{II}$ phase, with the average Co-O bonds significantly shorter in the former (1.9277 Å vs. 1.9905 Å for β$_1$.
compared to $\beta_{II}$). Given the theory presented by Arroyo-de Dompablo et al. concerning the Si-O-Co influence upon the Co$^{3+/2+}$ redox couple, the difference in bond length would qualitatively suggest a higher voltage for the $\beta_{I}$ material, though due to the many other contributing factors, others may be more dominant. Two distinct LiO$_4$ polyhedra are present in $\beta_{I}$ material, both of different volumes suggesting one site will be favoured for lithium removal.

![Schematic representations of $\beta_{I}$ Li$_2$CoSiO$_4$ (hydrothermal) structure, obtained from Rietveld refinement. Light blue Polyhedra LiO$_4$, Dark Blue (Li 95%/Co 5%)O$_4$, Grey polyhedra SiO$_4$, Green Polyhedra (Co 93%/Li 7%)O$_4$, Red spheres Oxygen atoms.](image)

The $\beta_{I}$ structure consists of alternating layers of polyhedra with their vertices aligned along the $c$ axis. Each layer consists of lines of alternating LiO$_4$ and SiO$_4$. 

Figure 4.3.5 Schematic representations of $\beta_{I}$ Li$_2$CoSiO$_4$ (hydrothermal) structure, obtained from Rietveld refinement. Light blue Polyhedra LiO$_4$, Dark Blue (Li 95%/Co 5%)O$_4$, Grey polyhedra SiO$_4$, Green Polyhedra (Co 93%/Li 7%)O$_4$, Red spheres Oxygen atoms.
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interspaced with lines of the two mixed metal oxide tetrahedra propagating along the $a$ axis. The above/below layer consists of similarly alternating polyhedra lines but their polyhedra facing in the opposite direction along the $b$ axis, as the (1,1,0),(1,0,1) projection shows in Figure 4.3.5.

![Figure 4.3.6](image)

**Figure 4.3.6** Schematic representation of a potential lithium insertion/removal pathway in $\beta_I$ Li$_2$CoSiO$_4$; Grey polyhedra SiO$_4$, Green polyhedra (Co 93%/Li 7%)O$_4$, Light blue spheres lithium, Dark Blue spheres mixed Li(0.95%) Co(0.05%) site, Red spheres Oxygen.

As demonstrated from the schematics of the $\beta_I$ material, there are distinct structural differences between the $\beta_I$ and $\beta_{II}$ polymorphs. Figure 4.3.6 highlights one possible lithium insertion/removal pathway (also seen as a ‘zigzag’ of dark/light blue polyhedra in schematic of $a,b$ plane in Figure 4.3.5). $\beta_I$ does not seem to present the direct $\text{Li}^+$ pathway seen in the $\beta_{II}$ structure, instead consisting of ‘zigzag’ tunnels along the $b$ axis. This may be indicative of distinct electrochemical behaviour between the $\beta_I$ and $\beta_{II}$ polymorphs.
4.2.1.3. Li$_2$CoSiO$_4$ γ$_0$ polymorph

West *et al.* noted that the phase boundary for the γ polymorphs lie above 1000°C but observed that the phase hysteresis caused by the sluggish phase conversions can be exploited to produce the γ polymorphs at room temperature. Because the material will naturally revert to the β polymorphs if allowed to slowly cool, the material must be rapidly cooled to maintain the γ structure. To this end it was found that by rapid quenching from above 850°C (removing the sample from the oven to room atmosphere) the γ$_0$ polymorph could be produced (diffraction pattern and refinement presented in Figure 4.3.7).

![Figure 4.3.7 X-ray diffraction pattern and Rietveld refinement of γ$_0$ Li$_2$CoSiO$_4$ material (produced by reheating hydrothermally lithium cobalt silicate to 1100°C and quenching to room temperature from 850°C).](image)
The material was refined with the P2₁/n space group and gave a good fit of \( R_{wp} = 7.55\% \). Table 3.3.7 shows that there is no observed site disorder within the cobalt and lithium sites in the material (again, confirmed by subsequent neutron diffraction work\(^{11}\)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Symbol</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>B(_{iso})</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1</td>
<td>4a</td>
<td>0.4967(4)</td>
<td>0.1643(2)</td>
<td>0.3106(4)</td>
<td>0.038(1)</td>
<td>1</td>
</tr>
<tr>
<td>Si1</td>
<td>4a</td>
<td>0.245(1)</td>
<td>0.4124(5)</td>
<td>0.310(4)</td>
<td>0.025(2)</td>
<td>1</td>
</tr>
<tr>
<td>Li1</td>
<td>4a</td>
<td>0.994(3)</td>
<td>0.155(1)</td>
<td>0.309(4)</td>
<td>0.012(9)</td>
<td>1</td>
</tr>
<tr>
<td>Li2</td>
<td>4a</td>
<td>0.221(4)</td>
<td>0.073(2)</td>
<td>0.704(5)</td>
<td>0.02(1)</td>
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<td>O1</td>
<td>4a</td>
<td>0.033(1)</td>
<td>0.3411(8)</td>
<td>0.213(2)</td>
<td>0.019(3)</td>
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</tr>
<tr>
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<td>0.4126(8)</td>
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<td>0.342(2)</td>
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<td>0.013(3)</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ a = 6.3064(1) \quad b = 10.6764(1) \quad c = 5.02334(7) \quad A = 90.0^0 \quad B = 90.587(2)^0 \quad C = 90.0^0 \]

Cell Volume = 338.213(8) Å\(^3\), \( R_p = 5.66\% \), \( R_{wp} = 7.55\% \), \( \chi^2 = 1.085 \)

Space Group: P2₁/n

Table 4.3.5 Refined lattice parameters of \( y_0 \mathrm{Li}_2\mathrm{CoSiO}_4 \).

<table>
<thead>
<tr>
<th></th>
<th>Li1-O</th>
<th>Li2-O</th>
<th>Co1-O</th>
<th>Si1-O</th>
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<td>1.984(9)</td>
<td>1.63(1)</td>
</tr>
<tr>
<td>O2</td>
<td>1.91(1)</td>
<td>2.08(2)</td>
<td>1.982(9)</td>
<td>1.620(8)</td>
</tr>
<tr>
<td>O3</td>
<td>2.024(9)</td>
<td>2.183(8)</td>
<td>2.03(1)</td>
<td>1.60(1)</td>
</tr>
<tr>
<td>O4</td>
<td>2.032(7)</td>
<td>1.892(7)</td>
<td>1.938(8)</td>
<td>1.603(8)</td>
</tr>
</tbody>
</table>

Average Bond Length Å

<table>
<thead>
<tr>
<th></th>
<th>Li1-O</th>
<th>Li2-O</th>
<th>Co1-O</th>
<th>Si1-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>1.973</td>
<td>1.99175</td>
<td>1.938</td>
<td>1.603</td>
</tr>
</tbody>
</table>

Tetrahedra volume Å\(^3\)

<table>
<thead>
<tr>
<th></th>
<th>Li1-O</th>
<th>Li2-O</th>
<th>Co1-O</th>
<th>Si1-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>5.05(3)</td>
<td>5.51(1)</td>
<td>5.11(4)</td>
<td>2.27(1)</td>
</tr>
</tbody>
</table>

Table 4.3.6 Selected polyhedra bond lengths and volumes for \( y_0 \mathrm{Li}_2\mathrm{CoSiO}_4 \) material.
Both the LiO$_4$ polyhedra present in the $\gamma_{II}$ phase are a smaller volume than their $\beta$ phase counterparts suggesting that if this presents a thermodynamic impediment to removing, it will require more energy to remove Li$^+$ from the structure.

Figure 4.3.8 Schematic representations of $\gamma_0$ Li$_2$CoSiO$_4$ (hydrothermal) structure, obtained from Rietveld refinement. Light blue Polyhedra LiO$_4$, Dark Blue (Li 95%/Co 5%)O$_4$, Grey polyhedra SiO$_4$, Green Polyhedra (Co 93%/Li 7%)O$_4$, Red spheres Oxygen atoms.

Figure 4.3.8 shows the $\gamma_0$ phase has notably lower symmetry than either of the $\beta$ polymorphs with layers in the c direction consisting of polyhedra with their vertices pointing in opposing directions (as shown in the a,b plane in Figure 4.3.8). The structure consists of clusters of 3 edge sharing tetrahedra with a central tetrahedron facing one way accompanied by two tetrahedra facing the opposite direction.
Figure 4.3.9 Schematic representation of a potential lithium insertion/removal pathway in $\beta_1$, $\text{Li}_2\text{CoSiO}_4$; Grey polyhedra $\text{SiO}_4$, Green polyhedra (Co/Li)O$_4$, Blue spheres lithium, Red spheres Oxygen.

Figure 4.3.9 shows a projection of the relatively open structure of $\gamma_0$. It does not possess the obvious lithium pathways of the $\beta_1$ and $\beta_{II}$ suggesting, that the electrochemical behaviour may be markedly different between the polymorphs.

West gives evidence for the existence of another polymorph, $\gamma_{II}$, produced from a fast, high temperature quench (>1000°C) of the $\beta_{II}$ phase$^{22}$. Though synthesis of this phase was attempted numerous times (via quenching at 1000°C from air into liquid nitrogen and similar quenching under an argon atmosphere) the $\gamma_{II}$ polymorph was never observed. The produced material was either a mixture of oxidised lithium silicates and cobalt oxides or one of the other previously observed polymorphs.
4.2.1.4. **Li$_2$CoSiO$_4$ $\beta_I$ (solid state) material**

Several attempts were made to natively produce other polymorphs through solid state synthesis, these attempts focussed primarily on the later heating regime of the solid state synthesis. It was determined that heating the precursor (a largely amorphous material, consisting of cobalt oxide/hydroxide and organic derivatives—see appendix iii) led to cobalt reduction and formation of lithium silicates, a possible consequence of organic components decomposing to reducing agents at higher temperatures$^{22}$. At lower temperatures $\beta_I$ remained the preferred phase no matter the quenching regime. This suggests that the solid state synthesis depressed the phase change from $\beta_I$ to $\beta_{II}$. The lack of doping in the Li1 site may also influence the phase behaviour.

![Figure 4.3.10 X-ray diffraction pattern and Rietveld refinement of $\beta$, Li$_2$CoSiO$_4$ prepared by solid state synthesis: A, Peak positions of Co$_3$O$_4$ impurity phase. B, Peak positions of $\beta_I$, Li$_2$CoSiO$_4$. □Unknown impurity peaks.](image-url)
As before the space group Pb\(_{n}\)2\(_1\) was used to refine the \(\beta_I\) structure. This produced a fit of \(R_{wp}= 20.33\%\) which is far from ideal. The presence of an unknown impurity (marked with an \(\square\) in Figure 4.3.10 and suspected to be a higher lithium silicate impurity \(\text{Li}_x\text{Si}_y\text{O}_z\)) and the known impurity of \(\text{Co}_3\text{O}_4\) (see peak marks \(A\)) combined to lower the fitting factors. Even after multiple attempts no impurity free materials were produced.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Symbol</th>
<th>(x/a)</th>
<th>(y/b)</th>
<th>(z/c)</th>
<th>(B_{iso})</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1</td>
<td>4a</td>
<td>0.491(1)</td>
<td>0.1647(6)</td>
<td>0.266(2)</td>
<td>0.031(3)</td>
<td>\text{Co 0.93/Li 0.07(3)}</td>
</tr>
<tr>
<td>Si1</td>
<td>4a</td>
<td>0.248(3)</td>
<td>0.410(1)</td>
<td>0.251(9)</td>
<td>0.039(5)</td>
<td>1</td>
</tr>
<tr>
<td>Li1</td>
<td>4a</td>
<td>0.96(1)</td>
<td>0.1748(6)</td>
<td>0.16(1)</td>
<td>0.02(8)</td>
<td>1</td>
</tr>
<tr>
<td>Li2</td>
<td>4a</td>
<td>0.69(2)</td>
<td>0.412(6)</td>
<td>0.24(2)</td>
<td>0.02(7)</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4a</td>
<td>0.031(5)</td>
<td>0.339(2)</td>
<td>0.154(5)</td>
<td>0.019(7)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>4a</td>
<td>0.254(6)</td>
<td>0.562(2)</td>
<td>0.151(5)</td>
<td>0.002(7)</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>4a</td>
<td>0.239(6)</td>
<td>0.411(2)</td>
<td>0.594(5)</td>
<td>0.007(7)</td>
<td>1</td>
</tr>
<tr>
<td>O4</td>
<td>4a</td>
<td>0.465(4)</td>
<td>0.337(2)</td>
<td>0.158(7)</td>
<td>0.010(8)</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ a = 6.271(4) \quad b = 10.689(7) \quad c = 4.930(3) \quad \text{Space Group: Pb}_n2_1 \]

\[ \text{Cell Volume} = 330.50(6) \text{ Å}^3 \quad R_p = 14.63\% \quad R_{wp}=20.33\%, \quad \chi^2 = 1.128 \]

Table 4.3.7 Refined parameters \(\text{Li}_2\text{CoSiO}_4\ \beta_I\) polymorph from solid state preparation.

Unlike the hydrothermally based \(\beta_I\), Table 4.3.7 shows that the solid state synthesis only has cation disorder on the cobalt site (in the same Co/Li ratio as seen in the hydrothermal \(\beta_I\)). This may infer that the disorder on the \(\text{Li}1\) site in the hydrothermal \(\beta_I\) phase is possibly an artefact of the disorder seen in the parent \(\beta_{II}\) phase and the subsequent \(\beta_{II}\) to \(\beta_{I}\) transformation, or at least show that the different
synthesis conditions between the $\beta_1$ hydrothermal and solid state polymorphs have a measurable structural effect on the final material.

As can be seen through the structural refinements of the various polymorphs there is a wide range of metal ion environments across the various polymorphs and different production methods. While determining electrochemical properties from structural information is speculative at best, the different environments provided by the polymorphs do at least suggest that the lithium polymorphs that were produced should have individual behaviour when lithium is removed (and replaced)

4.2.2. Morphological considerations

As each polymorph is produced under different conditions it is expected that each would have individual morphological characteristics. In an electrochemical context, having natively smaller particle sizes improves the lithium insertion/removal kinetics, reducing the ionic diffusion length of lithium in the bulk and exposing a greater surface area of the material to the electrolyte, increasing the rate of ionic and electron transfer. This enhanced interface area effect is balanced (and occasionally negated) by the possibility that the increased surface area will increase the rate of any parasitic side-reactions between the electrolyte and electrode (an extension of this problem on the nano-scale is the lowering of surface activation energy for very small particles$^{1,3,23}$). To this end transmission electron microscopy was undertaken to study the nano and microscopic nature of the various natively produced polymorphs.
4.2.2.1. \( \text{Li}_2\text{CoSiO}_4 \beta_{\text{II}} \) material

The hydrothermally prepared \( \beta_{\text{II}} \) material can be seen in the TEM image displayed in Figure 4.3.11. The image indicates that the hydrothermally prepared \( \beta_{\text{II}} \) material has an approximate diameter of 30-60 nm and relatively uniform particle size with only small variations between the width and length of the particles. This can be explained given the nature of hydrothermal production, where nucleation and crystal growth tends to be a lot faster (compared to solid state synthesis) and hence produce far smaller crystallites.\(^{19}\).

![TEM image of \( \beta_{\text{II}} \) Li\(_2\)CoSiO\(_4\) material](image)

Figure 4.3.11 TEM images taken of the hydrothermally prepared \( \beta_{\text{II}} \) \( \text{Li}_2\text{CoSiO}_4 \) polymorph.
4.2.2.2. \( \text{Li}_2\text{CoSiO}_4 \) \( \beta \text{i}(\text{hydrothermal}) \) material

It can be seen from the TEM image of the \( \beta \text{i} \) (hydrothermal) polymorph, shown in Figure 4.3.12, that the reheating process creates crystallites that are larger than its parent \( \beta \text{ii} \) material, most likely due to crystallite growth during the reheating/annealing stage. The particles have a range of 380 nm to 1 \( \mu \text{m} \) along their long axis and a range of approximately 160 nm to 500 nm across their width. It would appear that the crystal growth is anisotropic with the shorter axis having a value of 40-50\% of the long axis.

Figure 4.3.12 TEM images taken of the \( \beta \text{i} \) \( \text{Li}_2\text{CoSiO}_4 \) polymorph prepared through reheating hydrothermally prepared \( \beta \text{ii} \) material.
4.2.2.3. **Li$_2$CoSiO$_4$ $\gamma_0$ material**

As can be expected from the evidence observed for the $\beta_{\text{II}}$ to $\beta_{\text{I}}$ transition, the $\gamma_0$ material which is produced from reheating the $\beta_{\text{II}}$ hydrothermal product to 1100°C and rapidly quenching, also produces large crystallites. This is apparent in Figure 4.3.13. Similar to the $\beta_{\text{I}}$ phase, the $\gamma_0$ material can be seen to have a large range of crystallite sizes the smallest around 200nm on its long axis, up to over 1μm. The $\gamma_0$ phase looks to contain a greater range of irregular shaped particles compared to $\beta_{\text{I}}$, possibly due to the $\beta$ to $\gamma_0$ transition affecting the nature of crystal growth.

![TEM image of $\gamma_0$ Li$_2$CoSiO$_4$ phase obtained via reheating the hydrothermally produced $\beta_{\text{II}}$ phase.](image)

Figure 4.3.13 TEM image of $\gamma_0$ Li$_2$CoSiO$_4$ phase obtained via reheating the hydrothermally produced $\beta_{\text{II}}$ phase.
4.2.2.4. **Li$_2$CoSiO$_4$ $\beta_1$ (solid state) material**

From the TEM image (Figure 4.3.14) of the $\beta_1$ solid state material we can see that there appears to be non uniform particles with a range of diameters from ~200 to 900 nm across their length. Most particles are in the range of 250-400nm; the approximate dimensions roughly correlate to the $\beta_1$ hydrothermal material suggesting that the particle growth stage in both preparations may be similar irrespective of synthesis conditions.

![TEM image of pristine $\beta_1$ Li$_2$CoSiO$_4$ produced through solid state synthesis.](image)

**Figure 4.3.14** TEM image of pristine $\beta_1$ Li$_2$CoSiO$_4$ produced through solid state synthesis.
The size of the particles can not only offer an insight into the synthesis conditions but can be used to inform about the electrochemical behaviour of the crystallites. Given the important nature of surface based charge and ionic transfer reactions and diffusion lengths. With this in mind it is obvious that both $\beta_1$ and $\gamma_0$ are at a disadvantage (electrochemically) and this must be considered when investigating the electrochemical properties.

4.2.3. Electrochemical Performance of as Prepared Materials

Inherently the electrochemical behaviour of any new cathode material is of the utmost importance to its performance within the battery system. By using a variety of techniques to monitor the behaviour of a material when lithium is inserted or removed, a picture of the processes occurring within the material during battery cycling can be obtained.

To accommodate the possibility of poor electronic kinetics in the sample, as had been suggested by previous work on Li$_2$FeSiO$_4$\cite{17,24}, a slow cycling regime was chosen (C/16 equivalent to 10mA/g) in conjunction with elevated temperature (50$^\circ$C). The electrolyte chosen is a laboratory standard (denoted as LP30) which consists of a 1:1(M) mixture of ethyl carbonate and diethyl carbonate with 1M LiPF$_6$ salt added. The choice of electrolyte is crucial, controlling factors such as mass transport and mitigating possible parasitic side-reactions between the electrode and electrolyte. As well as being convenient, LP30 provides fairly good stability within the voltage range predicted (see figure 3.2.3. in chapter 3) for Li$_2$CoSiO$_4$ materials which, with its high predicted voltage $\sim$4.3V$^4$ discounts a significant number of other electrolyte systems.
Galvanostatic testing was undertaken using a 2 electrode ‘coin cell’ system incorporating a composite working electrode (consisting of the Li$_2$CoSiO$_4$ active material, a high surface area ‘Super S’ carbon as a conductivity enhancer and Kynar Flex 2801 binder in a 75:18:7 weight ratio respectively). The counter electrode was prepared from lithium foil, with all elements being sealed gas-tight within the coin cell under an argon atmosphere.

4.2.3.1. Li$_2$CoSiO$_4$ $\beta_{II}$ polymorph

Figure 4.3.15 $\beta_{II}$ material (1) Galvanostatic load curve; A) 1$^{st}$ cycle, B) 2$^{nd}$ cycle, C) 5$^{th}$ cycle, 4) 10$^{th}$ cycle (2) Variation of capacity vs. Cycle number; □Charging, ○Discharging - Electrolyte LP30, cycling Rate 10 mA/g at 50$^\circ$C.

Figure 4.3.15 shows the $\beta_{II}$ material gives a first charge capacity of over 210 mAh/g, which far exceeds the Li$_2$CoSiO$_4$ theoretical capacity (~162mAh/g) for 1 Li$^+$ removal. This ‘over capacity’ could be due to removal of more than one lithium per formula unit upon charging or perhaps, less desirable factors, such as side-reactions with the electrolyte. The voltage rapidly rises to the start of a plateau at approximately 4.2 V, the nearly flat plateau suggests a two phase reaction for Li$^+$ removal, a phase change from Li$_2$CoSiO$_4$ to LiCoSiO$_4$. The plateau gently slopes at a constant gradient.
until 4.35 V where the voltage begins to rise rapidly again. This most likely represents the removal of all (reversibly) accessible lithium. Given that the two Li\(^+\) ions occupy two structurally and energetically different sites, it would be expected that, if more than one lithium was being removed the voltage would shift significantly to accommodate the energy required to remove the second. This is not the case, as above 4.35 V the voltage slowly rises, the constantly changing voltage gradient indicates that this involves a significantly different process from the plateau and may not involve lithium insertion/removal at all. The \(\beta_{II}\) material has a first charge plateau capacity of \(\sim 150\) mAh/g, equivalent to removal of 92% of lithium in a \(\text{Li}_2\text{CoSiO}_4\) one electron oxidation process.

The presence of a discharge plateau beginning just below 4.2 V is encouraging as it suggests the presence of a reversible process of lithium insertion/removal, but the plateau capacity is much reduced compared to charging garnering only \(\sim 40\) mAh/g on the plateau (24% of available lithium) and 67mAh/g over all. Figure 4.3.15 (2) shows the large hysteresis between charge and discharge capacities is repeated through the cycling regime with the capacity generated on charge dropping rapidly until it reaches parity with the discharge capacities, where upon it stabilises and diminishes slowly.

The voltage difference between the charging and discharging plateau could be a purely polarisation artefact caused by poor conductivity or it could be caused by the introduction of a process (structural rearrangement etc.) between charging and discharging that causes a thermodynamic difference between removing and inserting lithium (i.e. the voltage shift).
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Subsequent structural refinement at the end of the first and tenth cycle showed no new phases present. The cycling was accompanied by slight volume reduction of the unit cell (primarily along the $b$ axis). This volume reduction may be down to lower lithium concentration within the material (something hard to accurately ascertain given the low scattering X-ray cross section of lithium). This may be due to the asymmetric charge and discharge capacities leading to lower lithium concentrations throughout the material (though it should be kept in mind that due to the recovery process of cycled material, good x-ray statistics are hard to achieve with cycled materials and the certainty in refinement values are subject to these limitations).

<table>
<thead>
<tr>
<th></th>
<th>Unit Cell parameters /Å</th>
<th>Cell volume/ Å$^3$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$b$</td>
</tr>
<tr>
<td><strong>Pristine β$_{II}$ material</strong></td>
<td>6.2694(4)</td>
<td>5.3563(4)</td>
</tr>
<tr>
<td><strong>β$_{II}$ material after 1 cycle</strong></td>
<td>6.269(3)</td>
<td>5.356(2)</td>
</tr>
<tr>
<td><strong>β$_{II}$ material after 10 cycles</strong></td>
<td>6.2610(5)</td>
<td>5.3557(4)</td>
</tr>
</tbody>
</table>

Table 4.3.9 Unit cell parameters of pristine β$_{II}$ material ($R_{wp}$ 8%), and after the first ($R_{wp}$ 4.77%) and second cycle ($R_{wp}$ 4.72%); space group Pmn2$_1$.

The slow sweep cyclic voltammetry shown in Figure 4.3.16 shows selected cycles of the β$_{II}$ material at a scan rate of 0.05 mV/s. The first sweep shows a sample free of any impurities with one defined oxidation peak at 4.36 V, assumed to be the removal of lithium from the sample (even at the slow sweep rate, the peak's voltage cannot be taken as absolute, given over-potential effects). Near the voltage cut-off the current begins to increase suggesting a secondary electrochemical process (most likely the same process that causes the sloping voltage rise after the plateau in the galvanostatic load curve); the reduction peak at 4.1 V is attributable to the lithium insertion process.
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On subsequent cycles the lithium removal and insertion peaks shift to more oxidising and reducing voltages respectively. The voltage difference is incremental through the cycles and when coupled with the minimal plateau shift in the galvanostatic load curves it is unlikely that the same drastic structural changes that are seen in Li₂FeSiO₄ on the first cycle \(^{25}\) are at work in \(\beta\) \(\text{Li}_2\text{CoSiO}_4\).

Given the poor capacity retention of the material the peak shift could be due to the reduction of accessible Li\(^+\) in the material on cycling manifesting itself as an increasing over-potential (hence peak shift) required to remove lithium.

From AC resistivity measurements in Figure 4.3.16 (2) we can see that, in the complex impedance plot, the material shows a classic double semi-circle thought to represent both the bulk diffusion process within the material and the grain boundary processes. Equivalent circuit refinements were carried out using the ECLab Zfit program, utilising an equivalent circuit of two Resistor(R)/Constant phase element(CPE) dipoles in series. The pseudo capacity values generated are quoted in Farads per second.
Figure 4.3.16 βII material: (1) Slow sweep cyclic voltammetry plot of selected cycles of the as prepared βII material; A) 1st cycle, B) 2nd Cycle, C) 5th cycle D) 10th cycle. - Electrolyte LP30, sweep rate 0.05mV/s at 50°C. (2) Nyquist plot of βII material between stainless steel blocking electrodes. The capacities of the high frequency and low frequency semi-circles are ~10⁻¹⁰Fs⁻¹ and ~10⁻⁹Fs⁻¹ respectively, inferring that the high frequency semi-circle is responsible for the bulk process and the low frequency semi-circle due to grain boundary effects. The measurements taken at room temperature and 50°C display a high frequency semi-circle at 6kHZ with conductivities (σ) (1/resistivity) of ~10⁻⁷S/cm.

<table>
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<th>AC Impedance</th>
<th>Room Temp.</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity/Ωm</td>
<td>High Freq.</td>
<td>Low Freq.</td>
</tr>
<tr>
<td>Resistivity/Ωm</td>
<td>2.02x10⁷</td>
<td>6.97x10⁸</td>
</tr>
<tr>
<td>Capacitance/Fs⁻¹</td>
<td>2.41x10⁻¹⁰</td>
<td>1.39x10⁻⁹</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>DC Resistivity</th>
<th>Room Temp.</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity/Ωm</td>
<td>1.54x10⁷</td>
<td>2.05x10⁶</td>
</tr>
</tbody>
</table>

Table 4.2.1 AC and DC resistivity details for βII material.

The capacities of the high frequency and low frequency semi-circles are ~10⁻¹⁰Fs⁻¹ and ~10⁻⁹Fs⁻¹ respectively, inferring that the high frequency semi-circle is responsible for the bulk process and the low frequency semi-circle due to grain boundary effects. The measurements taken at room temperature and 50°C display a high frequency semi-circle at 6kHZ with conductivities (σ) (1/resistivity) of ~10⁻⁷S/cm.

This is an improvement on reported values of the bulk contributions for LiFePO₄ by two orders of magnitude suggesting that the majority of transport
problems in $\beta_{II}$ Li$_2$CoSiO$_4$ must be ionic in nature. It is also worth noting that the bulk resistively changes little from 20$^0$C to 50$^0$C. The grain boundary (low frequency) semi-circle gives conductivity values of $\sim 10^{-9}$ and $\sim 10^{-10}$ S/cm for the room temperature and 50$^0$C samples respectively which is similar to other olivine materials$^{27}$.

From the DC resistively measurements shown in Table 4.3.10 it’s confirmed that the resistivity is mainly electrical in nature and dominated by bulk processes.
4.2.3.2. \( \text{Li}_2\text{CoSiO}_4 \beta_1 \) (hydrothermal) material

Compared to its \( \beta_{II} \) parent, the \( \beta_1 \) material, produced from reheating of the hydrothermal product, gives a diminished capacity; achieving a capacity of only \( \sim 125 \text{mAh/g} \) out of a possible \( 162 \text{mAh/g} \) on the first charge (approximately 80% of theoretical capacity), of which \( \sim 100 \text{mAh/g} \) can be ascribed to the plateau process \( 0 \). (\( \sim 0.6 \text{Li} \) per \( \text{Li}_2\text{CoSiO}_4 \) unit). As before the uninterrupted plateau suggests a two phase reaction. The reduced capacity could be due to the size differences between \( \beta_1 \) and \( \beta_{II} \) materials.

The voltage plateau sits at a slightly higher voltage in \( \beta_1 \) compared to its \( \beta_{II} \) counterpart (the plateau begins at 4.25V compared to 4.17 V for \( \beta_{II} \) material) and it could be the structural differences between \( \beta_1 \) and \( \beta_{II} \) \( \text{LiO}_4 \) polyhedra volume introduce a degree of polarisation resistance forcing the extraction voltage plateau to shift to a higher voltage. Considering the Co-O-Si triplet theory (i.e. a shorter Co-O bond suggests greater orbital overlap between cobalt and oxygen orbitals which in turn
increases the redox band-gap). Within the Co-O-Si triad, the average Co-O bond in $\beta_1$ is shorter than in $\beta_{\text{II}}$ (1.927 Å vs. 1.9905 Å respectively) which would, qualitatively suggest a higher voltage for the $\beta_1$ Co$^{3+/2+}$ redox couple. Most likely it is a combination of the greater thermodynamic penalty for removing Li$^+$ ions (hence greater polarisation of the electrode) coupled with the increased Co$^{3+/2+}$ redox level.

The discharge process bears similarities to the $\beta_{\text{II}}$ material, initially occurring at a voltage of 4.16 V and experiencing a 50 mV voltage drop between charging and discharging plateaus. At 50 mAh/g, the gross capacity of the discharge cycle is lower compared to the ~65 mAh/g achieved by the $\beta_{\text{II}}$ material (though the charge to discharge capacity ratio is higher for the $\beta_1$ vs. the $\beta_{\text{II}}$, 39% vs. 31% respectively).

The voltage plateau region accounted for the majority of the discharge capacity (approximately 35 mAh/g), but as with the $\beta_{\text{II}}$ polymorph there is a large disparity between the charge and discharge capacities. There was no noticeable difference between charge/discharge capacity ratios compared to when both stages were undertaken at a rate of 10 mAh/g, suggesting that the charge/discharge capacity difference was not based on a kinetic effect (or not a kinetic affect that is measurable by this magnitude of rate difference).

On subsequent cycling the charging plateau is less resolved, presumably being lost to polarisation effects as it becomes harder to remove lithium from the material. The discharge plateau is more stable but diminishes gradually as the capacity vs. cycle plot in Figure 4.3.17 (2) highlights.
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Figure 4.3.18 $\beta_1$ (hydrothermal) material: (1) Slow sweep cyclic voltammetry plot of selected cycles of the as prepared $\beta_{II}$ material; A) 1$^{st}$ cycle, B)2$^{nd}$ cycle, C)5$^{th}$ cycle D)10$^{th}$ cycle - Electrolyte LP30, sweep rate 0.05mV/s at 50°C; (2) Table 4.3.11 DC Resistivity measurements of $\beta_1$ (hydrothermal) material at room temperature and 50°C between 2 stainless steel electrodes

The slow sweep cyclic voltammogram of the $\beta_1$ polymorph displayed in Figure 4.3.18 (1) indicate similar behaviour to its $\beta_{II}$ analogue. There is one large oxidation peak (equivalent to the charging plateau process), albeit at a slightly higher voltage (4.41V) to its $\beta_{II}$ counterpart (4.37 V). As before there is slight over-potential effect compared to the voltage values from the galvanostatic plateau. The reduction peak gives a maximum current at 4.1V (compared to $\beta_{II}$ 4.085V) which, as expected, is shifted to a more reducing voltage compared to the mid-plateau voltage from the galvanostatic load curve.

As observed for the $\beta_{II}$ material there is no pronounced peak shift, only a gradual peak drift to higher voltages, presumably caused by the need for greater over potential, as removal of lithium from the material becomes more laboured (as suggested by the plateau polarisation seen in the load curve).
With structural refinement it was discovered that, after charging, conversion of the $\beta_I$ material (and in subsequent cycles) to the $\beta_{II}$ phase can be observed. The $\beta_{II}$ phase fraction (relative to the $\beta_I$ phase) grows with subsequent cycling until it becomes the dominant phase. The slow sweep C.V. shows no evidence of the expected shift in charging peak voltage to the lower value associated with the $\beta_{II}$ oxidation process (and there is no noticeable galvanostatic voltage plateau shift) but this may be occluded by greater polarisation effects present from factors such as the larger size of particles.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.3.19.png}
\caption{X-ray diffraction pattern and Rietveld refinement for $\beta_I$(hydrothermal) material after 9 cycles and 1 charge: A, Peak positions for the $\beta_I$ Li$_2$CoSiO$_4$ phase. B, Peak positions for the $\beta_{II}$ Li$_2$CoSiO$_4$ phase. □ Unknown impurity phase. $R_{wp}=5.63\%$, Phase ratio, $\beta_I:\beta_{II} 0.27:0.73$}
\end{figure}

The absence of $\beta_{II}$ activity in the electrochemistry is not easy to understand—one possible explanation is, as the $\beta_{II}$ is only created after the first charge sweep, its presence is harder to observe in the subsequent charging plateaus, due to polarisation effects obscuring the true plateau voltage (the $\beta_{II}$ and $\beta_I$ discharge voltages are almost
identical, in the $\beta_1$ case this may be due to an electrochemical contribution from the recently created $\beta_{II}$ phase.

### Table 4.3.12 Rietveld refinement parameters from cycled $\beta_1$(hydrothermal) material: $\beta_{II}$ phase space group $Pmn2_1$, $\beta_1$ phase space group, $Pbn2_1$

<table>
<thead>
<tr>
<th></th>
<th>Unit Cell parameters /Å</th>
<th>Cell vol. /Å³</th>
<th>Phase ratio</th>
<th>$R_{wp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pristine $\beta_1$ material</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{II}$ phase</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>17.32%</td>
</tr>
<tr>
<td>$\beta_1$ phase</td>
<td>6.2694(4) 5.3563(4) 4.9384(5)</td>
<td>165.96(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>1 Charge</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{II}$ phase</td>
<td>6.2733(1) 5.3549(6) 4.9341(5)</td>
<td>165.7(3)</td>
<td>0.28(2)</td>
<td>6.32%</td>
</tr>
<tr>
<td>$\beta_1$ phase</td>
<td>6.264(1) 10.712(2) 4.9377(8)</td>
<td>331.3(9)</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td><strong>9 cycles 1 charge</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{II}$ phase</td>
<td>6.2610(3) 5.3448(2) 4.9245(2)</td>
<td>164.79(1)</td>
<td>0.73(6)</td>
<td>5.63%</td>
</tr>
<tr>
<td>$\beta_1$ phase</td>
<td>6.255(1) 10.704(1) 4.9341(8)</td>
<td>330.39(8)</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td><strong>10 cycles</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{II}$ phase</td>
<td>6.251(2) 5.359(2) 4.961(1) 166.20(9)</td>
<td>0.68(5)</td>
<td>7.36%</td>
<td></td>
</tr>
<tr>
<td>$\beta_1$ phase</td>
<td>6.2673(5) 10.6986(7) 4.9307(3)</td>
<td>330.62(6)</td>
<td>0.32</td>
<td></td>
</tr>
</tbody>
</table>

There is also an unknown impurity present which appears in the later cycles (indicated in Figure 4.3.19). The impurity is possibly a lithium carbonate derivative which may form as part of the parasitic side reaction occurring in the higher voltage region (seen after the plateau in the galvanostatic load curves, or in the rapidly increasing current as the voltage sweeps towards the voltage cut-off in the cyclic
voltammograms). It may be that this impurity (or its associated side reaction) has an effect on the overall efficiency of the cycling process, causing the poor capacity retention seen in Figure 4.3.18 (during a $\beta_I - \beta_{II}$ transition, cobalt sites with a lowered surface activation energy may be exposed to the electrolyte, potential catalysing the dissolution of electrolyte with the transition metal ion, as has been observed in other systems$^{29,30}$).

It may be of some note that the presence of the $\beta_{II}$ phase is recorded at the end of the first charge. On later cycles the majority of the material is made up of $\beta_{II}$. The $\beta_I/\beta_{II}$ ratio seems to vary slightly with charge/discharge, most likely at each subsequent charge process more $\beta_{II}$ was created adjusting the phase ratio accordingly. This conversion mechanism must occur at similar voltages to lithium removal, given the lack of separate peaks in the cyclic voltammetry.

Attempts to measure the AC impedance of the pristine $\beta_I$ material provided few clues, with the impedance spectrum resolving to a single point characteristic of a ‘shunt’. The DC resistivity measurements show that the conductivity decreased with increased temperature (from $\sim10^{-8}$ to $\sim10^{-9}$ s/cm) this may suggest the $\beta_I$ (hydrothermal) does not fit the simple semi-conductor model (i.e. the presence of strain or more exotic charge carrier effects). The $\beta_I$ material has a lower DC conductivity compared to $\beta_{II}$ ($\sim10^{-7}$ s/cm) which is further evidence of its poor relative electrochemical performance.
4.2.3.3. \( \text{Li}_2\text{CoSiO}_4 \beta_1 \text{ (solid state) material} \)

For clarity the electrochemical results for \( \beta_1 \text{ (solid state)} \) are presented here to act as a useful comparison to the \( \beta_1 \text{ (hydrothermal)} \) material.

The composition vs. voltage profile of the \( \beta_1 \) material prepared from solid state synthesis is notably different from the \( \beta_1 \) material from hydrothermal reheating. Not only is the first charge capacity severely reduced (45 mAh/g vs. 125 mAh/g, solid state vs. hydrothermal respectively) but there is no defined plateau; instead there is a gentle slope running from 4.05 V to the 4.5 V cut-off. This starting voltage is significantly lower than \( \beta_1 \) (hydrothermal) material (~4.25 V) and \( \beta_{II} \) material (~4.14 V). The lower voltage for the pseudo-plateau could indicate the presence of another electrochemical process preceding lithium removal, the slight shoulder seen in the voltammogram in Figure 4.3.21 would seem to confirm this. Unlike the previous materials, there is no clear discharge plateau in the \( \beta_1 \text{ (solid state)} \) material, instead a voltage drop (~60mV) is observed, followed by a sharp slope which accounts for almost all of the 16 mAh/g.
capacity seen in the first discharge. On subsequent cycles the charging capacity quickly drops until it stabilises, in line with the discharge capacity of ~15mAh/g (shown in Figure 4.3.20.). Subsequent cycles show the decreasing starting voltage (and capacity) of the charging pseudo-plateau, insinuating that the pseudo-plateau process is diminishing.

![Graph](image)

**Figure 4.3.21** β₁ (solid state) material: (1) Slow sweep cyclic voltammetry plot of selected cycles of the as prepared β₁ solid state material; A) 1ˢᵗ cycle, B) 2ⁿᵈ cycle, C) 5ᵗʰ cycle D) 1₀ᵗʰ cycle - Electrolyte LP30, sweep rate 0.05mV/s at 5₀°C; (2) Table 4.3.13 DC Resistivity measurements of β₁ (solid state) material at room temperature and 5₀°C between 2 stainless steel electrodes

The cyclic voltammetry of the β₁ solid state material consists of a small shoulder preceding the current increase to the voltage cut-off, the lack of a major peak is no surprise given the galvanostatic profile (i.e. the lack of a plateau). The shoulder peak at 4.04 V bears a similarity to the larger β₁ (hydrothermal) and β₁ major oxidation peaks, in that it slowly fades with cycles, suggesting it could be an lithium insertion process (or an irreversible side-reaction with very slow kinetics). There does appear to be a more consistent reduction peak which doesn’t suffer the peak shifts seen in β₁ (hydrothermal) and β₁, but this may be to do with drastically lowered current density not exhausting the kinetic limitations of lithium insertion (and hence doesn’t require
an over-potential peak shift to remove lithium, as seen in the more electrochemically active $\beta_{II}$ and $\beta_{I}$ (hydrothermal) phases).

As before, the AC impedance spectrum resolved to a point. The DC conductivity is slightly higher than for the $\beta_{I}$ (hydrothermal) material and similarly shows a decrease in conductivity for the increasing temperature ($2 \times 10^{-9}$ S/cm at room temperature vs. $1 \times 10^{-9}$ S/cm) but the difference is less pronounced. The similarity between conductivities for the two $\beta_{I}$ materials suggest that the difference in performance is probably caused by something chemical (the different doping may affect the internal ionic kinetics) or physical (morphological, particle size) rather than electrical state of the solid state material.

The difference in electrochemical behaviour between the $\beta_{I}$ polymorphs is fairly pronounced but the structural differences are subtle. As both $\beta_{I}$ materials were natively produced with similar morphologies, the most notable difference between the two $\beta_{I}$ polymorphs is the change in fractional occupancies. It may be this ‘doping’ of lithium within the Co1 cobalt site alters the lithium insertion/removal properties of the material (or the lack of doping hinders the $\beta_{I}$(solid state) converting to $\beta_{II}$).
4.2.3.4. \( \text{Li}_2\text{CoSiO}_4 \) \( \gamma_0 \) material

\( X \) in \( \text{Li}_{1+x}\text{CoSiO}_4 \)

Figure 4.3.22 \( \gamma_0 \) material (1) Galvanostatic load curve; A) 1\textsuperscript{st} cycle, B) 2\textsuperscript{nd} cycle, C) 5\textsuperscript{th} cycle, 4) 10\textsuperscript{th} cycle (2) Variation of capacity vs. Cycle number; □Charging, ○Discharging - Electrolyte LP30, cycling Rate 10 mA/g at 50°C.

The \( \gamma_0 \) polymorph has greatly decreased capacity compared to the three other materials. It shares a similar profile to the solid state \( \beta_{\text{II}} \), again the particularly low electrochemical activity making it hard to discern what is due to lithium removal/insertion process and what is due to side reaction processes. As with \( \beta_{\text{I}} \) (solid state) the load curve begins with a rapid voltage increase until a sloping charge plateau is reached at 4.2 V. The plateau then gently increases up to 4.5 V voltage cut off. The plateau occupies a marginally higher voltage than the \( \beta_{\text{I}} \) polymorph, though whether this is indicative of an over-potential caused by poor sample conductivity (as highlighted in the DC conductivity measurements in Figure 4.3.23 (2)) or the different structural environment affecting the lithium removal voltage is difficult to tell. The initial plateau is in the correct range for a lithium removal process (at 4.2 V it sits between the initial plateau voltages of \( \beta_{\text{II}} \) and \( \beta_{\text{I}} \) (hydrothermal) materials).
The low capacity could be due to several factors; the pristine γ₀ material has relatively large particles causing unfavourable kinetics between the active material and the electrolyte. The γ₀ crystal structure consists of the smallest LiO₄ tetrahedra, theoretically making it harder to remove lithium. The average Co-O bond length in the Co-O-Si bonding triplet sits between the lengths of β_I and β_II which may explain the intermediate initial voltage at the start of the charging plateau. It is likely that a combination of these factors ensure that the γ₀ gives poor electrochemical performance, indeed on subsequent cycles the capacity produced is negligible (as is the discharge capacity).

Figure 4.3.23 γ₀ material: (1) Slow sweep cyclic voltammetry plot of selected cycles of the as prepared γ₀ material; A) 1st cycle, B) 2nd Cycle, C) 5th cycle D) 10th cycle - Electrolyte LP30, sweep rate 0.05mV/s at 50°C: (2) Table 4.3.14 DC Resistivity measurements of γ₀ material at room temperature and 50°C between 2 stainless steel electrodes

The cyclic voltammogram for the γ₀ polymorph is shown in Figure 4.3.23 and does show that there is a slight oxidation peak at 4.36 V (the same voltage peak as β_II) which diminishes on subsequent cycles until there is no obvious peak. The presence of
a reduction peak is encouraging as it suggests that, for what minimal lithium removal/insertion processes are present they appear to be repeatable. There is no voltage shift in the reduction peak. This may differ from previous polymorphs because the insertion of lithium process is not on a scale to be kinetically limited (and hence, force an over-potential).

Like the β_{II} and, different from the β_{I} (hydrothermal) material, the X-ray diffraction pattern after cycling did not show the presence of any new phases, or the presence of any impurities. Both these factors could be accounted for by the incredibly low electrochemical activity seen with the γ_{0} phase, ensuring minimal presence of products activated by electrochemical cycling.

<table>
<thead>
<tr>
<th>Unit Cell parameters /Å</th>
<th>Cell volume/ Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 6.3067(1)</td>
<td>338.237(8)</td>
</tr>
<tr>
<td>b 10.676(1)</td>
<td></td>
</tr>
<tr>
<td>c 5.02342(7)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3.15. Unit cell parameters of pristine γ_{0} material (R_{wp} 7.9%) , after the 10th cycle (R_{wp} 6.69%); Obtained from Rietveld refinement, space group P12_{1}/n1.

Table 4.3.15 indicates, as with the β_{II} material, there is a volume cell reduction after cycling, primarily caused by a reduction in the a axis of the unit cell (probably due to the removal of lithium which is not fully replaced by lithium insertion on discharge). There was no evidence of evolution of the β_{II} phase. This may be because the γ_{0} phase does not convert to β_{II} under cycling, or more likely the electrochemical activity is so low that it is hard to determine the actual behaviour of γ_{0} material under cycling.

As with the β_{I} materials the AC impedance spectrum was resolved to a point, leaving only DC resistivity measurements to provide an insight into the conductivity. As
expected from the $\gamma_0$ structure, morphology and galvanostatic behaviour, the $\gamma_0$ material has particularly low conductivity ($\sim 10^{10}$ S/M at room temperature and $\sim 10^{11}$ S/M at 50$^0$C) which may go some way to explaining the poor cycling performance, as with the $\beta_1$ materials the conductivity slightly decreases from room temperature to 50$^0$C.
4.3. **Conclusions and Further work**

Three polymorphs of Li$_2$CoSiO$_4$ were successfully produced using either a solid state or hydrothermal synthesis approach. The materials were characterised by X-ray diffraction and TEM. As suggested by West *et al.*$^{6,7}$ it was found that the phases follow their Li$_3$PO$_4$ analogues with both high temperature $\gamma$, and low temperature $\beta$ phases being preserved at room temperature. The hydrothermal synthesis offered the most convenient (and versatile) method of producing the three phases, allowing access to $\beta_{\text{I}}$ and $\gamma_{\text{O}}$ polymorphs, through reheating of the natively produced $\beta_{\text{II}}$ phase.

The electrochemical behaviour of the materials was characterised by galvanostatic testing in conjunction with slow sweep cyclic voltammetry, AC impedance spectroscopy, DC conductivity measurements as well as *ex situ* X-ray diffraction studies. The relatively superior performance of $\beta_{\text{II}}$ was observed, having a first charge capacity of nearly 210 mAh/g of which 150mAh/g (0.9 Li) which could be accurately described as due to lithium removal. This was ascribed to the previously discussed structural conditions and the low bulk resistivity established through AC impedance. It was shown that $\beta_{\text{II}}$ did not undergo a gross structural rearrangement in the first cycle, as had been reported for different silicate$^{17}$. Investigation of the electrochemical behaviour of the hydrothermally produced $\beta_{\text{I}}$ polymorph revealed a phase change to $\beta_{\text{II}}$ upon charging, a transformation that continued through subsequent cycles.

Both the hydrothermally reheated $\gamma_{\text{O}}$ and the $\beta_{\text{I}}$ phase produced through solid state synthesis showed poor cycling ability to an extent that it was hard to characterise the processes occurring on cycling. This was most likely due to the poor conductivity of
The lack of doping in the βI phases (present in the hydrothermal βI material). While the capacity retention for all phases was particularly poor, even over a relatively short number of cycles, the initial first charge performance of both the βII and βI phases show evidence of electrochemical activity.

This initial investigation into the properties of the Li$_2$CoSiO$_4$ material opened several interesting directions for future work. Further attempts to produce the γII phase observed by West et al. as well as accessing other phases through the solid state synthesis are obvious routes for future research. In order for Li$_2$CoSiO$_4$ to be a useful Li-ion battery cathode the capacity retention would have to be vastly improved and several easy methods exist for the optimisation of electrodes.

An investigation into the cause of different cycling behaviour of the solid state and hydrothermal βI phases, as well as the exact nature of the βI to βII conversion observed upon cycling would help to elucidate the nature of some of the processes occurring with cycling. Another area of investigation that may produce interesting insight, both of Li$_2$CoSiO$_4$ and possibly further afield is a quantitative study of the structural properties of the materials and their effects upon the cycling behaviour as well as establishing the exact affect of the Co-O-Si triad has upon the insertion/removal voltage of lithium.

This initial investigation of Li$_2$CoSiO$_4$ has provided an interesting overview of the possibilities offered by cobalt silicate olivines as cathode materials. Much work is still needed to establish the exact nature of the electrochemical processes occurring during battery cycling, but Li$_2$CoSiO$_4$ offers a useful insight into this growing area of cathode research.
4.4. References.

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27. C. Delacourt, L. Laffont, R. Bouchet, C. Wurm, J. Leriche, M. Morcrette, J. Tarascon, and
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Chapter 5. Li$_2$CoSiO$_4$ Electrochemical Optimisation

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5.1. Introduction

In an attempt to improve the cycling behaviour of Li$_2$CoSiO$_4$ the effect of mechanical milling and carbon coating upon $\beta_{II}$, $\beta_1$ and $\gamma_0$ materials was investigated. The materials were structurally and electrochemically characterised to determine the various effects of milling and coating.

There is substantial interest in electrode optimisation methods$^{1-8}$ due to the recent effort to commercialise LiFePO$_4$ materials which, though preferential to the LiCoO$_2$, suffer from low conductivity. Though the exact optimisation approach is tailor-made for the individual material, generally, areas such as electrode/electrolyte interface and electrode ‘wiring’ are sought out for improvement. It is hoped that by targeting the electronic and ionic movement in the bulk and at the interface a significant improvement in the electrochemical performance should occur.

LiFePO$_4$ type materials are known for their sluggish ionic and electronic conductivity$^{4,9-11}$ (as witnessed by the resistivity values of the three as-prepared polymorphs in the previous chapter), as such olivine optimisation approaches tend to focus upon improving conductivity. Two classic methods to improve the materials electronic properties are through reducing the particle size (thus reducing the ionic diffusion length) and surface coating the particles with a conducting material to improve ‘wiring’ between the particles and the performance of the material at the interface. Through mechanical milling and carbon coating the effects of these two processes on Li$_2$CoSiO$_4$ materials were investigated to gauge whether the electrochemical performance of Li$_2$CoSiO$_4$ could be easily improved.
5.2. Results and Discussion

The materials were produced hydrothermally (with re-heating to produce the β_i and γ_0 phases) as described in the experimental section in Chapter 3. It was felt that the hydrothermal method offered a far more convenient (and reproducible) alternative to the solid state method also discussed in Chapter 3 and, thus, was used exclusively to produce the β_II, β_I and γ_0 phases for the optimisation investigation.

As witnessed in the slow sweep cyclic voltammetry of the as-prepared material in Chapter 4, section 4.3, there is a noticeable current contribution in the voltage cut off region (near 4.5 V vs. Li⁺/Li). There is considerable precedent for this to be the consequence of side-reactions between the electrolyte and the electrode, especially at higher voltages associated with Li⁺ removal\textsuperscript{12-15}. It is generally thought this is an effect of exposure of the redox active cations (transition metal ions) to the electrolyte, which can catalyse reactions with the electrolyte and cause dissociation, when under increased thermodynamic ‘pressure’ (i.e. elevated voltages or lower activation energies during structural rearrangement from lithium removal/insertion). In theory NASICON type materials and their lithium analogues are better equipped to withstand electrolyte attack, the redox active cations being ensconced within a 3D poly-anion network, unlike their layered transition metal oxide counter-parts\textsuperscript{9}. Several different electrolyte systems were tested with the Li_2CoSiO_4 materials to find the most appropriate (see appendix iv) It was found that the electrolyte used to characterise the pristine material, LP30 (1:1 DMC:EC, 1M LiPF_6) still gave the best results, and so was used.
5.2.1. Mechanical Milling

A convenient method to reduce powder particle size is to mechanically mill materials in a hardened high energy ball milling vessel. The mill is sealed with the active material and two tungsten carbide bearings inside, the whole container is then vigorously mechanically shaken, the time length determining the size of the milled particles. By reducing the particle size and, thus, the Li$^+$ diffusion length within the particles of the material, the internal Li$^+$ diffusion kinetics should improve. Any internal benefit is also coupled with the increased electrode/electrolyte interface area due to the greatly increased surface area of the particles. Both effects should combine to give an improved capacity for each polymorph compared to their pristine analogue. While this simple method is easy to implement, its inherently energetic nature and the increase in particle surface area can introduce side-reactions and subsequent impurities during the milling process.

5.2.1.1. Structural and Morphological Effects of Mechanical Milling

In Figure 5.2.1 we can see a typical diffraction pattern of a Li$_2$CoSiO$_4$ polymorph after ball-milling. From the TEM images, displayed in Figure 5.2.2, we see that both $\beta_{I}$ and $\gamma_0$ polymorphs have reduced in size compared to their as-prepared counterparts (in the $\gamma_0$ case by an order of magnitude). The $\beta_{II}$ hydrothermal preparation is the only material without a significant change in particle size on milling, in this case, the ball milling may even be counter-productive, as the high energy milling process may allow some of the smaller particles to sinter together, creating larger, less
desirable, particles. This may well be the case as seen by the larger range in particle sizes observed in the ball milled material (Ø ~20-150nm) compared to the more homogeneous as-prepared material (Ø ~60-100nm seen in Chapter 4, section 4.3.2).

![Figure 5.2.1. Comparison of (normalised) X-ray diffraction patterns for β\textsubscript{i} Li\textsubscript{2}CoSiO\textsubscript{4} material; (1) As prepared material, (2) After 60 minutes ball-milling.](image)

As the T.E.M. images in Figure 5.2.2 highlight, the ball-milling process produces a fairly homogenous particle size across all materials. Both the β\textsubscript{i} and γ\textsubscript{0} polymorph

![Figure 5.2.2. TEM images of Li\textsubscript{2}CoSiO\textsubscript{4} polymorphs ball-milled for 60 minutes; (1) γ\textsubscript{0} polymorph, (2) β\textsubscript{II} polymorph, (3) β\textsubscript{i} polymorph.](image)
show significant particle size reduction with the majority of the ball-milled material having a diameter of less than 100nm (both $\beta_i$ and $\gamma_0$ materials contained particles with $\phi>500$nm prior to ball milling). The $\beta_{II}$ material only experienced a marginal change in particle size, with the particles seeming to increase diameter after ball-milling (from 60nm $\phi$ as-prepared to $>100$nm $\phi$ after ball-milling).
5.2.1.2. Electrochemical Effects of Ball-milling

![Galvanostatic load curves of ball-milled Li₂CoSiO₄ polymorphs; a) first cycle, b) second cycle, c) fifth cycle, d) tenth cycle – Electrolyte LP30, cycle rate 10mA/g at a temperature of 50°C.](image)

Figure 5.2.3. Galvanostatic load curves of ball-milled Li₂CoSiO₄ polymorphs; a) first cycle, b) second cycle, c) fifth cycle, d) tenth cycle – Electrolyte LP30, cycle rate 10mA/g at a temperature of 50°C.

It is apparent from Figure 5.2.3 that ball-milling significantly alters the galvanostatic behaviour of the Li₂CoSiO₄ polymorphs. The γ₀ polymorph is the only material whose electrochemical performance is visibly improved after ball-milling. This is not surprising given that the γ₀ material shows the greatest change in particle size after milling, from particles of over 1μm Ø to an approximate particle size of less than 100nm Ø. The first charge capacity of ~130 mAh/g is notably better than the pristine
material (~8 mAh/g). This improvement could be due to kinetic enhancement brought about by reduction in particle size from milling, in-turn reducing lithium (and electronic) diffusion lengths as well as potentially improving the ‘wiring’ between particles through energetic sintering of particles during the milling process. There is also a distinct possibility that the large capacity merely represents a side reaction caused by the more reactive smaller particles.

The whole first discharge process develops a capacity of ~50 mAh/g and, where a discharge pseudo-plateau is identifiable, it comes after significant polarisation (~600mV between charge and discharge process, compared to ~500mV for as-prepared β polymorphs). This poor electrochemical performance, despite the, presumably, greatly enhanced surface area, suggests that the structure of γ₀ phase presents considerable obstacles to the efficient insertion and removal of Li⁺ ions from the structure.

While the capacity retention upon cycling does show improvement over the as-prepared γ₀ material, this is to be expected given the near negligible electrochemical activity exhibited in the as-prepared material and both charge and discharge capacities of the ball-milled materials quickly dissipate in subsequent cycles (as can be seen in Figure 5.2.4).

Unlike the ball-milled γ₀ phase, the β₁ and β₁₁ phases show significantly reduced electrochemical performance compared to their as-prepared material. For the β₁ phase this is counter-intuitive given the reduction of particle size post-milling (particles were reduced from up to 500nm Ø down to particles under 100nm Ø). Structural refinement
was attempted to determine if the ball-milled $\beta_{II}$ material was structurally different to its as-prepared counterpart.

![Graphs of Capacity Vs. Cycle number for ball-milled Li$_2$CoSiO$_4$ $\beta_{II}$, $\beta_{I}$ and $\gamma_0$ materials.](image)

Figure 5.2.4 Capacity Vs. Cycle number for ball-milled Li$_2$CoSiO$_4$ $\beta_{II}$, $\beta_{I}$ and $\gamma_0$ materials.-Electrolyte LP30, cycle rate 10mA/g at a temperature of 50$^\circ$C

The refinement did not provide any clear answers, though it inferred that milling may globally increase disorder in the cobalt and lithium sites. Although given the poor state of the ball-milled diffraction pattern, the refinement results should be treated with a large degree of caution.

The reduction in capacity of ball-milled $\beta_{II}$ on first charge is perhaps to be expected given the slight increase in particle size post-milling. Looking closer at the profiles of the $\beta$ polymorph it can be seen that the voltage plateaus seen on charge (and to a certain extent on discharge) in the as-prepared materials have been replaced by sloping pseudo-plateaus for the ball-milled samples. The lack of any single
electrochemical process (i.e. a voltage plateau) suggests that side-reactions are present, and perhaps prevalent, a notion which may explain Figure 5.2.4 which displays the capacity versus cycle number of the ball-milled material over 10 cycles and shows diminished capacity retention compared to the as-prepared material.

As with the pristine material, the charge capacity drops off sharply after the first cycle but capacity loss slows on subsequent cycles. The discharge capacity reduction is not so severe but (as with the pristine material) the discharge capacity continues to significantly lag the charge capacity. As this effect seems to be ubiquitous (i.e. the improvement in the first charge capacity of the γ₀ ball-milled material is not matched in an equally improved discharge capacity) it would seem there is fundamentally a problem with reinserting lithium into the once occupied sites; whether this is a result of structural impediments or parasitic side-reactions is unclear.

The apparent change in cycling behaviour on ball-milling was investigated further using AC impedance and DC resistivity measurements. If the reduction in performance is caused by the loss of lithium or other elements at the surface during milling, this ‘delithiated’ phase may subsequently form a surface layer, which should become apparent with AC impedance. This process has been witnessed with the more air sensitive iron silicates\(^{12}\) and under the energetic environment of ball-milling the surface layers may be more susceptible to reaction with the atmosphere\(^{16,17}\) (attempts were made to mill the materials under argon but similar electrochemical results were achieved, suggesting that it may not be a surface oxidation layer forming during ball-milling \textit{per se} but a loss of lithium/ions and subsequent reactions in the cell that causes the reduced performance).
As with the pristine materials, the only phase that displays a complex impedance spectrum is the \( \beta_{II} \) material (the other materials resolving to a single point about zero on both impedance axis, i.e. an electrical ‘shunt’).

An identical equivalent circuit to the one used for the pristine material was employed (-Resistor\(_1\)/Constant Phase element\(_1\) + Resistor\(_2\)/Constant Phase Element\(_2\)) fitted using a least square refinement. Compared to the as-prepared material, the high frequency semi-circle (traditionally assigned to the bulk processes) is severely depressed relative to the low frequency semi-circle (thought to be produced by particle surface/grain boundary effects). This indicates that the surface/grain boundary effect is the dominating feature.

The values generated from the impedance spectrum are displayed in Table 5.2.1. Traditionally the high frequency (bulk) semi-circle is expected to have a capacitance of hundreds of picoFarads, while the low frequency (surface/grain
boundary) semi-circle is of the order of nanoFarads. The ball-milled βII material is found to have a high frequency capacitance of $\sim 10^{-10}$ Fs$^{-1}$ suggesting a bulk contribution, but the low frequency capacitance is in the order of $\sim 10^{-7}$Fs$^{-1}$ which is a considerably lower capacitance than expected for a surface/grain contribution. The low capacitance may be due to oxygen deficiencies or loss of other ions at the surface of the grains or other intricate effects such as increased strain, resulting in a low permittivity.

### AC Impedance

<table>
<thead>
<tr>
<th></th>
<th>Room Temp.</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Freq.</td>
<td>Low Freq.</td>
</tr>
<tr>
<td>Resistivity/Ωm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.02x10^4</td>
<td>9.45x10^6</td>
<td></td>
</tr>
<tr>
<td>Capacitance/Fs$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.41x10^{-10}</td>
<td>1.39x10^{-7}</td>
<td>2.57x10^{-9}</td>
</tr>
</tbody>
</table>

### DC Resistivity/Ωm

<table>
<thead>
<tr>
<th></th>
<th>Room temp.</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>βII material</td>
<td>4.51x10^6</td>
<td>1.16x10^7</td>
</tr>
<tr>
<td>βI material</td>
<td>1.36x10^9</td>
<td>9.80x10^9</td>
</tr>
<tr>
<td>γ0 material</td>
<td>1.09x10^9</td>
<td>1.74x10^9</td>
</tr>
</tbody>
</table>

Table 5.2.1. Results obtained from AC impedance spectroscopy of ball-milled βII material, using a - $R_1$/CPE$_1$ + $R_2$/CPE$_2$- equivalent circuit. DC Resistivity data for βII (taken for the 3-4.5 volt region), βI and γ0 materials at room temperature and 50°C.

The resistivity and capacity for the bulk process within the ball-milled βII material was $\sim 10^5$Ωm and $\sim 10^{-10}$Fs$^{-1}$ respectively, changing to $\sim 10^6$Ωm and $\sim 10^{-9}$Fs$^{-1}$ at 50°C. Compared to the as-prepared material, the bulk resistivity is reduced while the grain boundary resistance remains similar.

One possible explanation for the bulk resistivity reduction is the loss of lithium during ball-milling. As the silicate materials are expected to be semi-conductors$^9$, the loss of Li$^+$ ions could result in P-type doping within the bulk material, this in turn could improve the conductivity (i.e. reduce the resistivity). Ball-milling is known to increase
internal strain within crystallites\textsuperscript{18,19}, due to the presence of lattice distortion at the grain boundary, possible from the accentuation of dislocation density due to prolonged milling. From the DC resistivity measurement it would seem that the electrical resistance is dominated by the grain boundary resistance which may explain why $\beta_{II}$ and $\beta_{I}$ and $\gamma_{0}$ do not show altered performance.

The DC voltage vs. current profile of ball-milled $\beta_{II}$, $\beta_{I}$ and $\gamma_{0}$ materials showed non-linear behaviour (an example is given with the $\beta_{II}$ material in appendix v). This may explain why the polymorphs deviate from ‘classic’ semi-conductor behaviour, i.e. their resistance increases with temperature. The resistivity measurements were calculated for the region 2 - 4.5 V and produced values that were lower than the pristine material for the $\beta_{II}$ polymorph but higher for $\beta_{I}$ and $\gamma_{0}$ materials ($\sim 10^7$, $10^7$ and $10^9$ $\Omega$m for the as-prepared $\beta_{II}$, $\beta_{I}$ and $\gamma_{0}$ respectively). The improvement in the DC resistance of the $\beta_{II}$ material could be explained by particle sintering (seen in the TEM image) improving the ‘wiring’ between crystallites, an effect that is outweighed by the dominating features of the higher resistance surface/grain boundary layer which is much more ubiquitous in the after milled $\beta_{I}$ and $\gamma_{0}$ materials compared to their as-prepared counterparts.

From the electrochemical and structural study it is clear that the $\gamma_{0}$ polymorph initially experiences an improvement in the electrochemical performance either from particle size reduction (by an order of magnitude) or side reactions, but the performance of the $\gamma_{0}$ phase quickly diminishes and (while an improvement on the pristine $\gamma_{0}$ material) overall the ball-milled material does not perform particularly well.
When the change in particle size is less dramatic (i.e. $\beta_1$ and $\beta_{II}$) no apparent improvement in electrochemistry is observed. This is seen in both $\beta_{II}$ and $\beta_1$ galvanostatic load curve which show diminished first charge (and discharge) capacities and poor capacity retention over cycling, compared to the pristine material.

The electrochemical behaviour of all materials post-milling is most telling. All materials display a first charge pseudo-plateau which gently slopes upwards to the voltage cut-off. The lack of reversible discharge, or subsequent charging plateaus strongly suggests that the pseudo-plateau is not formed by reversible lithium removal. Instead it would seem that it is the consequence of irreversible side-reactions probably initiated by some lithium removal from the structure (hence the plateau starts around the lithium removal voltage seen in the as prepared material). The side reactions may not be as prevalent on subsequent cycles because their products may be passivating, causing a reduction in electrochemical activity.

Both $\beta_1$ and $\beta_{II}$ polymorphs show reduced capacities compared to their non-milled counterparts. With the $\gamma_0$ material it is possible that initially a balance is struck, on the first cycle at least, between the benefits of reducing the particle size versus the debilitating effects of side reactions that seem to occur due to the increased particle surface area/electrolyte interaction.

It would seem that ball-milling is not an ideal technique for Li$_2$CoSiO$_4$ electrode optimisation as the reduced particle size does not offer a remedy to the poor capacity retention. This infers that ionic conductivity (in the bulk at least) may not be the determining factor on the capacity retention with cycling, given that, in the $\beta_1$ and $\gamma_0$ materials such a large reduction in bulk diffusion length is not met with an
improvement in the electrochemical behaviour. This is hard to give this as absolute, as negative effects associated with particle size reduction, (i.e. side reactions) may diminish any kinetic benefit gained from reducing particle size. It is clear that the next stage of work on particle size reduction would have to investigate the nature of the side reactions and establish a method to negate them.
5.2.2. Carbon Coating of Li$_2$CoSiO$_4$

Another established approach to improve electrode performance is to coat the particles with a conducting surface to improve electronic connections between particles and electron conduction at the particle surface$^{1,8,13,17,20-23}$. This method has an advantage over ball-milling as (assuming the coating is near total) the surface covering can act as a barrier against side reactions between the cathode and electrolyte$^{13,20,21,24}$. The simplest conductive additive to employ (and most favoured from an industrial perspective) is carbon. It is cheap, ubiquitous, non-toxic and offers a wide variety of coating methods. In the case of Li$_2$CoSiO$_4$, due to the pyrolysis temperature of the carbon precursors (to ensure a complete coating regime) and subsequent graphitisation temperatures (to optimise conductivity) special consideration of coating technique is necessary as the coating procedure may involve temperatures in the region of Li$_2$CoSiO$_4$ polymorphic phase change.

Various forms of carbon coating were investigated to determine the optimum carbon precursor, including sucrose (mixed in with the hydrothermal precursors or dispersed in acetone and mixed with the fully formed $\beta_{II}$ material), citric acid sol-gels and xerogel polymers (added as precursors at the hydrothermal stage, as well as pre-prepared xerogels after hydrothermal synthesis or as pre-prepared Li$_2$CoSiO$_4$ material added during gelation stage of the xerogel). Each coating approach gave a different product, depending greatly on the carbon decomposition process.
As a degree of graphitisation was required to produce a conductively beneficial carbon coating, temperatures near 700°C were necessary during the carbon coating process. It was discovered that, as graphitisation temperatures are approached, the Li$_2$CoSiO$_4$ is highly susceptible to side-reactions with the carbon coating itself or the pyrolysis decomposition products. It may be that as Li$_2$CoSiO$_4$ nears the phase change boundary it forms an intermediate or transitionary phase which, given its meta-stable nature, may have significantly lower activation energy than its more thermodynamically stable parent phases. This makes it significantly more reactive to the pyrolysis decomposition products and reduction. Impurities observed from the carbon coating processes tended to be Li$_2$SiO$_3$, other higher order silicates, Li$_2$CO$_3$ or cobalt metal, indicative of reductive reactions.

The least disruptive coating process utilised xerogel added to the hydrothermal β$_{\|}$ material prior to the final pyrolysis stage of xerogel formation. The xerogel was mixed into β$_{\|}$ material in acetone; once the acetone had evaporated the mixture was heated to an appropriate pyrolysis temperature in an oven under flowing argon.

Xerogels are high surface area polymers, consisting of aromatic and extended carbon chains formed through an acid or base catalysed polymerisation of resorcinol and formaldehyde as shown in Figure 5.2.6.
Xerogel has the potential advantage over other types of carbon treatment as it consists of a large network of interconnected high-surface area pores built from a scaffold of conjugated and aromatic bonded carbons, requiring less graphitisation\textsuperscript{25}. Xerogels have previously been successfully employed to improve the electrochemical performance of the iron polyanion silicates\textsuperscript{26} with impressive results, and thus, were a natural choice for investigation as a conductive additive for cobalt silicate materials.

The Xerogel synthesis involved several stages; the precursors (formaldehyde, resorcinol and lithium carbonate as a catalyst) are mixed together in water then heated to gelation. Subsequent heating removes the water from the polymer matrix.
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and forms a brittle solid. This is then mixed with the active cathode material and heated under flowing argon to pyrolyse the carbon and coat the active material. At each stage there is the opportunity to alter the conditions and, hence, change the nature of the final xerogel material. By pyrolysing the xerogel with the active material (and thus, choosing a relatively high temperature for xerogel pyrolysis) much of the structural and morphological nature of the material is lost.

The pyrolysis stage of carbon coating involves delicate manipulation of heating and argon flow rates to minimise the effects of the reductive carothermal pyrolysis. The xerogel undergoes several reactions as it decomposes to carbon, notably water and hydroxide loss below 200°C and subsequent hydrogen gas evolution between 350-500°C, as polymer chains are carbonised\(^2\). Hydrogen gas is a strong reducing agent and the management of its evolution within the heated xerogel/\( \text{Li}_2\text{CoSiO}_4 \) system became an important factor in producing a (relatively) pure product, with the argon gas flow requiring careful control to ensure that low concentrations of hydrogen gas were produced and could be quickly removed by the flowing argon.

Various approaches were employed to try and produce the 3 previously synthesised \( \text{Li}_2\text{CoSiO}_4 \) phases, but with limited success. Considerable effort was employed to produce a fast quenching, gas tight apparatus, to form the \( \beta_{\text{II}} \) and \( \gamma_0 \) phases. Failure to produce a pure \( \gamma_0 \) material appeared to be caused by a chemical rather than technological obstacle, given that the starting \( \beta_{\text{II}} \) phase was always reduced to cobalt metal and lithium silicates at temperatures above 800°C and no remaining \( \text{Li}_2\text{CoSiO}_4 \) phases were observed. This may suggest that the \( \beta \) to \( \gamma \)
transformation created a reactive intermediate or that the higher temperature produced a more reducing environment (or a combination of the two), hence producing the mentioned impurities, irrespective of the cooling regime. Pure carbon coated $\beta_{\text{II}}$ also proved elusive, as after heating to the $\beta_{\text{II}}/\beta_{\text{I}}$ phase boundary region, carbon coating seemed to introduce considerable hysteresis in the reverse (kinetically dependent) $\beta_{\text{I}}$ to $\beta_{\text{II}}$ transformation, always producing a mixed phase no matter the cooling regime. These effects, combined with the limitations imposed by the graphitisation temperature ($600^\circ$-$900^\circ$C) ensured that a mixed phase of $\beta_{\text{I}}/\beta_{\text{II}}$ was universally produced, with heating time having little effect on the relative phase ratios.

To this end it was established that a heating ramp of $3.14^\circ$C min$^{-1}$ to an oven temperature of $710^\circ$C for 4hrs while incorporating an argon gas flow of two litres a minute and allowing the material to cool with the oven, gave impurity free Li$_2$CoSiO$_4$. 
5.2.2.1. Structural Characterisation of Carbon Coated Li$_2$CoSiO$_4$

Figure 5.2.7 X-ray diffraction pattern and Rietveld refinement parameters of carbon coated β$_1$ Li$_2$CoSiO$_4$ (10% Xerogel precursor by pre-fired weight): A) Li$_2$CoSiO$_4$ β$_{II}$ polymorph peak positions, B) Li$_2$CoSiO$_4$ β$_{I}$ polymorph peak positions. $R_{wp}$ 13.64%.

Figure 5.2.7 shows the X-ray diffraction pattern obtained from the carbon coated material. A superficial analysis of the carbon coating diffraction pattern (and in deference to the synthesis conditions) suggested that the β$_{I}$ polymorph is produced through the coating and subsequent heating process. On closer investigation it was revealed that a phase mixture of β$_{II}$ and β$_{I}$ gave the best Rietveld fit (the best purely β$_{I}$ fit gave $R_{wp}$=22%, when Co/Li mixed sites were allowed to achieve up to 70/30 disorder).

Compared to the pristine β$_{I}$ material the carbon coated diffraction pattern shows altered relative intensities in the (1,1,1) peak ($2\theta$ = 30.854) compared to its
(1,2,0) (2Θ =28.43) and (1,1,0) (2Θ =27.54) neighbours indicative of the presence of the βII phase (using a ‘βI only’ fit this can be partially accounted for by strongly increasing the disorder in cobalt 4a site).

Table 5.2.2 shows the refinement parameters of the carbon coated Li2CoSiO4 material. The best Rietveld fit was achieved with a relative βII:βI phase ratio of approximately 7:1. This is surprising as the synthesis does not employ the fast cooling supposedly required to produce βII material after heating to relatively high (600-850°C) temperatures. It is possible this is caused by the initial βII material not undergoing a phase change due to the ‘barrier’ effects of the carbon coating on the crystallites thus, not allowing the usual conversion of βII to βI at higher temperatures.

The parameters obtained through Rietveld refinement (shown in Table 5.2.2) suggest that there is little difference between the as-prepared βII phase and the βII material present within the carbon coated mixture, apart from a slight change in the overall stoichiometry (from Li2.06Co0.94SiO4 as-prepared to Li2.1Co0.9SiO4 when carbon coated). Though this may have limited significance given the assumed natural variation in stoichiometry between batches.

The βI polymorph present in the carbon coated material is also broadly similar to its as-prepared analogue. The overall stoichiometry is closer to the ideal, at Li1.99Co2.01SiO4 compared to Li2.02Co0.98SiO4 for the as-prepared βI material; this is primarily due to loss of lithium from the mixed cobalt position.
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**Table 5.2.2** Refinement parameters achieved from carbon coated $\text{Li}_2\text{CoSiO}_4$: $\beta_{\text{II}}$ Polymorph and $\beta_{\text{I}}$ polymorph gave $R_{\text{wp}}=13.64\%$ at a relative phase ratio of $\beta_{\text{II}}:\beta_{\text{I}}=7:1$.

TEM images in of the carbon coated material (Figure 5.2.8) show that there is none of the particle growth seen previously when the $\beta_{\text{II}}$ material was heated (i.e. to access the $\beta_{\text{I}}$ and $\gamma_0$ phases). There is also an absence of an obvious thick carbon

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surface layer sometimes associated with high degrees of carbon coating\textsuperscript{20}. The lack of particle growth again suggests that the carbon acts to retard crystal growth which may be crucial for the $\beta_{\text{II}}$ to $\beta_{\text{I}}$ transformation.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{TEM micrograph image of carbon coated $\text{Li}_2\text{CoSiO}_4$ material.}
\end{figure}

Further investigation showed that, when purely xerogel underwent an identical heating regime, a large weight loss was observed, the xerogel losing over 70\% of its mass. This is to be expected given the transformation of hydrolysed polymer to graphitic carbon thought to occur during heating\textsuperscript{25}. As a rough approximation (using volume and surface area of the particles, and the densities and ratios of involved materials) a starting pre-fired mixture of 90\% active material and 10\% wt. Xerogel precursor would result in only ~1 Å deep universal carbon coating covering the particles which would explain why a clear surface layer isn’t observed in the TEM image. It could well be that the carbon only covers patches of the particles.
While the physical presence of the carbon coating may be only slight, it is clear that the xerogel treatment has an effect upon the nature of the material and it is expected that the carbon coating should also have some effect on the electrochemical performance of the material.

5.2.2.2. Electrochemical Behaviour of Carbon Coated Li$_2$CoSiO$_4$

![Galvanostatic load curve for carbon coated Li$_2$CoSiO$_4$ material: Electrolyte LP30, cycle rate 10 mA/g at a temperature of 50°C](image)

The electrochemical behaviour shown in Figure 5.2.9 is improved compared to the pristine (and ball-milled) $\beta_i$ material (Chapter 3, Section 4.3.3 and Figure 5.2.3 respectively). The first charge shows a defined plateau beginning at 4.21V, slightly higher than the as-prepared $\beta_{\text{III}}$ material but clearly a single plateau (i.e. not 2 separate plateaus for $\beta_{\text{II}}$ and $\beta_i$ phases). This would suggest that the major contribution to the electrochemical behaviour comes from the $\beta_{\text{III}}$ phase. Approximately 150mAh/g capacity passes before the 4.5V cut-off, which is significantly less than the 210 mAh/g capacity observed in the $\beta_{\text{III}}$ as-prepared material. There is a 300mV hysteresis between
charge and discharge plateaus, a reduction of ~200mV compared to the observed charge/discharge polarisation in the pristine $\beta_{II}$ material. While this polarisation reduction suggests that the carbon coating goes some way to mitigating the ohmic effects between charge and discharge, it either does not fully negate the kinetic impediment, or perhaps, it hints at a process that is not improved by the benefit provided by carbon coating (e.g. a slightly different thermodynamic process between initiating lithium removal and lithium insertion). The first discharge capacity is slightly larger than its un-coated counterpart (110mAh/g vs. 103mAh/g) but it is in the subsequent cycles that a difference in behaviour becomes more noticeable as Figure 5.2.10 shows.

![Graph](image)

**Figure 5.2.10.** Capacity Vs. Cycle number for $\beta_{I}$ carbon coated material: □ Capacity on Charge, ○ Capacity on discharge – Electrolyte LP30, cycle rate 10mA/g at a temperature 50°C

As with the pristine material the carbon coated material shows a diminished second cycle capacity in both charge and discharge (~60% and 3% reduction respectively, compared to ~62% and 24% drop for the pristine material) and continues
this trend through the following cycles, showing a second to tenth cycle reduction of ~40% for charging capacities and 26% for discharge capacities

The improved capacity retention is indicative that the carbon coated material is able to improve the cycling behaviour of the Li$_2$CoSiO$_4$ material and, as witnessed by the selected galvanostatic cycles in Figure 5.2.9, it reduces the polarisation seen on charging and discharging. It is not clear whether the carbon coating acts solely as a barrier to the side reactions assumed to be present (as identified in the as-prepared and ball-milled materials). There is a chance the carbon coating improves the surface kinetics of the particles, diminishing the ohmic drop between the surface of the particles and the LiCoSiO$_4$/Li$_2$CoSiO$_4$ interface (the reduction of charge/discharge polarisation would suggest this). Most likely it is a combination of the two factors.

Figure 5.2.11. (1) Nyquist plot of carbon coated Li$_2$CoSiO$_4$ taken between stainless steel blocking electrodes: □Room temperature, ○ 50°C; Inset high frequency region. (2) Equivalent circuit used to model carbon coated AC impedance. Spectrum taken using two stainless steel blocking electrodes.
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The AC impedance spectrum from the carbon coated material was notably different from the as-prepared (and ball-milled) β₈ material, suggesting the carbon coating process had changed the electronic nature of the material. Instead of a clear high frequency and low frequency semi-circle, representing the bulk and grain boundary process respectively, there appears to be a more complex system at work. Several equivalent circuits were developed and tested, modelling various different scenarios (e.g. complete coating of particles with carbon, partial covering, and replacement of surface layer with carbon etc.). It was found that the circuit that gave the best fit (i.e. the lowest \( \chi^2 \) value for the non-linear least squares fit) represented the carbon coating (and possibly the β₈ phase electronic contributions) as a single resistor in parallel with the dipole that is assumed to include the surface/grain boundary contribution (equivalent circuit shown in Figure 5.2.11 (2), It has been used previously to model similar situations\(^1\)).

### AC impedance

<table>
<thead>
<tr>
<th></th>
<th>Room Temp.</th>
<th>50°C</th>
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</thead>
<tbody>
<tr>
<td><strong>Resistivity/ ΩM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High Freq.</td>
<td>1.26 x 10⁶ ((R₁))</td>
<td>2.3 x 10⁸ ((R₁))</td>
</tr>
<tr>
<td>Low Freq.</td>
<td>7.59 x 10⁶ ((R₂))</td>
<td>7.59 x 10⁶ ((R₂))</td>
</tr>
<tr>
<td><strong>Capacity/ F⁸⁻¹</strong></td>
<td>5.31 x 10¹¹ ((CPE₁))</td>
<td>1.84 x 10¹⁰ ((CPE₁))</td>
</tr>
<tr>
<td></td>
<td>2.57 x 10⁻⁴ ((CPE₂))</td>
<td>1.12 x 10⁻⁶ ((CPE₂))</td>
</tr>
</tbody>
</table>

### DC Resistivity

<table>
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<tr>
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<th>Room Temp.</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Resistivity/ Ωm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.39 x 10⁵</td>
<td>2.22 x 10⁶</td>
</tr>
</tbody>
</table>

Table 5.2.3. AC impedance and DC Resistivity details for carbon coated Li₂CoSiO₄.
The capacities of the high frequency and low frequency semi-circles are $\sim 10^{-11}$ F$^{n-1}$ and $\sim 10^{6}$ F$^{n-1}$ ($\sim 10^{-10}$ F$^{n-1}$ and $\sim 10^{6}$ F$^{n-1}$ for 50$^0$C respectively), inferring that the high frequency semi-circle is again responsible for the bulk process. The low frequency semi-circle is of a lower capacity traditionally associated with purely grain boundary effects (normally quoted as nF)$^{2,28}$. If the low frequency semi-circle includes the surface/grain boundary effects then the process of carbon coating has intimately affected the electrical properties of the boundary regions. The lower capacity could hint that there could be a distribution of relaxation times within the low frequency semi-circle. This is consistent with the complicated nature of surface coatings and their interactions with grain boundary contributions (pitting effects etc.$^{29}$

The measurements taken at room temperature and 50$^0$C display a high frequency semi-circle at 0.5kHZ with conductivities (1/resistivity) of $\sim 10^{-7}$ S/cm. This is a lower conductivity than the as-prepared $\beta_{II}$ material (though in line with olivine materials such as LiFePO$_4^{10,30}$). Which suggests that the bulk $\beta_{II}$ phase within the carbon coated material may be subtly (electronically) different to the as-prepared material.

As with pristine material there is little change in the bulk conductivity between the room temperature and 50$^0$C measurements. The grain boundary (low frequency) contribution gives conductivity values of $\sim 10^{-7}$ s/cm for both the room temperature and 50$^0$C samples, while the extra resistance contribution ($R_3$) develops a resistivity of $\sim 10^9$ and $10^{10}$ $\Omega$/m respectively. The $R_3$ resistance is likely to be the sum of a combination of factors, with surface coatings being notoriously complex to analyse, especially if the carbon coating process produced incomplete coverings.
Given that only the as-prepared $\beta_{II}$ gave quantifiable AC impedance data, the AC data is most likely to represent the $\beta_{II}$ material, with contributions from the $\beta_I$ material, the carbon coating and other effects represented in the $R_3$ contribution. The DC resistivity measurements show that the purely electronic (i.e. DC) contributions are lower than the resistivity observed in the individual bulk or surface/grain boundary contributions, suggesting that the AC resistivity has other factors other than purely electronic contributions. The carbon coated $\text{Li}_2\text{CoSiO}_4$ material has DC resistivity values that sit between the values of the $\beta_I$ and $\beta_{II}$ phases. The increase in DC resistivity (and in $R_3$) resistance at 50°C again suggests that a simplistic semi-conductor does not fit with the $\text{Li}_2\text{CoSiO}_4$ material, and further work is needed to fully explore the charge carriers present in the silicate materials.

While the carbon-coated cycle retention is greatly improved compared to the as-prepared material it still represents a considerable loss of capacity over a short number of cycles. The effect of different amounts of carbon loading on the electrode performance was investigated. Figure 5.2.12 shows the result of the carbon loading series (5-30% (wt.) of xerogel precursor) on the charging capacity over ten cycles.
While the pristine material has the highest first charge capacity, relatively low carbon loading (5 & 10% loading) perform better over ten cycles. The loss of capacity with subsequent cycles levels off for all carbon coated materials, where the pristine material continues to lose significant capacity with each cycle. It would seem that higher loading of carbon (>15%) had a detrimental effect on the charging capacity of the material. This may be caused by the coating became thick enough to present an obstacle to lithium diffusion at the electrode/electrolyte interface. In the case of higher carbon loading it also became increasingly difficult to produce impurity free material, the prevalence of pyrolysis decomposition side-reactions increasing with increasing carbon loading.
5.3. Conclusions and Further Work

Both ‘classical’ approaches to electrode optimisation provided mixed results. Some benefit was observed with ball-milling Li$_2$CoSiO$_4$ materials (namely the $\gamma_0$ phase). This performance improvement is assumed to be due to a large particle size reduction. Any benefit from ball-milling was significantly counter-balanced by the negative effects of ball-milling, such as increased contributions from side reactions, to the extent that materials not known to suffer from chronically low ionic/electronic kinetics (the $\beta_{II}$ and $\beta_I$ Li$_2$CoSiO$_4$ polymorphs) performed worse after ball milling due to the presence of these side-reactions.

Carbon coating of the material improved the capacity retention (though some capacity loss with cycling was still observed) but the inability to produce carbon coated $\beta_I$ or $\gamma_0$ polymorphs or phase pure $\beta_{II}$ materials is disappointing. While it appears that the ‘LP30’ solvent/salt combination was the optimum electrolyte for the relatively high voltage Li$_2$CoSiO$_4$ cathode, the apparent presence of parasitic side-reactions suggests that further investigation into the electrode/electrolyte reactions could improve many of the factors influencing Li$_2$CoSiO$_4$ electrode performance.

Several important factors need to be addressed in order to fully understand the Li$_2$CoSiO$_4$ system namely the role of any side-reactions seemingly enhanced by mechanical-milling which may be studied by in situ techniques such as IR or AC impedance. Further investigation into the nature of the effect of carbon coating on the crystal growth may point the way to producing phase pure coated materials, as well as fully establishing the carbon/active material ratio in the coated material. Exploration of
different coating materials (such as metal oxides$^{13,17,20,21}$) whose favourable coating regimes may allow access to the $\gamma_0$ phase and phase pure $\beta_{II}$ and $\beta_{I}$, in conjunction with improving capacity retention over repeated cycling, are necessary in order for the cobalt silicate materials to be seriously considered as cathode materials.
5.4. References

Chapter 6. LiVO₂ as a Lithium Intercalation Anode
Chapter 6: LiVO$_2$ as a Lithium intercalation Anode

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Chapter 6. LiVO$_2$ as a Lithium Intercalation Anode.

6.1. Introduction

Layered compounds of the composition Li$_x$MO$_2$ are traditionally seen as cathode materials, recent work has shown that the group of compounds may provide a useful alternative to the graphite anode$^{1-4}$. This chapter focuses on the new anode material LiVO$_2$ and its subsequent characterisation.

Traditionally graphite has been the anode of choice$^{5-12}$. Since the introduction of a lithium ion host as both anode and cathode in the early 1990’s graphite has dominated the anode market due to it being cheap, ubiquitous and non-toxic, most importantly graphite has a capacity (370mAh/g) that easily exceeds the capacity of most cathodes; hence the focus of research normally falls on cathodes. Unfortunately the electrochemical process of intercalating lithium into graphite is not ideal. Graphite has an inherently low energy density (0.0372 kWh/kg) as well as the low lithium intercalation voltage (about 0.1V away from the Li/Li$^+$ equilibrium voltage) which can cause lithium plating when a high over-potential is applied$^{7,9-11}$; hence, alternatives to graphite are now being actively sought.

Recent investigations into non-graphitic anodes have produced materials that utilise more complex electrochemical behaviour, such as conversion reactions of CoO$^{13}$, tin based alloy systems$^{14}$ and titanate based, zero strain intercalation materials$^{8,15}$. However, these materials come with their own problems, most notably large voltage hysteresis between charge and discharge process, large volumetric changes and high intercalation voltages respectively.
Research has begun into layered transition metal oxides as anodes. Traditionally seen as cathodes, materials such as LiCoO$_2$ and LiMn$_{0.5}$Ni$_{0.5}$O$_2$\textsuperscript{1-3,16-19} have been investigated as potential anodes partly due to the existence of the Li$_2$MO$_2$ phase. It is thought that a LiMO$_2$ to Li$_2$MO$_2$ phase conversion can take place during cycling and had been observed to a limited extent with the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ materials\textsuperscript{19}. LiVO$_2$ offers similar structural characteristics as LiMO$_2$ materials and is thought to have a low (0.2V) $V^{3+/2+}$ redox couple\textsuperscript{20} and high material density (4.29g/cm$^3$), ensuring high power densities, combined with a theoretical specific capacity close to graphite (298 mAh/g). Recent work has found that LiVO$_2$ will undergo reversible cycling at low voltages\textsuperscript{21-23} but the electrochemical processes and the nature of the LiVO$_2$ to Li$_2$VO$_2$ phase conversion has yet to be fully established.
6.2. Results and Discussion

6.2.1. Structural Characterisation

Li$_{1+x}$V$_{1-x}$O$_2$ materials were synthesised using a solid state method as described in the experimental section, special attention was needed prior to calcinations to ensure an argon atmosphere was maintained during ball milling, due to the reactive nature of the V$_2$O$_3$ starting material. Various stoichiometries were produced using differing amounts of excess lithium in the starting materials. Doped Li$_{1+x}$V$_{1-x}$O$_2$ products with the starting stoichiometries of x = 0, 0.025, 0.05, 0.07, 0.1 and 0.2 were produced. The X-ray diffraction patterns of the various doped materials can be seen in the inset of Figure 6.3.1. All materials could be indexed to a $R3m$ space group based on the classic $\alpha$-NaFeO$_2$ structure. A typical refinement is shown in Figure 6.3.1 where the nominally 5% lithium excess material was refined, giving a good fit of $R_{wp} = 3.35\%$. A list of refinement parameters is given in Table 6.3.1.
Chapter 6. LiVO\textsubscript{2} as a Lithium Intercalation Anode.

Figure 6.3.1 X-ray diffraction pattern and Rietveld fitting of Li\textsubscript{1.08}V\textsubscript{0.92}O\textsubscript{2} (nominally Li 5% excess). Insert X-ray diffraction patterns of Li\textsubscript{x}V\textsubscript{1-x}O\textsubscript{2}: A) X=0 (nominal Li 0% excess lithium) $R_{wp}$=4.65\%, B) X=0.01 (nominally Li 2.5% excess) $R_{wp}$= 1.35\%, C) X=0.08 (nominally Li 5% excess) $R_{wp}$=3.1\%, D) X=0.13 (nominally Li 7% excess) $R_{wp}$=3.72\%, E) X=0.17 (nominally Li 10% excess) $R_{wp}$=3.52\%, F) X=0.21 (nominally Li 20% excess) $R_{wp}$= 3.4\%.

<table>
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<th>Wyckoff Symbol</th>
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<th>y/b</th>
<th>z/c</th>
<th>$B_{iso}$</th>
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</tr>
<tr>
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<td>0.00</td>
<td>0.00</td>
<td>0.030(1)</td>
<td>Li\textsubscript{0.92}/V\textsubscript{0.08}(8)</td>
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<tr>
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<td>6c</td>
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<td>0.00</td>
<td>0.2560(1)</td>
<td>0.032(1)</td>
<td>1</td>
</tr>
</tbody>
</table>

$a = 2.8438(4)$  $b = 2.8438(4)$  $c = 14.791(3)$  

Cell Volume = 103.59(3)

Space group: $R^3m$  $R_p$= 2.36\%  $R_{wp}$=2.98\%  $\chi^2$ = 1.023

Table 6.3.1 Refined parameters of Li\textsubscript{1.08}V\textsubscript{0.92}O\textsubscript{2} (nominally 5% excess lithium).

The material is analogous to the well known $\alpha$-NaFeO\textsubscript{2} structure, or the layered transition metal oxide cathode materials, primarily associated with LiCoO\textsubscript{2}\textsuperscript{5,24-27}. The structure is based around a scaffold of hexagonally close packed oxygen anions, with
layers of transition metal ions (in this case vanadium) occupying octahedral holes forming VO$_6$ octahedra, alternating with layers of octahedrally coordinated lithium ions forming a layer of LiO$_6$ with an ABC... structure. A schematic representation of the structure is shown in Figure 6.3.2. It is the tetrahedral sites in the LiO$_6$ ‘slabs’ that the lithium is expected to intercalate into.

![Schematic representation of the LiVO$_2$ structure: Purple polyhedra VO$_6$, Blue Spheres lithium, Red spheres oxygen.](image)

**Figure 6.3.2 Schematic representation of the LiVO$_2$ structure: Purple polyhedra VO$_6$, Blue Spheres lithium, Red spheres oxygen.**

It was found that the doped lithium could be modelled as lithium within the 3a vanadium site (displacing the vanadium). This was seen to cause a slight expansion along the $a$ (and $b$) axis and a contraction along the $c$ axis. It should be noted that replacement of lithium by vanadium in lithium 3b sites was also considered, but the refinement model suggested this was unlikely to have occurred in the materials).

With reference to the LiVO$_2$ structure displayed in Figure 6.3.1, the structural changes upon doping corresponds to the VO$_6$ slabs getting closer together via
contraction of the LiO$_6$ layers. This is due to the occupation of some of the octahedral vanadium sites with lithium. The 6 coordinate Li$^+$ ion has a radius of 90 pm while the V$^{3+}$ ion in octahedral coordination has a radius of 78pm, which causes an expansion of the V(Li)O$_6$ slab volume and consequently compressing the LiO$_6$ slab volume (the structure seemingly pinned by the electrostatic repulsion of the hexagonal oxygen lattices, allowing for the compression of the wider LiO$_6$ layer). This effect is slightly counter-balanced by the introduction of a small amount of the (smaller) V$^{4+}$ ions in the VO$_6$ layers, necessary to maintain charge balance due to the replacement of V$^{3+}$ with Li$^+$ in the VO$_6$ layer (the presence of V$^{4+}$ was confirmed with double titration oxidation sate analysis, mentioned in Figure 6.3.3, and subsequent computer modelling discussed later in this section).

The change in c axis and c/a axis ratio with lithium content is displayed in Figure 6.3.3 (2). It is clear that the nature of lithium doping mechanism and the effect this has upon the unit cell defies a simple explanation. The stoichiometry of lithium in the starting materials compared to the stoichiometry of the final material also bears closer inspection, seemingly increasing the amount of excess lithium during the reaction.
The refinements were repeated several times with separately prepared materials to confirm the accuracy of values (Subsequent joint x-ray and neutron refinement work by Dr Armstrong also showed good agreement with the un-doped and 5% excess lithium materials. The difference in the final stoichiometry of the 5% material ($\text{Li}_{1.07}\text{V}_{0.93}\text{O}_2$ by joint neutron/X-ray diffraction, compared to $\text{Li}_{1.08}\text{V}_{0.92}\text{O}_2$ from X-ray only) is within the error margin, see submitted paper in appendix vii).

The large contraction in the $c$ axis length with the replacement of ~ 8% lithium in the octahedral vanadium sites seems out of place with the trend of gradual reduction in $c$ axis length with increasing lithium/vanadium disorder (though not without some precedent\textsuperscript{28}). It would seem (as observed through the change in $c/a$ axis with composition) that the $a$ axis remains largely unperturbed by the inclusion of lithium into the vanadium layer.

Figure 6.3.3 (1) Lithium composition of doped material. (2) Variation in LiVO\(_2\) $a$ (□) and $c$ (○) unit cell axis with lithium content.
The complicated structural behaviour observed with doping may be a consequence of the intricate defect chemistry caused by the inter-play between $V^{3+}$, $Li^+$ and $V^{4+}$ ions in the vanadate layer. The exact conformation of $Li^+$ and $V^{4+}$ ions in a layer of $V^{3+}$ may change drastically with the introduction of a little extra lithium in the layer perhaps incurring a shift to a subtly different solid solution structure shifting the overall unit cell parameters with greater lithium.

It is also notable that Figure 6.3.3 (1) shows the lithium stoichiometry of the product increases over the synthesis compared to the reagents. It is common with solid state reactions containing lithium oxides to observe lithia loss over the course of the heating stage of the reaction because of the relatively high volatility of lithium oxides\textsuperscript{29-31} but it would appear (somewhat unusually) that the materials suffer from vanadium loss. The oxidation state of the vanadium was independently confirmed in the ~8% doped material by double titration giving a gross vanadium oxidation state of +3.18 (equivalent to 8.25% lithium doping). The difference between starting and refinement stoichiometry is probably based in the diminished accuracy of weighing the (moisture sensitive) starting materials in a controlled atmosphere. Since the oxidation state and refinement data are in agreement, it is more appropriate to use the refinement data to quote the stoichiometry.

The TEM image, shown in Figure 6.3.4., confirms that the classic solid state synthesis procedure produces uniform particles with particle sizes of 70-200 nm, suggesting that gross kinetic transport issues should not be a problem given the small size of the crystallites.
Figure 6.3.4 TEM image of as prepared $\text{Li}_{1.08}\text{V}_{0.92}\text{O}_2$. 
6.2.2. **Electrochemical Behaviour**

6.2.2.1. **Influence of Lithium Doping**

The electrochemical behaviour displayed a strong dependence upon the amount of doped lithium present in the material. Figure 6.3.5 shows the effect of doping upon the galvanostatic profile of some selected materials.

![Figure 6.3.5. Voltage change with lithium composition for selected doped Li$_{1-x}$V$_{1-x}$O$_2$ materials; A) Undoped LiVO$_2$ material, B) Li$_{1.08}$V$_{0.92}$O$_2$ C) Li$_{1.12}$V$_{0.88}$O$_2$. Inset: Incremental capacity plot for A) Undoped LiVO$_2$ material, B) Li$_{1.08}$V$_{0.92}$O$_2$ C) Li$_{1.12}$V$_{0.88}$O$_2$. - Electrolyte LP30, cycling rate 10 mA/g at a temperature of 30°C](image)

All materials display a shoulder at 0.8V, assumed to be part of the SEI formation procedure, given its existence has been observed with other (graphitic) anode systems$^{12}$, as expected this shoulder then disappears on subsequent cycles. The voltage composition plots show a heavy doping dependence, with the un-doped
material showing significantly poorer performance than the 8% and 12% doped materials (which display reasonably similar behaviour). The un-doped material has a particularly short 1st discharge plateau of 40 mAh/g near 0V. Although as the majority of this capacity is evolved in the near lithium plating region it is possible that the 40mAh/g is just a consequence of lithium deposition.

The doped materials show ~310 mAh/g and ~300 mAh/g discharge capacity for the 8% and 12% doped materials respectively. Figure 6.3.6 shows that the largest discharge (and charge) capacity from all the doped materials was achieved with the 8% material, which may be a consequence of the subtle structural differences between the doped materials seen in Figure 6.3.3.

![Graph showing discharge and charge capacities of doped Li\(_{1+x}\)V\(_{1-x}\)O\(_2\) materials.](image)

**Figure 6.3.6 First discharge and charge capacities of doped Li\(_{1+x}\)V\(_{1-x}\)O\(_2\) materials:** □ Discharge capacity, ○ Charge capacity - Electrolyte LP30, cycling rate 10 mA/g at a temperature of 50°C

Both the doped materials in Figure 6.3.5 evolved a second shoulder around 0.4V which is not present in the un-doped material. This suggests that the second shoulder could be a consequence of lithium activity at the anode (absent in the almost inert un-doped material), though it does not look like ‘classic’ intercalation behaviour (which
would be shown as a flat plateau for a two phase reaction or a constant gradient slope for a solid solution with lithium intercalation). It could be further SEI formation which has been suggested before with >1Li insertions in LiMO2 structures\textsuperscript{1,32,33} (incidentally the absence of peaks associated with the shoulder processes in the incremental capacity plots is due to the lack of constant rate of change of capacity with voltage hence not appearing as peaks in the dQ/dE plot). There is a possibility that this ‘shoulder’ region also represents structural changes occurring within the LiVO\textsubscript{2} material prior to a LiVO\textsubscript{2} to Li\textsubscript{2}VO\textsubscript{2} phase conversion associated with the plateau voltage region.

The flat voltage plateau suggests a two phase reaction and is reached after \textasciitilde70 mAh/g capacity has passed. From the incremental capacity plots it can be seen that the first discharge of the 8% doped material (and to a lesser extent the 12% doped material) consists of two electrochemical processes (one of which disappears on repeated cycling) indicated by the two peaks in the incremental capacity plot. The peak at 0.1V disappears after the first cycle as the peak at \textasciitilde0.05V dominates.

During the charging processes the incremental capacity plot there is only a slight difference in the peak voltages between doped materials (2.99V vs. 2.95V of 8% and 12% doping respectively) more indicative of a polarisation (ohmic drop) difference between the two materials, rather than two distinct electrochemical processes.
Chapter 6. LiVO\textsubscript{2} as a Lithium Intercalation Anode.

The ability of a small amount of lithium doping to ‘switch on’ the intercalation process bears closer inspection. It is unlikely that the doping alters the kinetic behaviour of the LiVO\textsubscript{2} materials, as highlighted in Figure 6.3.7, where there is little difference between the GITT (pseudo-equilibrium) profiles and the galvanostatic profiles (taken at 10mA/g) of the un-doped material and the 8% doped material.

When the material was cycled using a galvanostatic intermittent titration (GITT) regime the ‘equilibrium’ voltage/composition profile (ostensibly a galvanostatic profile at 0 mA) can be used to find the absolute voltage plateau.

![Figure 6.3.7 1st discharge Galvanostatic profiles of un-doped and 8% doped Li\textsubscript{1+x}V\textsubscript{1-y}O\textsubscript{2}: A) Un-doped LiVO\textsubscript{2} galvanostatic profile cycling rate; 10 mA/g, B) Un-doped LiVO\textsubscript{2} GITT, C) Li\textsubscript{1.08}V\textsubscript{0.92}O\textsubscript{2} Galvanostatic profile cycling rate 10 mA/g cycling rate, D) Li\textsubscript{1.08}V\textsubscript{0.92}O\textsubscript{2} GITT – electrolyte LP30, temperature 30°C](image)

As Figure 6.3.7 shows in the un-doped material both the GITT and galvanostatic profile have near identical total capacities suggesting that cycling at 10mA/g does not kinetically hinder the material. The 8% lithium doped material has a larger capacity.
when discharged under equilibrium type conditions, suggesting that there is a slight kinetic impediment to be considered when discharging the material, especially in the region above ~0.2V, which appears to be kinetically limited, producing more capacity with slower cycling. More importantly there is still a significant difference between the doped and un-doped material, even when transport effects are removed. The undoped material producing very little capacity until the voltage drops into the lithium plating region. This suggests that the difference between the doped and un-doped material is more intricate, perhaps relying on the subtle structural differences.

From the structural refinement it can be seen that there is no vanadium in the lithium layer in either of the doped and un-doped materials, removing the possibility of vanadium pinning, which may have inhibited shearing on any LiVO₂ to Li₂VO₂ phase conversion.

6.2.2.2. Computational studies

To explore the difference between doped (Li₁₀⁷V₀⁹³O₂) and un-doped (LiVO₂) materials atomistic modelling was undertaken, although this work was not directly undertaken by C. Lyness. It provides vital insight into the structural affects associated with doping the LiVO₂ structure with excess lithium and so, it is beneficial to discuss the work here. The work was carried out, in collaboration with Professor Peter Bruce and Dr. Rob Armstrong, by Dr. Pooja Panchmatia and Professor M. Saiful Islam of the University of Bath (further technical details can be found in the paper attached in the appendix vii).
Chapter 6. LiVO₂ as a Lithium Intercalation Anode.

Atomistic modelling has a history of providing useful insights into defect chemistry\(^{34-37}\) and so was an obvious choice to investigate the LiVO₂ materials, providing a perspective which would be hard to obtain from X-ray (or neutron) refinement alone. LiVO₂, Li\(_{1.07}\text{V}_{0.93}\)O₂ (stoichiometry as per the joint refinement) and Li\(_2\)VO₂ were all successfully modelled in good agreement with the joint x-ray and neutron diffraction refinements undertaken by Dr Armstrong (and data presented in this chapter). It was found that a significant 3eV energy penalty existed for introduction of vanadium into a 3b lithium site further confirming the absence of vanadium pinning in any of the materials. As expected from the double titration information and structural refinements, introducing Li\(^+\) ions into the V\(^{3+}\) layer was found to cause charge compensation in the surrounding vanadium sites forcing some local vanadium to a V\(^{4+}\) oxidation state. The computer model found that, out of the various conformations considered, the most likely (i.e. most stable) vanadium/lithium ion conformation was two V\(^{4+}\) ions edge sharing with the octahedral lithium ion. The free energy of the trimer was suitably lower than isolated defects (though, due to similar energies, the exact conformation of the trimer structure (out of a choice of three) was hard to deduce.

The possibility of larger agglomerations of trimer clusters was also investigated. It was discovered that even the lowest energy cluster (a dodecamer) had a significantly higher energy (by 0.35eV) than the isolated trimer cluster environment, suggesting a prevalence of the trimer conformation throughout the structure.

The nature of the doping effect on lithium intercalation was also investigated. As there are no empty octahedral sites in the \(\bar{R}3m\) structure, the intercalating lithium is

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expected to insert into a tetrahedral site in the lithium layer. An issue with this insertion mechanism was found when the inserted \( Li^+ \) has to face share with an octahedral \( V^{3+} \) (inevitable in the \( LiVO_2 \) material, while in \( Li_{1.07}V_{0.83}O_2 \) there is the possibility of face sharing with a doped octahedral \( Li^+ \) site). It was discovered that the energetic cost of inserting lithium into a tetrahedral site in the alkali layer is 0.62 eV higher if that site face shares with a \( V^{3+} \) ion, compared to a \( Li^+ \) ion from the vanadate layer, showing obvious favour to the doped material which has contains lithium in the 3a vanadium site.

Due to lack of \( Li^+ \) face sharing in the un-doped material, it was determined that un-doped \( LiVO_2 \) would require a voltage of 2.98 V to insert lithium into the alkali tetrahedral site, far below the voltage at which lithium would start plating (0V) and consequently occlude any further reactions. In contrast, \( Li_{1.07}V_{0.93}O_2 \) was found to intercalate lithium into its alkali tetrahedral sites at 0.58V, a voltage that may explain some of the extended voltage shoulders prior to the plateau seen in the galvanostatic profiles (Figure 6.3.5). This suggests that prior to any phase conversion, some lithium intercalation into the tetrahedral sites may be necessary.

Further computational work showed that the lithium inserted into tetrahedral sites in the alkali layer causes large lattice distortions. This was due to the inserted lithium ion being displaced slightly towards the octahedral \( Li^+ \) face and the resulting \( Li^+-Li^+ \) repulsion distorting the octahedral lithium ion causing it to maintain three short Li-O bonds (1.91 Å) and 3 long Li-O bonds (2.45 Å) compared to the ubiquitous Li-O bond length (1.99 Å) prior to tetrahedral lithium insertion. The effects of this distortion are felt throughout the local lattice causing the anionic sub-lattice to distort.
(the O-O bond length altering form 2.93 Å to 3.0 Å). These changes could possibly herald the onset of shearing, required if the LiVO$_2$ $R\overline{3}m$ structure was to undergo phase change to the Li$_2$VO$_2$ $P\overline{3}m1$ material.

It is thought that the four Li$^+$ face sharing environment of the inserted Li$^+$ ion (three in the alkali layer, one from doped lithium in the vanadate layer) is enough to trigger a shearing event (primarily caused by Li$^+$-Li$^+$ repulsion). The new Li$_2$VO$_2$ structure can then adopt all the lithium from the alkali layer in the original LiVO$_2$ material, and allow one new lithium to be inserted into the empty tetrahedral site now present within the Li$_2$VO$_2$ material, allowing for Li$_2$VO$_2$ stoichiometry to be adopted.

The new structure is stabilised by the absence of face sharing, with all the tetrahedral sites filled and all octahedral sites empty within the alkali layer. DFT calculations give the phase conversion reaction a voltage of +0.23V, a difference of ~0.1V with the experimentally observed voltage plateau, an incongruity expected from previous DFT work$^{37-39}$ and allowing for the possible need for a slight over-potential for the kinetically inhibited LiVO$_2$ material.
6.2.2.3. The Discharge Process

To further investigate the nature of the over-lithiated phase of LiVO$_2$, X-ray diffraction patterns were collected of the material at different stages of discharge (shown in Figure 6.3.8). There is a clear phase transition from the previously identified LiVO$_2$ phase to what has been ascribed the Li$_2$VO$_2$ phase refined using a Li$_2$MnO$_2$ model$^{40}$ with the space group $P\bar{3}m1$. The refinement of the material after 115mAh/g is given in Figure 6.3.9 as an example, with the associated Li$_2$VO$_2$ refinement parameters displayed in Table 6.3.2.

![X-ray diffraction patterns](image)

**Figure 6.3.8** Selected regions of X-ray diffraction patterns taken at different lithium compositions during cycling: P1 and P2 are selected peaks of Phase 1 (LiVO$_2$) and Phase 2 (Li$_2$VO$_2$) respectively.
The 30-50 2Θ regions displayed in the insets in Figure 6.3.8 show that there is no detectable new phase growth during the ‘SEI’ stage of the cycle (i.e. no ‘P2’ peaks up to 70mAh/g). As the discharge plateau proceeds, the presence of the Li$_2$VO$_2$ phase becomes apparent (observed as minor peaks at 38 and 47 degrees in Figure 6.3.9). This phase comes to dominate by the end of the discharge plateau.

The Li$_2$VO$_2$ phase is made up of hexagonally close-packed oxygen scaffold with layers of lithium ions occupying all tetrahedral sites, alternating with layers of vanadium situated in the ocatahedral sites (a schematic is displayed in Figure 6.3.9). This structure is isostructural with previously documented materials such as Li$_2$NiO$_2$,$^{41}$ Li$_2$MnO$_2$,$^{42,43}$ and Li$_2$Mn$_{0.5}$Ni$_{0.5}$O$_2$.{$^2$}

Figure 6.3.9. X-ray diffraction pattern and Rietveld refinement parameters for Li$_{1.08}$V$_{0.92}$O$_2$ at 115mAh/g (~0.3Li) discharge capacity, $R_{wp}=4.34$: A) LiVO$_2$ phase peak positions, B) Li$_2$VO$_2$ phase peak position. Inset: schematic representation of Li$_2$VO$_2$ structure along the $a$ direction.
Within the partially cycled material it became particularly hard to (reliably) identify the amount of mixing between the metals in the vanadium/lithium sites (i.e. manually altering the fractional occupancies of the 2d and 1a site did not significantly alter the quality of the fit). This was due in part to the poor quality of the recovered materials (and X-ray diffraction patterns) and not helped by lithium’s small X-ray scattering cross-section.

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<th>y/b</th>
<th>z/c</th>
<th>B_{iso}</th>
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\[ a = 3.0998(3) \quad b = 3.0998(3) \quad c = 5.2207(8) \quad \text{Cell Volume} = 43.351(8) \]

Space group: \( P\bar{3}m1 \)

\[ R_p = 3.24\% \quad R_{wp} = 4.34\% \quad \chi^2 = 1.621 \]

* Values produced from two phase refinement from material recovered at 115mAh/g

Table 6.3.3. Refinement parameters of (nominally) Li\(_2\)VO\(_2\) derived from X-ray diffraction of Li\(_{1.08}\)V\(_{0.92}\)O\(_2\) materials after 115mAh/g of discharge.

In subsequent work utilising neutron diffraction (see appendix vii) the presence of the Li\(_2\)VO\(_2\) phase was further confirmed throughout the cycle. Table 6.3.3 displays some refined parameters of the recovered material collected at different points during discharge. It becomes clear that the processes occurring during cycling are considerably more complicated than the simplistic picture painted by the electrochemical plateau.

Throughout discharge the LiVO\(_2\) unit cell is seen to expand slightly, this can be understood by the reduction of the small amounts of V\(^{4+}\) in the structure (thought to be present to balance the replacement of some V\(^{3+}\) with Li\(^+\)). The reduction to V\(^{3+}\) is expected to be accompanied by an increase in the V-O bond lengths, due to the
differing charge densities of $V^{4+}$ and $V^{3+}$ ions. There is also a possibility that the insertion of Li$^+$ ions into the tetrahedral sites in the LiO$_6$ layer causes lattice expansion prior to a shearing event. The relationship between the relative phase ratio is harder to understand and suggests that more than one electrochemical process may occur during the plateau region possibly due to the onset of lithium plating near the Li/Li$^+$ equilibrium voltage.

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<th>$b$</th>
<th>$c$</th>
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<th>Phase Ratio</th>
<th>$R_{wp}$ (joint)</th>
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<td></td>
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<td>2.845(2)</td>
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<td>103.59(2)</td>
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<td>3.35%</td>
</tr>
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<td>X</td>
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<td>43.66(6)</td>
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Table 6.3.3 Selected Refinement parameters from the X-ray diffraction patterns taken at different points during discharge of Li$_{1.08}$V$_{0.92}$O$_2$.  

175
The Li$_2$VO$_2$ phase appears to undergo little change in the unit cell parameters during discharge and it is mainly due to the ratio relationship between the two phases that the discharge picture becomes more complicated. It would seem that the majority of the LiVO$_2$ to Li$_2$VO$_2$ phase transformation occurs during the first half of the plateau (primarily between the 45-90 mAh/g region). After 90mAh/g of ‘plateau’ capacity has passed, little more phase transformations occurs, with the majority of the material consisting of Li$_2$VO$_2$ after 205mAh/g (135mAh/g of plateau capacity).

This raises the question of what other reduction process is producing the subsequent capacity and more importantly why does the LiVO$_2$ stop converting to Li$_2$VO$_2$. The amount of capacity passed during the ‘phase change’ section of the plateau is similar to the reversible capacity seen in subsequent cycles (Figure 6.3.13) suggesting that the excess capacity (i.e. the capacity produced after Li$_2$VO$_2$ was the large majority phase) is due to an irreversible process occurring after the formation of Li$_2$VO$_2$ in the first discharge (this may explain the two electrochemical processes seen on discharge in the incremental capacity plot in Figure 6.3.5).

To better understand the results of the first discharge structural study further electrochemical analysis was undertaken. Figure 6.3.10 displays the first discharge of Li$_{1.08}$V$_{0.92}$O$_2$ under multiple cycling rate regimes, from this information can be derived about the transport properties of the Li$_{1.08}$V$_{0.92}$O$_2$ material.
Figure 6.3.10 First discharge voltage vs. composition profiles of Li$_{1.08+x}$V$_{0.92}$O$_2$ at different rates: A) 200 mA/g, B) 125 mA/g, C) 75 mA/g, D) 30 mA/g, E) 20 mA/g, F) 10 mA/g, G) 5 mA/g, H) 0 mA (equilibrium GITT measurement). Inset: Plateau capacity vs. rate – Electrolyte LP30 at a temperature 30°C.

The slow decrease in plateau voltage with cycling rate is indicative of an ‘over-potential’ effect, seen in the faster rate regimes because of the increase in polarisation resistance effects (amongst others) upon lithium insertion voltage. The reduction in capacity with rate is due to the inability to completely insert lithium at the faster rate before the voltage cut off. Both the SEI layer formation at ~0.8V and the subsequent shoulder process at ~0.5V are rate dependent (reducing in capacity with faster rate). The ratio of capacity produced by ‘shoulder’ processes to plateau capacity does alter with different cycling rate suggesting that the two have different rate dependencies, and thus are linked to different electrochemical processes. As the
insert shows in Figure 6.3.10, the plateau capacity slowly decreases with rate in a roughly exponential manner.

Combining the information of the different cycling rates we can gain further insight into the processes occurring as the Li$_{1.08}$V$_{0.92}$O$_2$ material undergoes discharge. The polarisation resistance at different lithium compositions can be determined by the ohmic drop at a certain lithium composition$^{44}$. This is found by (at a given Li$^+$ composition) plotting the voltage of the system at different current rates and finding the gradient (i.e. finding $V/I = R$ at different lithium compositions by measuring the voltage response at different current rates). The results are shown in Figure 6.3.11

![Figure 6.3.11 Polarisation resistance at different lithium compositions for Li$_{1.08}$V$_{0.92}$O$_2$](image)

Whenever there is a pronounced change in polarisation, it can be assumed that this is instigated by either a dominating side-reaction or a new structural process. It would seem that there are 4 distinct processes at the start of the doped LiVO$_2$ discharge; these match up closely with the different processes observed with the
galvanostatic profile. Stages I to III all start as more insulating their resistances then drop. As Stage I and II have been ascribed to SEI formation previously in the literature\textsuperscript{12} it might be assumed that stage III, also follows similar resistance behaviour, is part of an SEI formation (or some sort of amorphous electrode/electrolyte surface layer formation). However the computer modelling, discussed previously, would suggest that this region may also account for lithium insertion into empty tetrahedral sites in the alkali layer, prior to possible phase conversion of LiVO\textsubscript{2} to Li\textsubscript{2}VO\textsubscript{2} material. The decreasing polarisation resistance may be due to the structure becoming more ‘open’ prior to shearing, with it reaching a critical concentration of tetrahedrally intercalated lithium at around 0.2V when it is easiest to insert Li\textsuperscript{+} into the tetrahedral site (hence lowest resistance) and when it begins to shear (hence proceeding voltage plateau). This ties in well with the expanded structure seen in the unit cell volume increase in the \textit{ex situ} refinement of the LiVO\textsubscript{2} material at 70mAh/g.

Phase IV displays different polarisation resistance behaviour, initially with a low polarisation resistance (0.7Ω/g) and then slowly increasing as the plateau lengthens. This is behaviour that would be expected during lithium intercalation, with the relative resistance increasing as the LiVO\textsubscript{2} material is over-lithiated and the structure undergoes significant changes to convert to Li\textsubscript{2}VO\textsubscript{2}. Both the break-up of contiguous LiVO\textsubscript{2} domains and the gradual filling of the empty tetrahedral sites in the Li\textsubscript{2}VO\textsubscript{2} structure may be expected to increase the resistance of the material.
Investigating the AC impedance in situ provides a different perspective on the cycling behaviour. Figure 6.3.12(1) displays the AC impedance of the battery system as a whole and how this changes with lithium composition.

The AC modelling of the complete battery system is inherently more complicated than for an individual material, factors such as the system resistance (comprising of the ohmic resistance of the electrolyte, leads, current collectors, various electric fields etc.) as well as the surface film resistance, SEI layer resistance and the charge transfer resistance must be taken into account along with the effects of semi-infinite diffusion of the lithium ions and various double layer capacitances.

While several models have been proposed for two electrode battery systems\textsuperscript{14,45-48} it is generally accepted that the high frequency intercept is given over to the ohmic resistance (including leads and other system resistance), the high frequency semi-circle (labelled A in Figure 6.3.12) is a consequence of the surface film resistance $R_f$ and the low frequency semi-circle (labelled B) is due to the charge transfer resistance $R_{ct}$ associated with the solid/electrolyte interface and hence represents the electrochemical behaviour of the system. The low frequency ‘tail’ is thought to be from the semi-infinite diffusion (Warburg) of lithium ions in bulk processes. The values for $R_{ct}$ match up well with previously reported charge transfer resistances, for example LiMn$_{0.5}$Ni$_{0.5}$O$_2$\textsuperscript{49}
Chapter 6. LiVO$_2$ as a Lithium Intercalation Anode.

Figure 6.3.12 (1) Nyquist plots of AC impedance spectrum of a 2 electrode Li$_{1.08+x}$V$_{0.92}$O$_2$ | Lithium battery system taken at different states of discharge. (2) Various resistance parameters obtained from the Impedance spectrums at different states of charge. Inset: close up of 90-325 mAh/g region for $R_{ct}$ – Electrolyte LP30, cycling rate 10mA/g at a temperature of 30°C

The in situ impedance lines up well with the previously discussed data in both Figure 6.3.11 (ex situ X-ray diffraction data) and Figure 6.3.8 (polarisation resistance) comprising of three fairly well defined regions. With reference to Figure 6.3.12(2) we can see that the charge transfer resistance ($R_{ct}$) undergoes large changes from the 0-100 mAh/g region starting at almost 180 Ω and eventually dropping to ~70Ω with the onset of the plateau region and lithium intercalation at around 70 mAh/g.

This 0-70 mAh/g region consists of SEI formation and the large fluctuations in $R_{ct}$ is commensurate with the observations from the polarisation resistance in Figure 6.3.11 which suggest that there is more than one type of SEI formation. The presence of a third definable semicircle between the ‘high’ and low’ frequency semi-circles is also noted. This exists up until around 70mAh/g and has a resistance value in between
R_f and R_{ct}. It could represent the presence of an insulating layer upon the active material which disappears with the onset of lithium intercalation.

The region from 70 mAh/g up to ~175mAh/g presents relatively little change in the charge transfer resistance, from the x-ray diffraction, this region is associated with the single electrochemical process of LiVO_2 to Li_2VO_2 conversion and is expected to be a monotonic charge transfer process.

After ~200mAh/g the charge transfer resistance begins to alter, settling at the higher resistance of ~70 Ω, indicative of a different process compared to the 70-175mAh/g region. During this process the R_{ct} is relatively unchanging perhaps suggesting that the capacity of this region is generated by a single process. While the charge-transfer resistance only confirms the presence of different process during discharge, it correlates well to the previously observed regions through polarisation resistance and X-ray diffraction, though it does not directly show what causes the change in R_{ct}.

A self-consistent picture begins to emerge between the galvanostatic, X-ray diffraction and AC impedance information. There are 3 distinct stages occurring through discharge. Initially, what is believed to be SEI formation occurs with little change to the LiVO_2 material except with a slight expansion. This is possibly a consequence of intercalation of Li^+ into the tetrahedral sites in the alkali layers of LiVO_2. This stage is followed by the onset of full lithium intercalation causing LiVO_2 to Li_2VO_2 phase transformations. Finally the LiVO_2 phase transformation slows, to be replaced by a process which does not produce any crystalline products.
While not explicitly showing the processes occurring during LiVO$_2$ discharge, both the \textit{in situ} AC impedance and polarisation resistance are consistent with the \textit{ex situ} diffraction data (and to a certain extent, the computer modelling). All techniques point to a complicated first discharge process, this does not bode well for the long term cycling of LiVO$_2$ material with the intercalation seemingly dependent on multiple inter-connected processes.

As Figure 6.3.13 shows, the capacity retention over even a short number of cycles is poor with the discharge capacity diminishing by almost 70% over 10 cycles (though this value is closer to 50% when you consider just the ‘reversible’ capacity from the plateau of the first discharge). The charging capacity fares a little better losing ~55% of the capacity after ten cycles (due to the lack of irreversible capacity on the first charge). It would seem that the lithium intercalation process is fairly efficient, with similar amounts of lithium being removed as charge is inserted in the previous discharge cycle. The slow reduction in capacities seen in Figure 6.3.13 (2) is monotonic and shows no signs of stabilising after the ten cycles.

It was not clear whether the poor capacity retention is a consequence of side reactions (although any side reactions are probably not electrolyte specific, given that the capacity decline was observed with other electrolytes, see appendix vi). Since altering electrochemical factors made little difference, the poor performance could be rooted in a physical process such as dissolution of the electrode.
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Figure 6.3.13. (1) Selected cycles of Voltage vs. composition plots of Li$_{1.08+x}$V$_{0.92}$O$_2$: A) 1$^{st}$ cycle, B) 2$^{nd}$ cycle, C) 5$^{th}$ Cycle, D) 10$^{th}$ cycle. (2) Capacity vs. cycle number for Li$_{1.08}$V$_{0.92}$O$_2$ material. - Electrolyte LP30, cycling rate 10mA/g at a temperature 30$^\circ$C.

The stoichiometry of the Li$_2$VO$_2$ phase (i.e. lack of lithium/vanadium site mixing) may explain the poor capacity retention over repeated cycles. While it is apparent from the atomistic modelling that a small amount of doping is crucial for LiVO$_2$ to Li$_2$VO$_2$ phase conversion the same may not be true for the reverse process; the nature of the LiVO$_2$ material created from de-lithiation of Li$_2$VO$_2$ is of crucial importance. Due to the large structural rearrangement occurring when LiVO$_2$ shears to Li$_2$VO$_2$ it would appear that the doping in the vanadate layer is not retained (at least it is not obvious from the refinement of the recovered material). It is likely that this ‘un-doped’ stoichiometry is maintained when Li$_2$VO$_2$ undergoes phase conversion to LiVO$_2$, which as the modelling suggests would seriously hamper subsequent intercalation of Li$^+$ into the LiVO$_2$ material and may be the cause of the poor capacity retention seen in Figure 6.3.13.
6.3. Conclusions and Further Work

Various doped LiVO$_2$ materials were produced using a solid state synthesis. Subsequent structural characterisation revealed a complicated relationship between the unit cell dimensions and the amount of lithium doping. The electrochemical behaviour of the LiVO$_2$ material was found to be closely linked with the amount of doped lithium present with the 8% excess lithium residing in the vanadium layer giving the highest first discharge capacity.

A self consistent picture emerged of the electrochemical processes occurring within the doped LiVO$_2$ material under galvanostatic cycling. It was ascertained from various observations that from 0-70mAh/g there is a region of sloping voltage shoulders as more charge is inserted into the electrode. There is a gradual reduction in charge transfer resistance and no detectable change in the x-ray diffraction patterns during this stage. In conjunction with previous studies this suggests the growth of various amorphous SEI layers.

After ~70mAh/g there is a period marked by a flat galvanostatic voltage plateau and a gradual increase in polarisation resistance. There is observed growth, and subsequent domination, of a second phase in the X-ray diffraction patterns that can be refined using a $P\bar{3}m1$ Li$_2$VO$_2$ model. This region is marked with little change in the charge transfer resistance and thus is ascribed to LiVO$_2$ to Li$_2$VO$_2$ transformation. This lasts until ~180mAh/g of charge has been inserted after which, although little change is seen in the galvanostatic plateau voltage, no new Li$_2$VO$_2$ growth (or other phase) is seen in the X-ray diffraction pattern. The charge transfer resistance is seen to increase
from the previous region to stabilise at around 70 Ω which suggests some subtle change has occurred in the electrochemical behaviour. The resilience of the voltage plateau despite the lack of new Li$_2$VO$_2$ growth in the diffraction patterns suggest that some lithium insertion (i.e. triggering the $V^{3+/2+}$ redox couple) is occurring but no crystalline phases are being produced, or the voltage is close enough to the lithium Li$^+$/Li equilibrium voltage to start depositing lithium metal.

While this work has explored the nature of the electrochemical processes occurring within the LiVO$_2$ system, further characterisation is needed to fully understand the complicated anodic nature of LiVO$_2$. Further *in situ* studies perhaps utilising IR, Raman and NMR techniques may help to investigate the nature of the SEI layer formation (or lithium intercalation) and the subsequent drop off in LiVO$_2$ to Li$_2$VO$_2$ phase conversion. A more in depth *ex situ* analysis of the structures of LiVO$_2$ and Li$_2$VO$_2$ on repeated cycling would help to establish if the doping of the 3a octahedral vanadate site is carried through on phase conversion. Establishing the full nature of the first discharge process may go some way into determining methods to increase the cyclability of the material and would be an important step into establishing LiVO$_2$ as a viable anode.
6.4. References

Chapter 7. Preliminary Investigation into Layered Transition Metal Oxide Anodes
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7.1. Introduction

Several transition metal oxide (LiMO₂) systems were investigated for their ability to convert to layered Li₂MO₂ materials upon over-lithiation (> 1Li⁺ per unit cell). A preliminary investigation concerning the structural nature of the LiCoO₂, LiMn₀.₅Ni₀.₅O₂ and LiNi₀.₃₃Co₀.₆₆O₂ systems during electrochemical discharge was undertaken.

Layered oxide anodes remain an undeveloped area of research; although there has been some work (mainly by Thackeray et al.) little is understood about which systems can successfully undergo addition of lithium at low voltages. It is thought that layered LiMO₂ (where M= Co, Ni, Mn, V, Ni₀.₅Mn₀.₅...) type materials can undergo several types of reaction with >1Li⁺ intercalation. Three of the best understood reactions are:

**Equation 1** \( \text{LiMO}_2 + \text{Li} \rightarrow \text{Li}_2\text{MO}_2 \) addition reaction

**Equation 2** \( \text{LiMO}_2 + \text{Li} \rightarrow \text{Li}_2\text{O} + \text{MO} \) decomposition reaction

**Equation 3** \( \text{LiMO}_2 + 3\text{Li} \rightarrow \text{M} + 2\text{Li}_2\text{O} \) displacement reaction

Reaction (1) has been observed in the LiVO₂ system (as discussed in the previous chapter), as well as, tentatively, for the LiNi₀.₅Mn₀.₅O₂ system¹ which has been the focus of several articles by Thackeray et al.¹⁻⁵. Other materials known to form Li₂MO₂ phases (albeit through chemical rather than electrochemical methods) include Li₂MnO₂⁶ (which adopts a similar hexagonal structure to Li₂VO₂ and Li₂Mn₀.₅No₀.₅O₂) and Li₂NiO₂⁷,⁸ (which forms both rhombohedral and orthorhombic structures) and Li₂CuO₂ which is known to adopt an orthorhombic structure⁹,¹⁰.
The electrochemical addition reaction is advantageous because it involves a ‘simple’ phase conversion rather than a separate electrochemical process which may incur a variety of products and a large thermodynamic (i.e. voltage) difference between the discharging and charging reaction. The conversion of LiMO$_2$ materials to $P\bar{3}m1$ type Li$_2$MO$_2$ materials (i.e. not destroying the rhombohedral symmetry) is an attractive solution to anode design as it would promote higher capacity and longevity given the, presumably, lower energy cost of the phase change process compared to decomposition or displacement type reactions.

Decomposition and displacement reactions represent other types of processes occurring upon $>1$Li$^+$ being adding to the system. In the case of equation 2 the ternary oxide decomposes to the monoxide (or potentially, a higher $M_xO_y$ oxide) and lithium peroxide (Li$_2$O). In equation 3 the metal is displaced to its elemental form by extrusion from the LiMO$_2$ structure upon excess lithium insertion. There is a strong possibility that both equations 2 and 3 could happen simultaneously or sequentially leading to multiple products (such as metal monoxide (MO) from equation 2 displacing to give the metal and lithium peroxide (a reaction that has been further investigated for its anodic properties$^{11,12}$). It is thought that this may explain the behaviour of LiCoO$_2$$^{13}$.

Thackeray et al suggest that it is the balance struck between thermodynamic and kinetic factors of the over-lithiation reaction which determine the reaction pathway$^5$. The work concluded that the explanation is inherently complex and various physical and structural factors can influence the type of reaction pathway when the system is over-lithiated.
7.2. Results and Discussion

All materials were initially cycled from 3.0V to establish the presence of any plateaus and determine the most appropriate cycling regime.

7.2.1. LiMO$_2$

Several systems were assessed for possible addition type behaviour (eq. 1) a selection of their voltage composition profiles are displayed in Figure 6.3.1.

![Graph showing voltage vs. lithium composition for selected layered transition metal compounds](image)

**Figure 7.3.1.** 1st and 2nd cycles of voltage vs. lithium composition for selected layered transition metal compounds – Electrolyte LP30, cycling rate 10mA/g at a temperature 30°C  A)LiMn$_{0.5}$Co$_{0.5}$O$_2$, B)LiMnO$_2$, C)LiMn$_{0.33}$Co$_{0.33}$O$_2$

As can be seen from the galvanostatic profiles in Figure 6.3.1. the layered transition metal oxides display a wide variety of behaviour upon over-lithiation. The different voltages of the first discharge plateaux of the three materials indicate either differing redox couples or discrete thermodynamic processes which occur at different
voltage. It would seem that, given the similar plateau voltages, both the LiMn$_{0.33}$Ni$_{0.33}$Co$_{0.33}$O$_2$ and LiMn$_{0.5}$Co$_{0.5}$O$_2$ materials utilise the same process (at least on the first discharge). The previously reported ability of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ to undergo addition of lithium using the Mn ion$^5$ would suggest that perhaps the manganese ion is the redox active component of the Ni/Mn system. Indeed Thackeray has proved, theoretically, that LiMn$_{0.5}$Co$_{0.5}$O$_2$ would contain a tetravalent Mn ion$^5$ (this is especially pertinent as the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ to Li$_2$Mn$_{0.5}$Ni$_{0.5}$O$_2$ transition is thought to occur at a similar voltage to the LiMn$_{0.5}$Co$_{0.5}$O$_2$ plateau). Though without further experimental proof of the oxidation states of the transition metal ions it is difficult to ascertain which ions are likely to undergo reduction. The nearly symmetric charge and second discharge profile of the LiMn$_{0.5}$Co$_{0.5}$O$_2$ material suggests a reversible reaction, hinting at a possible LiMn$_{0.5}$Co$_{0.5}$O$_2$ to Li$_2$Mn$_{0.5}$Co$_{0.5}$O$_2$ phase change.

The LiMn$_{0.33}$Ni$_{0.33}$Co$_{0.33}$O$_2$ displays an initial (and 2$^{nd}$) discharge capacity ($\sim$750 mAh/g), far in excess of the theoretical capacity for a lithium addition reaction ($\sim$280 mAh/g). The lack of symmetrical charge and discharge profile suggests the plateau reaction is not reversible. Perhaps the Mn is reduced upon discharge, as has been observed in other binary metal systems (hence the similar plateau voltage to LiMn$_{0.5}$Co$_{0.5}$O$_2$) on charge another process likely occurs.

The layered LiMnO$_2$ material shows an entirely different first discharge plateau at $\sim$0.4V, indicative of a distinct process. Given the large difference between initial discharge capacity and subsequent charge and 2$^{nd}$ discharge capacities it is unlikely that LiMnO$_2$ undergoes a simple addition type reaction to produce Li$_2$MnO$_2$. This hints at the complicated nature of how the addition/decomposition/displacement reactions
are determined, as $\text{Li}_2\text{MnO}_2$ is a known, thermodynamically stable, material\textsuperscript{14} which would suggest that, thermodynamically at least, a reversible LiMnO$_2$ to $\text{Li}_2\text{MnO}_2$ transition should be possible.

LiCoO$_2$ and solid solutions of LiMn$_x$Ni$_{1-x}$O$_2$ and LiNi$_x$Co$_{1-x}$O$_2$ were also investigated and these are explored in further depth, as these materials displayed behaviour exemplifying either addition type reactions or displacement/decomposition reactions.
7.2.2. LiCoO\textsubscript{2}

Figure 6.3.2 shows the galvanostatic profile of LiCoO\textsubscript{2} when cycled from 3V-1.1V. Previously it has been suggested that LiCoO\textsubscript{2} cannot undergo an addition type reaction\textsuperscript{5} and when cycled it is clear that the first discharge far exceeds the theoretical capacity (~274mAh/g) for an addition type reaction (as do subsequent discharge plateaus).

![Figure 7.3.2. 1st and 2nd cycle of LiCoO\textsubscript{2} Voltage vs. Lithium composition profile - Inset: Incremental capacity plot of 1\textsuperscript{st} and 2\textsuperscript{nd} cycle of LiCoO\textsubscript{2} - Electrolyte LP30, cycling rate 10 mA/g at a temperature 30°C.](image)

The near flat voltage plateau at 1.24V suggests a monotonic reaction (without any of the SEI formation seen in the LiVO\textsubscript{2} system), which undergoes a large hysteresis of approximately 1 V upon charging. From the incremental capacity plot in the inset it can be seen that there is a large difference between the discharge and charging peaks. The discharge is characterised by a single large peak which shifts to a lower voltage on further cycles. This would tend to suggest that simple sequential reactions (i.e. a combination of eq. 2 and 3) are not occurring, as these would be expected to produce different voltage plateaus during discharge. Although the discharge appears to be a
single process, the charging process indicates multiple reaction types at different voltages which may reflect the discharge products reacting on lithium removal to form multiple products. The subsequent second discharge cycle has three identifiable processes, the first two occurring in the region at ~1.5V, and may represent reactions between the some of the products from the charging reaction and lithium (or indeed a sequential type displacement/decomposition reaction). The third discharge peak process represents the galvanostatic voltage plateau and occurs at a slightly reduced voltage compared to first discharge plateau which may be indicative of a simple over-potential (IR drop) or may hint at a distinctly new process.

From the ex situ diffraction patterns in Figure 6.3.3 It can be seen that the LiCoO₂ does not undergo a ‘classic’ phase change on over-lithiation. After 100mAh/g capacity has passed there is very little change to the diffraction pattern, indeed it is only at the end of discharge that a noticeable change is observed with the introduction of the Li₂O phase. The Li₂O material is thought to be produced through both dissociation and displacement reactions (eq. 2 and 3). The lack of any CoO or Co metal products in the X-ray diffraction pattern is likely due to the nanoscopic and/or amorphous nature of the extruded products⁴,¹⁵ which makes them weak coherent scatterers of X-rays.

Without any other obvious crystalline cobalt products in the fully discharged X-ray diffraction pattern it is hard to say whether a dissociation or displacement reaction dominates when over-lithiating of LiCoO₂ and further work using small-angle or non-diffraction based techniques is needed to further elucidate the nature of the ~1V discharge reaction. What is clear is that no LiCoO₂ to Li₂CoO₃ phase conversion occurs.
Figure 7.3.3. X-ray diffraction patterns and Rietveld refinement of LiCoO$_2$ material through discharge to 1.1V: A) Pristine LiCoO$_2$ material, B) LiCoO$_2$ after 100 mAh/g capacity, C) LiCoO$_2$ discharged to 1.1V.

Although not a candidate for a layered oxide ‘addition’ anode, the LiCoO$_2$ system should not be neglected, as it may offer valuable insight into the mechanisms which favour displacement/ dissociation over addition type reactions.
7.2.3. LiMn$_{0.5}$Ni$_{0.5}$O$_2$

An ‘addition’ type phase transformation is expected for LiMn$_{0.5}$Ni$_{0.5}$O$_2$ after the presence of Li$_2$Mn$_{0.5}$Ni$_{0.5}$O$_2$ was experimentally confirmed by Thackeray et al$^3$. The galvanostatic profile is displayed in Figure 6.3.4.

![Graph](image)

Figure 7.3.4. 1$^{st}$ and 2$^{nd}$ cycle of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ Voltage vs. Lithium composition profile - Inset: Incremental capacity plot of 1$^{st}$ and 2$^{nd}$ cycle of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ – Electrolyte LP30, cycle rate 10mA/g at a temperature of 30$^\circ$C

This profile is markedly different from LiCoO$_2$ material, with the first and second discharge voltage plateaus showing gently sloping behaviour at similar voltages (~1V) with no obvious discharge peak shift seen between the first and second cycles (seen in the incremental capacity plot). In many ways the first discharge profile of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ is similar to the LiVO$_2$ material discussed in the previous chapter. It has multiple voltage ‘shoulders’ before reaching the voltage plateau (presumably due to a similar process that occurs within the LiVO$_2$ system). There is also a large irreversible capacity on the first discharge, with the second discharge only having a capacity of ~150 mAh/g (0.5Li). The LiMn$_{0.5}$Ni$_{0.5}$O$_2$ system deviates from the LiVO$_2$ archetype on
charging, where (from the incremental capacity plot in Figure 6.3.4) it can be seen that there are clearly two processes occurring. It appears that the approximate capacities (derived from area under the peak) for each peak are similar (~60mAh/g for the peak at 1.6V and ~80mAh/g for the peak at 1.9V). The reason for the two peaks may be down to the more intricate redox chemistry present in the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ system.

LiMn$_{0.5}$Ni$_{0.5}$O$_2$ represents a slightly more complicated electrochemical system than LiCoO$_2$ as it contains more than one redox couple (Mn$^{x+/x}$ and Ni$^{y+/y}$). It has been previously established theoretically$^5$ that the nickel adopts a +2 oxidation state and the manganese shows a +4 oxidation state within the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ system. Hence the nickel redox couple is thought to be only active above 2V$^{16-18}$ (i.e. when the material is used as a cathode) utilising the Ni$^{3+/2+}$ and Ni$^{3+/4+}$ redox couples either as sequential one electron reactions or a direct Ni$^{4+/2+}$ reduction/oxidation. Conversely below 2V the manganese redox couple is active, again either through one electron reactions or a direct Mn$^{4+/2+}$ couple. Depending on the nature of this reaction this can introduce the problematic Jahn-Teller structural distortion associated with the octahedral Mn$^{3+}$ ion— which has a history of debilitating the performance of systems which contain Jahn-Teller active ions$^{19-24}$.

From the incremental capacity plot it would seem that the single discharge process is a consequence of Mn$^{4+/2+}$ reduction and the two processes observed on charging are a sequential Mn$^{4+/3+}$, Mn$^{3+/2+}$ oxidation (while it could be argued that the 0.5 Li plateau on 2$^{nd}$ discharge may suggest a 1 electron process on discharge, the presence of the 2 charging peaks in the incremental plot insinuates a 2 electron oxidation which could only happen with a full 4+ to 2+ reduction on discharge).
The *ex situ* X-ray diffraction pattern taken after 160mAh/g of discharge (displayed in Figure 6.3.5) confirms the behaviour that was first observed by Thackeray *et al.*\(^3\) with the apparent growth of the Li\(_2\)Mn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) phase. The Li\(_2\)Mn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) phase can be refined to a \(\bar{P}\overline{3}m1\) space group, iso-structural to Li\(_2\)NiO\(_2\), Li\(_2\)VO\(_2\) and Li\(_2\)MnO\(_2\)\(^{25}\) type materials.

![X-ray diffraction patterns and Rietveld refinements](image)

Figure 7.3.5. X-ray diffraction patterns and Rietveld refinements for nominally LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) materials at different states of discharge: A) Pristine LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) as received from Fluka, B) LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) after 160mAh/g of discharge, □ Unknown impurity.

The joint refinement gives a fit of \(R_{wp} = 9.57\%\) and a phase ratio of approximately 0.4:0.6 LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) : Li\(_2\)Mn\(_{0.3}\)Ni\(_{0.7}\)O\(_2\). Selected parameters are given below for the Li\(_2\)Mn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) phase, due to the similar X-ray scattering cross sections of manganese and nickel (combined with the poorer X-ray statistics from the recovered
powder sample) the model showed very little bias for fractional occupancies in the 1a site and thus the ratio was fixed at 1:1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Symbol</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>B_{iso}</th>
<th>Occupancy</th>
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<td>0.00</td>
<td>0.022(1)</td>
<td>Mn0.51/Ni0.49(1)</td>
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<tr>
<td>O1</td>
<td>2d</td>
<td>0.333</td>
<td>0.667</td>
<td>0.249(5)</td>
<td>0.084(2)</td>
<td>1</td>
</tr>
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</table>

\[a = 3.150(1) \quad b = 3.150(1) \quad c = 5.139(2) \quad \text{Cell Volume} = 44.17(4)\]

Space group: \(P\bar{3}m1\) \(R_p = 7.2\%\) * \(R_{wp} = 9.57\%\) * \(\chi^2 = 1.597\) *

* Values produced from two phase refinement from material recovered at 115mAh/g

Table 7.3.1. Refinement parameters of (nominally) Li$_2$Mn$_{0.5}$Ni$_{0.5}$O$_2$ derived from X-ray diffraction of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ material after 160mAh/g of discharge.

The refinement gave similar (if slightly reduced) lattice parameters to the material reported by Thackeray et al.\(^3\) The growth of the new phase can be clearly seen in the selected 2θ regions throughout the discharge process displayed in Figure 6.3.6. While the majority of the phase conversion occurs by 160mAh/g the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ material does not suffer as strongly from the effect seen with the LiVO$_2$ material which seemingly stopped the LiVO$_2$ to Li$_2$VO$_2$ change half way through the plateau. One clue as to the cause of ‘non phase conversion’ capacity may be the impurity peaks seen in the X-ray diffraction pattern taken at 160mAh/g (and present in the later diffraction patterns).
Figure 7.3.6. selected X-ray diffraction peaks through cycling of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ material – Electrolyte LP30, cycling rate 10 mA/g at a temperature of 30°C

The nature of this impurity was not discovered after various obvious materials failed to fully account for all the peaks (i.e. NiO and other dissociation/displacement type products). It is likely that the peaks represent various products from side-reactions with the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ materials, possibly as a consequence of reactions during phase change or indeed more exotic dissociation reactions occurring from the start of discharge.

One feature highlighted in the diffraction sections shown in Figure 6.3.6 is the splitting of the prominent LiMn$_{0.5}$Ni$_{0.5}$O$_2$ peak (~ 23.5°) during discharge (this also explains the slightly diminished fitting around the strong LiMn$_{0.58}$Ni$_{0.5}$O$_2$ peaks in the diffraction pattern taken at 160mAh/g). The phase change may induce stacking faults that initially cause widening of the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ peak at 23.5° (h,k,l, = 0,0,3) then, eventually, separation into 2 different peaks. Stacking faults are known to cause the
widening of peaks\textsuperscript{26}, in this case possibly brought about by reordering of the LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} structure (prior to over-lithiation and shearing) into either of its proposed theoretical structures (i.e. the Mn/Ni organised in a striped or zigzag layers\textsuperscript{5}).

Interestingly it appears that when the LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} reforms on charging, the LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} is dominated by only one peak (seen in the single peak in 0.8V charged X-ray diffraction pattern segment in Figure 6.3.6). The dominant peak seen upon charging appears in the same place as the peak that splits from the pristine material on discharge, suggesting this new ‘sub-phase’ is more favourable to convert to from Li\textsubscript{2}Mn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}. The peak splitting may offer insight into the nature of the addition process and would be worthy of further study (possibly shedding light on some of the nebulous data produced from LiVO\textsubscript{2} concerning the shearing process – see appendix \textit{vii}).
7.2.4. LiNi$_{0.33}$Co$_{0.66}$O$_2$

A further material that displayed promising addition type of behaviour was LiNi$_x$Co$_{1-x}$O$_2$ (where X=0.33, 0.5, 0.66). Previously un-investigated as an anode, LiNi$_x$Co$_{1-x}$O$_2$ has been intensely researched as a possible cathode material$^{27-30}$. In a computational study on mixed metal layered oxide anodes$^5$ it was determined that the Ni/Co LiMO$_2$ system would have the largest change in reaction energy upon lithium insertion between the Ni/Co, Ni/Mn and Mn/Co binary metal LiMO$_2$ series (suggesting that this would be the most favourable system). The same study suggested that for Ni/Co, Ni/Mn and Mn/Co LiMO$_2$ systems, a displacement reaction is the most thermodynamically favourable reaction hinting that, when addition does occur, kinetic factors may be dominant in the systems that display Li$_2$MO$_2$ conversions). In the study it was suggested that a LiNi$_{0.5}$Co$_{0.5}$O$_2$ material would have both Ni$^{3+}$ and Co$^{3+}$ present causing the Ni ion to undergo strong Jahn-Teller distortion which may produce structural strain, inducing instabilities upon cycling.

It was found that the LiNi$_{0.33}$Co$_{0.66}$O$_2$ showed marginally better performance thus LiNi$_{0.33}$Co$_{0.66}$O$_2$ is used as an example in the following analysis.
The galvanostatic profile of LiNi$_{0.33}$Co$_{0.66}$O$_2$ does not show any of the voltage ‘shoulders’ seen with the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ material (or the LiVO$_2$) instead the first discharge is defined by 2 processes (indicated by the 2 peaks in the incremental capacity plot) and can be identified by the steeply or gently sloping regions of the first discharge. Neither process is repeated on the second discharge instead being replaced by a single plateau at a voltage mid-way between both first discharge plateaus. The charge and 2$^{nd}$ discharge processes are almost symmetrical with the plateaus of both producing comparable capacity, suggesting that the charging processes is reversible with the second discharge. The first discharge exceeds the theoretical one Li$^+$ addition reaction of LiNi$_{0.33}$Co$_{0.66}$O$_2$ (as does the second to a lesser extent)(~274mAh/g if both metal ions utilise a one electron redox couple or ~180 mAh/g if just the Co$^{3+}$ is active) but the plateau is dissimilar to the ‘runaway’ plateaus of LiMnO$_2$ and LiCoO$_2$. 

Figure 7.3.7. 1$^{st}$ and 2$^{nd}$ cycle voltage vs. composition profile for LiNi$_{0.33}$Co$_{0.66}$O$_2$. Inset: 1$^{st}$ and 2$^{nd}$ incremental capacity plot – Electrolyte LP30, cycling rate 10mA/g at a temperature of 30$^\circ$C.
Given the sloping nature of the first plateau it is possible that the initial sloping ‘pseudo-plateau’ is a consequence of prolonged SEI formation and the latter plateau represents a LiNi$_{0.33}$Co$_{0.66}$O$_2$ to Li$_2$Ni$_{0.33}$Co$_{0.66}$O$_2$ structural conversion or the two electrochemically distinct voltage plateaus may represent distinct cobalt or nickel clusters known to be present within LiNi$_x$Co$_{1-x}$O$_2$ systems$^{31,32}$.

The charging process appears to be a simple monotonic process with only one prominent peak shown in the incremental capacity plot. The same appears to be true for the second discharge, the altered voltage plateau suggesting a new phase is produced on charging which then undergoes lithiation on the second discharge.

The nature of the first discharge process was further investigated by ex situ X-ray diffraction patterns as seen in Figure 6.3.8. The diffraction pattern taken at 200mAh/g of discharge revealed the growth of a second phase. The second phase was refined using a $P\overline{3}m1$ space group initially based on the (theoretical) Li$_2$Ni$_{0.5}$Co$_{0.5}$O$_2$ model produced by Thackeray et al.$^5$ The model gave a joint refinement fit of $R_{wp}=7.68\%$ (the majority of the misfit coming from the LiNi$_{0.33}$Co$_{0.66}$O$_2$ phase) suggesting that, for the first time, a Li$_2$Ni$_x$Co$_{1-x}$O$_2$ material has been experimentally observed.
Figure 7.3.8. X-ray diffraction patterns and Rietveld refinement of LiNi$_{0.36}$Co$_{0.64}$O$_2$ at different stages of discharge: A) Pristine (nominally) LiNi$_{0.33}$Co$_{0.66}$O$_2$ material, B) (nominally) LiNi$_{0.33}$Co$_{0.66}$O$_2$ after 200mAh/g of discharge, C) (nominally) LiNi$_{0.33}$Co$_{0.66}$O$_2$ material discharged to 1V.
The lattice parameters (displayed in Table 6.3.1) confirm a reasonable unit cell, commensurate with the previous theoretical work on Li$_2$Ni$_{0.5}$Co$_{0.5}$O$_2$.

<table>
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</table>

$a = 3.1003(6)$  $b = 3.1003(6)$  $c = 5.1608(9)$  

Cell Volume = 42.96(1)

Space group: $P\bar{3}m1$  

$R_p = 6.12\%$  $R_{wp} = 7.68\%$  $\chi^2 = 2.202$

* Values produced from two phase refinement from material recovered at 115mAh/g

The refinement taken at the end of discharge (1V) shows that both phases are still present, with a phase ratio of 0.13 (LiNi$_{0.36}$Co$_{0.64}$O$_2$):0.87 (Li$_2$Ni$_{0.4}$Co$_{0.6}$O$_2$) suggesting a continued LiNi$_{0.64}$Co$_{0.36}$O$_2$ to Li$_2$Ni$_{0.4}$Co$_{0.6}$O$_2$ phase change throughout the plateau.

The lack of evidence of any other phase (or other material) lends more support to the idea that the first sloping section seen in the galvanostatic profile is SEI formation and the amorphous organo-metallic product is transparent to X-ray diffraction techniques. Indeed it highlights that the preceding voltage ‘shoulders’ are not necessary for
addition type reactions contrary to what the LiMn_{0.5}Ni_{0.5}O_2 and LiVO_2 systems may suggest.

As highlighted by the insets in Figure 6.3.8 (2) and (3), LiNi_{0.33}Co_{0.66}O_2 material does not undergo the peak splitting (of the (0,0,3) peak) observed in LiNi_{0.5}Mn_{0.5}O_2 system which may suggest a subtly different process occurring on over-lithiation, with stacking faults precluded by the different structural chemistries of the LiMn_{0.5}Ni_{0.5}O_2 and LiNi_{0.33}Co_{0.66}O_2 (it is thought that Jahn-Teller distortion present in LiNi_{0.33}Co_{0.66}O_2 means the ‘zigzag’ and ‘striped’ ordering difference theoretical thought to exist in LiNi_{0.5}Mn_{0.5}O_2 can’t occur\(^5\)). Unlike the LiMn_{0.5}Ni_{0.5}O_2 material there was no impurity observed during LiNi_{0.33}Co_{0.66}O_2 discharge suggesting that the nickel/cobalt material may be more stable on longer cycling regimes.

The presence of the previously unreported Li_{2}Ni_{0.4}Co_{0.6}O_2 phase suggests that the over-lithiation of (nominally) LiNi_{0.33}Co_{0.66}O_2 may provide a viable anode system. Certainly the lack of impurities produced on discharge and the more symmetric charge and 2\(^{nd}\) discharge galvanostatic profile may make it a more favourable material compared to the nickel/manganese system

A more in-depth study is needed to establish the nature of the charging process and the cause of the change in plateau voltage in the subsequent discharge but the presence of a Li_{2}Ni_{0.33}Co_{0.66}O_2 phase is an encouraging place to start.
7.3. Conclusions and Further Work

Although only a brief overview, several interesting areas of research have been highlighted for more in-depth study. The effect of over-lithiation of LiCoO\textsubscript{2} was reported using ex situ X-ray diffraction. It was found that Li\textsubscript{2}O is produced during discharge, strongly suggesting that a dissociation or displacement reaction occurs. The lack of cobalt materials indicated that the extruded cobalt oxide or cobalt metal or transparent to X-rays suggesting either nanoscopic and/or amorphous reaction products. Establishing the nature of the over-lithiation reaction either through small-angle scattering techniques or electron microscopy would go some way towards establishing the nature of the over-lithiation reaction.

The occurrence of the phase change of LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} to Li\textsubscript{2}Mn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} was also investigated. It was established that the LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} systems is similar to the LiVO\textsubscript{2} material in many ways, both consisting of multiple first discharge processes, with the majority of the LiMO\textsubscript{2} to Li\textsubscript{2}MO\textsubscript{2} phase change occurring in the first part of the discharge plateau. Unlike LiVO\textsubscript{2}, LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} undergoes a 2 part charging process, possibly due to the two electron Mn\textsuperscript{4+/2+} redox couple. The discharge process also indicated that some localised structural rearrangement occurs in the LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} prior to phase change to Li\textsubscript{2}Mn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}. This may go some-way to explaining the complicated structural conversion from LiMO\textsubscript{2} to Li\textsubscript{2}MO\textsubscript{2}. Further study of LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} may be able to answer several questions applicable to the LiMO\textsubscript{2}/Li\textsubscript{2}MO\textsubscript{2} system as a whole, not least the nature of the lithium insertion process during phase change and the redox environment of the transition metal ion during charge and discharge. To accomplish this, an in-depth neutron diffraction study of materials at different states of discharge/charge (which would also help identify the unknown
impurity) coupled with an *in situ* XPS study would enable better understanding of the system through cycling.

A LiNi$_x$Co$_{1-x}$O$_2$ material was shown, for the first time, to undergo an addition type reaction to form a Li$_2$Ni$_x$Co$_{1-x}$O$_2$ type material at low voltage discharge. The Li$_2$Ni$_{0.4}$Co$_{0.6}$O$_2$ was identified through *ex situ* X-ray diffraction and found to be structurally analogous to previously reported Li$_2$Ni$_{0.5}$Ni$_{0.5}$O$_2$ and Li$_2$VO$_2$ materials. The nature of the discharge/charge process was found to be subtly different to the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ material as there were no voltage ‘shoulders’ upon initial discharge, seemingly replaced by two voltage plateaus, sloping at slightly different gradients.

The incremental capacity plots also showed that charging bore a single electrochemical process, something mimicked by the second discharge process which shifted to a different voltage compared to first discharge. Both factors indicate that the electrochemical nature of the LiMO$_2$/Li$_2$MO$_2$ phase change is slightly different for the Ni/Mn and Ni/Co systems. The altered Ni/Co electrochemical behaviour would provide a useful counter-point to the Ni/Mn system and a similarly in-depth structural and redox study of the system would complement the investigation into its LiNi$_{0.5}$Mn$_{0.5}$O$_2$ counterpart.

The LiMO$_2$/Li$_2$MO$_2$ system may yet provide a useful anode material; certainly the results from this preliminary investigation are promising with several possible Li$_2$MO$_2$ systems identified. Much work is needed before a transition metal layered oxide anode would be ready for commercialisation with the most prevalent problem being the understanding of the varied electrochemical behaviour of the LiMO$_2$ system and the factors that allow it to convert to its Li$_2$MO$_2$ analogue.
7.4. References

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8.1. **Conclusions.**

This thesis has focussed on synthesis and subsequent structural and electrochemical characterisation of novel electrode materials and processes. Three polymorphs of Li$_2$CoSiO$_4$ were produced and a comparison between their structural nature and electrochemical behaviour was undertaken. Further research was initiated in order to improve the electrochemical performance of the material. A novel class of layered LiMO$_2$ anode was examined, primarily the material LiVO$_2$, which, in conjunction with LiMn$_{0.5}$Ni$_{0.5}$O$_2$ and LiNi$_{0.5}$Co$_{0.5}$O$_2$, was found to undergo lithium addition upon discharge, causing a phase change to a layered Li$_2$MO$_2$ structure.

8.2. **Li$_2$CoSiO$_4$**

The compound Li$_2$CoSiO$_4$ was found to have three easily synthesised phases produced either through solid state or hydrothermal methods, denoted β$_{I}$, β$_{II}$ and γ$_{0}$ as described previously by West and Glasser$^1$ (a fourth phase, γ$_{II}$, reported by West and Glasser could not be realised). The phase was dependent on the synthesis conditions, primarily the final heating stage and it was found that the hydrothermal synthesis produced the most consistent material. Depending on the heating conditions, reheating of the hydrothermally produced β$_{II}$ phase allowed access to phase pure β$_{I}$ and γ$_{0}$ materials.

The phases were structurally characterised via x-ray diffraction and refined using the Rietveld method (the results have subsequently been corroborated with neutron diffraction and a $^7$Li NMR study$^{2,3}$). It was found that, as suggested by previous studies$^{1,4,5}$, the Li$_2$CoSiO$_4$ polymorphs form structures based around distorted forms of
the classic Li$_3$PO$_4$ structure. The hydrothermally produced β$_{II}$ material could be indexed to a \textit{Pmn2$_1$} space group. The structure takes the form of rows of offset LiO$_4$, CoO$_4$/LiO$_4$ and SiO$_4$ tetrahedron with mixing in the cobalt/lithium 4a site approximately 50/50. All polyhedra within β$_{II}$ are arranged so that the vertices of the corner sharing tetrahedra point along the \textit{c} axis. With the disordered lithium/cobalt tetrahedra translating along the \textit{a} axis and alternating chains of LiO$_4$ and SiO$_4$ tetrahedra running in parallel. TEM imaging showed that the hydrothermal synthesis produced roughly spherical particles of β$_{II}$ material, with a diameter of 30 - 100nm.

Electrochemically, it was found that the β$_{II}$ material has a first charge capacity of nearly 210 mAh/g, of which 150mAh/g (0.9 Li) could be assigned to the voltage plateau at 4.2V. The first discharge plateau had a significantly smaller capacity of 40 mAh/g occurring at a voltage of 4.15V. The material suffering a 50mV polarisation between the start of charge and discharge plateaus. Although subsequent \textit{ex situ} Rietveld refinement showed little structural changes after 10 cycles, the performance of the cathode diminished quickly, producing approximately 18mAh/g and 15mAh/g on charge and discharge respectively by the 10$^{th}$ cycle. Unlike what has been reported for the Li$_2$FeSiO$_4$ material\textsuperscript{6-8} there was no obvious phase change or plateau voltage shift during first discharge.

The β$_I$ structure was indexed to a \textit{Pbn2$_1$} space group, consisting of alternating layers of polyhedra with their vertices aligned along the \textit{c} axis. Each layer consists of lines of alternating LiO$_4$ and SiO$_4$, interspaced with lines of the two mixed metal oxide tetrahedra (LiO$_4$ or CoO$_4$), propagating along the \textit{a} axis. There was some cation mixing in the cobalt and one of the lithium sites, with approximately 7% lithium in the cobalt
site and 5% cobalt in the lithium site. The TEM imaging revealed that with reheating of the hydrothermal $\beta_{II}$ material to form the $\beta_{I}$ polymorph large particles were formed with diameters up to 1μm. The difference between the particulate dimensions of hydrothermally produced parent material is presumably a consequence of crystallite growth during the subsequent heating.

Electrochemically, the $\beta_{I}$ material had an initial charging plateau around 4.25V vs. $\text{Li}^+/\text{Li}$ which produced a capacity of approximately 100 mAh/g. The discharge plateau had an initial voltage of 4.16V and produced a capacity of around 35mAh/g. It was found that the structure underwent a phase change upon cycling, with the initial $\beta_{I}$ phase changing to a $\beta_{II}$ structure during charging. This complicated electrochemical behaviour is perhaps reflected in the cycling performance of the $\beta_{I}$ material, as the capacity diminished over a relatively small number of cycles and by the tenth cycle produced only 10mAh/g for both charge and discharge. It is difficult to tell the electrochemical contribution solely from the $\beta_{I}$ phase, especially as in later cycles the contributions from both $\beta_{I}$ and $\beta_{II}$ were occluded by polarisation effects.

The $\gamma_{0}$ material was indexed to a $P2_1/n$ space group and consisted of layers along the a,b, plane of $\text{LiO}_4$, $\text{CoO}_4$ and $\text{SiO}_4$ tetrahedra with their vertices pointing in opposing directions. The structure consists of clusters of 3 edge sharing tetrahedra, with a central tetrahedron accompanied by two tetrahedra facing the opposite direction. Unlike the two $\beta$ polymorphs there is no site sharing or disorder between the lithium and cobalt ions. As with the $\beta_{I}$ material, TEM images showed the particles, formed by reheating of $\beta_{II}$ material to be up to 1μm in diameter.
Electrochemically, the $\gamma_0$ phase appeared to be almost inert, producing a total first charge capacity of only 8 mAh/g without a distinct voltage plateau. On first discharge there was negligible capacity produced, a situation that did not improve on subsequent cycling. Unsurprisingly, there was no structural change on cycling, presumably due to the limited electrochemistry of the material.

The only polymorph successfully produced through solid state synthesis was the $\beta_1$ phase, this material had subtle differences compared to its hydrothermally based $\beta_1$ counterpart. While cation disorder was observed in both the cobalt and one of the lithium sites for $\beta_1$ material made from reheating hydrothermally prepared material, the solid state $\beta_1$ polymorph showed cation disorder only within the cobalt site, with approximately 7% lithium occupancy. TEM imaging showed that the solid state material was made up of particles with approximately the same dimensions as the hydrothermally prepared $\beta_1$ analogue (particle diameters up to 1μm).

The electrochemistry of the solid state $\beta_1$ polymorph was poorer than its hydrothermally based counterpart, producing a first charge capacity of only 40 mAh/g and a first discharge capacity of around 17 mAh/g, both of which diminished with subsequent cycling. Apparently the subtle structural differences between the two polymorphs were enough to instigate the difference in electrochemical behaviour.

### 8.2.1. $\text{Li}_2\text{CoSiO}_4$ Electrode Optimisation

In an attempt to improve the cycling behaviour of $\text{Li}_2\text{CoSiO}_4$ the effect of mechanical milling and carbon coating upon hydrothermally produced $\beta_{1u}$, $\beta_1$ and $\gamma_0$
materials was investigated. The materials were structurally and electrochemically characterised to determine the various effects of milling and coating. It was found that, in general, mechanical milling had a negative effect on the cycling performance of the materials, seemingly encouraging spurious side-reactions. The $\gamma_0$ material was the only phase that had a noticeable improvement (showing a first charge capacity of 140 mAh/g) but it was unclear whether this was due to the large particle size reduction (1μm to 100nm before and after ball-milling respectively) or side reactions enhanced by the increased surface area of the electrode/electrolyte interface. The capacity of the first charge was not maintained on discharge or on subsequent cycles and any benefit was significantly offset by reduction in capacity retention on multiple cycles. This was a problem ubiquitous through all polymorphs, highlighted by the poor performance of the $\beta_{II}$ and $\beta_I$ materials.

Carbon coating was successfully undertaken using a procedure that had been employed previously with Li$_2$FeSiO$_4$ materials. The $\beta_{II}$ polymorph and a formaldehyde/resorcinol xerogel were mixed together, to complete the xerogel graphitisation process, the mixture was then heated and the produced material was a mixture of the $\beta_{II}/\beta_I$ material in a 7:1 phase ratio, with approximately 3% carbon by weight. The carbon coated material did not show significant first charge improvement on the previously observed pristine $\beta_{II}$ material but the electrochemical performance was seen to improve over a limited number of cycles, with approximately 45% of the charging capacity being retained after 10 cycles (compared to around 25% for the pristine material).
8.2.2. **Li$_2$CoSiO$_4$ Future Work**

While the initial investigation into Li$_2$CoSiO$_4$ materials and subsequent electrode optimisation opened several interesting avenues of potential research, it is crucial that fundamental questions are answered, namely the nature of the disparity between charging and discharging regimes, the poor cycling lifetime of the material and the phase change observed on inserting lithium into the $\beta_I$ structure. Numerous techniques could be employed: *in situ* analysis would be possibly the most useful with X-ray/neutron diffraction providing the most precise information of the structural changes occurring with cycling. If this was undertaken in conjunction with *in situ* AC impedance and Infra-red spectroscopy a far more intricate picture would appear of the processes occurring with cycling. Further computational studies of the nature of the structural effects on the Co-O-Si triplet system and this effect on the lithium insertion and removal voltage would provide valuable information about the behaviour of the different phases under cycling. This may point to suitable adjustments to the structures or electronic nature of the materials that could be made with doping of the silicon site or indeed introducing solid solutions of cobalt, iron and manganese materials, which would add a useful versatility to the silicate polyanion class of cathodes. Investigation of further optimisation techniques such as utilising different conductive coating techniques which do not require such vigorous preparation conditions may allow the preservation of the pure $\beta_{II}$, $\beta_I$ and $\gamma_0$ phases after coating as well as potentially further improving the long term cycle performance of the materials.

Much work is needed to develop the Li$_2$CoSiO$_4$ materials, but the versatile polyanion structure and the varied electrochemistry they exhibit ensure that it would be a worthwhile venture, allowing greater understanding of the burgeoning class of
lithium silicate polyanion cathode materials and perhaps producing useful, viable cathode materials in the future.

8.3. LiVO$_2$

Various Li$_{1+x}$V$_{1-x}$O$_2$ materials (where x=0 to 0.2) were produced through solid state synthesis and were structurally characterised using X-ray diffraction and subsequent Rietveld refinement. The electrochemical behaviour of the system was studied through galvanostatic methods as well as *in situ* AC impedance and X-ray diffraction patterns taken at different lithium compositions during discharge.

The electrochemical behaviour of LiVO$_2$ was found to be heavily dependent on the amount of doped lithium present. The stoichiometric material had a very poor discharge capacity and showed no evidence of a plateau, where as the lithium doped material showed a voltage plateau at approximately 0.1V vs. Li$^+/\text{Li}$. The capacity varied with doping amount, highlighting a complicated relationship between discharge capacity and amount of lithium doping. It was found that the 8% lithium doped material showing the highest capacity of around 310mAh/g for the initial discharge. This was in excess of the theoretical capacity (298mAh/g) but a large irreversible capacity was observed on the first discharge which was not present on subsequent charge and discharge cycles.

Combining the structural and electrochemical analysis taken throughout the discharge of Li$_{1.08}$V$_{0.92}$O$_2$ a self consistent picture begins to emerge. There were three
clear stages during discharge; from 0-70mAh/g of capacity, from 70-180mAh/g and from 180-310mAh/g.

The region from 0-70mAh/g is characterised by sloping voltage shoulders in the galvanostatic profile. The *ex situ* X-ray diffraction study showed little structural changes during this region and combined with the *in situ* AC impedance and polarisation resistance data (and previous studies) it is suggested that this represents a region of extended SEI growth. Between 70-180mAh/g a new Li$_2$VO$_2$ phase was observed in the X-ray diffraction patterns, and a voltage plateau was observed in the galvanostatic profile. Relatively little change was observed in the charge transfer resistance seen in the AC impedance measurements.

After 180mAh/g of capacity had passed the X-ray diffraction patterns showed relatively little new growth of the Li$_2$VO$_2$ material, which contrasts with the galvanostatic profile which displays little change to the voltage plateau (the process responsible for the plateau assumed to be the LiVO$_2$ to Li$_2$VO$_2$ phase change). The charge transfer resistance was seen to undergo a change corresponding to the altered structural behaviour, which suggests the presence of a distinct electrochemical process after 180mAh/g, the nature of which could be from the LiVO$_2$/Li$_2$VO$_2$ material itself or an external process, possibly lithium deposition.

Extensive computer modelling, undertaken by the Islam group at Bath University in conjunction with the work of this thesis suggested that the doping dependence of Li$_{1+x}$V$_{1-x}$O$_2$ was a consequence of the extra lithium presence in the vanadium layer in LiVO$_2$. Due to the presence of a small amount of octahedral lithium in the vanadium layer the energy penalty of tetrahedral lithium insertion in the
adjacent lithium layer (required to convert to Li$_2$VO$_2$ structure) was considerably reduced allowing lithium to be inserted at a voltage that is high enough to avoid the dominating effects of lithium deposition (i.e. greater than 0V vs. Li$^+$/Li).

8.3.1. LiVO$_2$ Future Work

Further characterisation is required in order to fully understand the complicated processes present with lithium insertion into LiVO$_2$ materials, especially with respect to the SEI formation process at the beginning of discharge and the drop off in LiVO$_2$ to Li$_2$VO$_2$ phase conversion mid way through the voltage plateau. The incorporation of further in situ techniques such as Raman and NMR may help to answer some of the questions raised by the discharge behaviour. The poor capacity retention on repeated cycling should also be investigated and research into the nature of lithium doping in the 3a vanadium site upon repeated discharge and charge cycles may suggest useful avenues to follow when trying to improve the cycle lifetime.

8.4. LiMO$_2$

Several transition metal oxide (LiMO$_2$) systems were investigated for their ability to convert to layered Li$_2$MO$_2$ materials upon over-lithiation (> 1Li$^+$ per unit cell). A preliminary investigation concerning the structural nature of the LiCoO$_2$, LiMn$_{0.5}$Ni$_{0.5}$O$_2$ and LiNi$_{0.33}$Co$_{0.66}$O$_2$ systems during electrochemical discharge was undertaken.

The voltage plateau for the over-lithiation process of LiCoO$_2$ occurred at 1.25V and had a first discharge capacity of almost 550mAh/g the charging process showed no
corresponding voltage plateau. On subsequent discharge a similar voltage plateau evolved at around 1.2V but only produced around 300 mAh/g of capacity. Through ex situ X-ray diffraction it was established that LiCoO$_2$ did not convert to Li$_2$CoO$_2$ when cycled. The presence of Li$_2$O, seen in x-ray diffraction patterns of cycled material strongly suggested a ‘dissociation’ or ‘displacement’ type reaction, most likely producing a combination of amorphous cobalt metal and cobalt oxide products along with Li$_2$O.

LiMn$_{0.5}$Ni$_{0.5}$O$_2$ underwent a Li ‘addition’ type reaction to form Li$_2$Mn$_{0.5}$Ni$_{0.5}$O$_2$, as suggested by the previous work of Thackeray$^{10-13}$. Upon initial discharge LiMn$_{0.5}$Ni$_{0.5}$O$_2$ was seen to undergo a similar process to LiVO$_2$ with multiple sloping voltage shoulders until a voltage plateau was reached around 1V with the initial discharge producing around 300mAh/g capacity. On charge it was observed that there were two distinct electrochemical processes compared to the monotonous discharge process. It is possible that this reflects multiple redox couples active at different states of charge. X-ray diffraction confirmed the presence of Li$_2$Mn$_{0.5}$Ni$_{0.5}$O$_2$ on discharge, which was seen to be the dominant phase by the end of discharge. Local structural rearrangement was also observed for the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ material during first discharge.

For the first time a Li$_2$Ni$_x$Co$_{1-x}$O$_2$ (0<X>1) material was been observed. It was found that on over-lithiation the material LiNi$_{0.33}$Co$_{0.66}$O$_2$ was seen to convert to Li$_2$Ni$_{0.4}$Co$_{0.6}$O$_2$. The LiNi$_{0.33}$Co$_{0.66}$O$_2$ material had different first discharge behaviour to its LiVO$_2$ and LiMn$_{0.5}$Ni$_{0.5}$O$_2$ counter parts, with no sloping voltage shoulders observed. Instead a sloping voltage pseudo-plateau was observed beginning at 1.4V and finishing after approximately 450mAh/g of capacity had passed near 1V. There was still the
familiar irreversible capacity of first discharge, with the subsequent discharge achieving approximately 300mAh/g of capacity. Unlike its Mn/Ni counterpart, the LiNi$_{0.33}$Co$_{0.66}$O$_2$ seemingly utilised the same redox couple during both discharge and charge. The \textit{ex situ} X-ray diffraction study showed the presence of a Li$_2$Ni$_{0.4}$Co$_{0.6}$O$_2$ phase during discharge, and the material was seen not to undergo the peak splitting seen previously in the LiMn$_{0.5}$Ni$_{0.5}$O$_2$ material on conversion to Li$_2$Mn$_{0.5}$Ni$_{0.5}$O$_2$.

8.4.1. \textbf{LiMO$_2$ Future Work}

The variation in electrochemical and structural behaviour of the LiMO$_2$ materials certainly merits closer inspection. Further identification of similar systems that will and will not undergo ‘addition’ type reactions would better inform about the complicated processes that determine the reactions of layered transition metal oxides on over lithiation. The structural changes that occur during LiMO$_2$ to Li$_2$MO$_2$ phase conversion require further research and an in-depth investigation, akin to the LiVO$_2$ research, into the behaviour of the LiMn$_{x}$Ni$_{1-x}$O$_2$ and LiCo$_{x}$Ni$_{1-x}$O$_2$ system would answer questions about the process of over lithiation. It may also be pertinent to investigate the lithium doping effect on the layered transition metal oxide anodes and whether this has an effect on the addition/displacement/dissociation reaction pathway selection.
8.5. **Summary**

The aim of this thesis was to undertake original research into novel lithium host materials. This investigation centred around two areas, namely the cathode material $\text{Li}_2\text{CoSiO}_4$ and the $\text{LiMO}_2$ class of anode. The behaviour of both types of material upon electrochemical lithium insertion and removal were explored, using structural and electrochemical characterisation to understand the nature of the processes occurring within the materials undergoing electrochemical cycling. The research successfully highlighted several viable materials for lithium host electrodes that could be utilised in lithium-ion battery systems and identified numerous interesting avenues for further investigation.

Energy storage technology is constantly evolving to meet new social, economic and environmental pressures facing modern society. There is an urgent need to provide innovative, novel and versatile solutions to the problem of on demand power production. Much research is still needed, even at a fundamental level, to bring energy storage technology to maturity and it is hoped that the work of this thesis can be used to inform future research of lithium host materials and eventually be used to help bring about an improvement in the increasingly vital field of energy storage.
8.6. References

Appendix i

Published Paper:

The Lithium Intercalation Compound Li$_2$CoSiO$_4$ and Its Behaviour as a Positive Electrode for Lithium Batteries.

C Lyness, B Delobel, AR Armstrong, PG Bruce - Chemical Communications, 2007, 4892
The lithium intercalation compound \( \text{Li}_2\text{CoSiO}_4 \) and its behaviour as a positive electrode for lithium batteries†

Christopher Lyness, Bruno Delobel,‡ A. Robert Armstrong and Peter G. Bruce*

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The electrochemical behaviour of 3 polymorphs of the lithium intercalation compound \( \text{Li}_2\text{CoSiO}_4 \), \( \beta_h \), \( \beta_I \) and \( \gamma_0 \), as positive electrodes in rechargeable lithium batteries is investigated for the first time.

The layered Li intercalation compound, \( \text{LiCoO}_2 \), is used as the cathode in the majority of commercial rechargeable lithium-ion batteries.\(^1\)\(^2\) Alternative compounds, such as \( \text{LiNiO}_2 \) or \( \text{LiMnO}_2 \) have also been considered; their solid solutions, e.g. \( \text{Li}(\text{Co}_{1/3}\text{Mn}_{2/3})\text{O}_2 \), \( \text{Ni}_{1/2}\text{O}_2 \) are used in the latest commercial products.\(^3\)\(^4\) Recognition that compounds based on the phosphate anion, such as the olivine \( \text{LiFePO}_4 \), could act as lithium intercalation hosts, and could operate as cathodes in rechargeable lithium batteries, represented a significant breakthrough.\(^6\) Bonding of the oxygen to the phosphorus stabilises the former with respect to evolution from the structure, an important problem on charging simple transition metal oxides. Recently, an entirely new class of lithium intercalation compounds based on silicates, \( \text{Li}_x\text{MSiO}_4 \), where \( M = \text{Fe}, \text{Mn}, \text{Co} \), has been described.\(^7\) Of these the most studied is \( \text{Li}_2\text{FeSiO}_4 \), it has been shown that at \( 60 \, ^\circ\text{C} \) \( 165 \, \text{mA h g}^{-1} \) of charge may be extracted, corresponding to one lithium per formula unit; with reversible lithium cycling over the range \( \text{Li}_x\text{FeSiO}_4 \), \( 1.15 < x < 2 \), corresponding to \( 140 \, \text{mA h g}^{-1} \) when suitably carbon coated and with a particle size of \( 150 \, \text{nm} \).\(^7\)\(^8\) Si doped \( \text{LiCoO}_2 \) gave \( \text{Li}_2\text{CoSiO}_4 \) as an impurity with enhanced electrochemical properties but behaviour of the pure phase was not reported.\(^8\) Here we present the first preliminary report on the electrochemistry of three polymorphs of the compound \( \text{Li}_2\text{CoSiO}_4 \).\(^8\)

The \( \text{Li}_x\text{MSiO}_4 \) compounds (\( M = \text{Fe}, \text{Mn}, \text{Co} \)) belong to a family of materials known as the tetrahedral structures.\(^9\) They are composed of tetragonally packed oxide ions (a distorted form of hexagonal close packing) within which half the tetrahedral sites are occupied by cations such that face sharing between the pairs of tetrahedral sites is avoided.\(^10\) The tetrahedral structures exhibit a rich polymorphism, with more than eight polymorphs known. They may be divided into two families, designated \( \beta \) and \( \gamma \). In the case of the former all the tetrahedra point in the same direction, perpendicular to the close-packed planes, and share only corners with each other, whereas, in the case of the \( \gamma \) polymorphs, the tetrahedra are arranged in groups of three with the central tetrahedron pointing in the opposite direction to the outer two, with which it shares edges, Fig. 1. Where both \( \beta \) and \( \gamma \) polymorphs exist for a given compound the latter is stable at higher temperatures, with the \( \beta \) to \( \gamma \) transformation involving inversion of half the tetrahedral sites.\(^11\) Several variants of both \( \beta \) and \( \gamma \) exist, involving either ordering or distortions of the parent structures, they are designated \( \beta_h \), \( \gamma_0 \), \( \gamma_1 \), etc. In many cases these phases may be quenched to room temperature, where they exhibit long-term stability. Originally the different polymorphs were distinguished only on the basis of differences in their powder X-ray diffraction patterns.\(^7\) More recently, the complete crystal structures of a few isolated examples have been solved.\(^12\)

\( \text{Li}_2\text{CoSiO}_4 \) compounds were synthesised by initial hydrothermal reaction which produces the \( \beta_\text{H} \) polymorph. The \( \beta_h \) form was obtained by heating the \( \beta_\text{H} \) phase in air to \( 700 \, ^\circ\text{C} \) for \( 2 \, \text{h} \). The \( \gamma_0 \) phase was formed by heating the \( \beta_\text{H} \) polymorph to \( 1100 \, ^\circ\text{C} \) for \( 2 \, \text{h} \), then lowering the temperature to \( 850 \, ^\circ\text{C} \) whereupon the material was quenched to room temperature. Powder X-ray diffraction patterns of as-prepared \( \text{Li}_2\text{CoSiO}_4 \), and those heated to 700 and \( 1100 \, ^\circ\text{C} \) are presented in Fig. 2 (Stoe STADI/P diffractometer, Fe-K\( \alpha \)). They correspond to the three polymorphs \( \beta_\text{H}, \beta_\text{I} \) and \( \gamma_0 \) respectively. Their structures have been refined by the Rietveld method (TOPAS).\(^13\) Full details are beyond the scope of this communication but will be reported later. The structures of \( \beta_\text{H}, \beta_\text{I} \) and \( \gamma_0 \) are shown in Fig. 1.

![Fig. 1 Crystal structures of three tetrahedral polymorphs of Li2MXO4: (a) βH, (b) βI, (c) γ0. Grey tetrahedra: XO4, blue: MO6, green: LiO4.](image-url)
The extraction of 180 mA h g\(^{-1}\) results in a gentle increase in potential on the first charge, corresponding to Co\(^{2+}\) to Co\(^{3+}\). The first discharge capacity is much smaller at around 30 mA h g\(^{-1}\). Subsequent cycling leads to further capacity fade, such that after 10 cycles the cell capacity is negligible. Turning to the \(\beta\)\(_b\) polymorph, cycled under the same conditions, the shape of the first charge curve is similar, although with some additional structure evident. The first charge capacity is significantly lower at only 80 mA h g\(^{-1}\). The discharge capacity on the first cycle was again around 30 mA h g\(^{-1}\), although by virtue of the lower charge capacity the efficiency had improved from 14\% for \(\beta\)\(_b\) to 38\% for \(\beta\)\(_b\). Again after 10 cycles the capacity of the \(\beta\)\(_b\) polymorph was negligible, Fig. 3(b). The \(\gamma\)\(_0\) polymorph also exhibits a slow potential rise on the first charge corresponding to a capacity of 100 mA h g\(^{-1}\) and around 30 mA h g\(^{-1}\) on discharge, again with negligible capacity after 10 cycles.

Although the load curves in Fig. 3, despite a low rate of 10 mA g\(^{-1}\), may still be somewhat influenced by kinetics, it is interesting to note that the charge and discharge potentials are all similar, suggesting that the structural differences in the three polymorphs are not sufficient to induce major changes in the Li\(^+\) and e\(^-\) chemical potentials. Also the values are in broad agreement with those predicted by DFT + U calculations for Li\(_2\)CoSiO\(_4\) (4.4 V).\(^7\,\text{de}\) They are higher than Li\(_2\)FeSiO\(_4\) (~3 V) and Li\(_2\)MnSiO\(_4\) (~4.2 V).

Although ball-milling aids the distribution of carbon within the composite electrode, carbon coating the particles would further improve the efficiency of the “wiring”, as has been demonstrated for LiFePO\(_4\).\(^14\) It is necessary to pyrolyse the carbon precursors above 650 °C to form sufficient sp\(^2\) linkages to promote good electron transport. All our attempts to carbon coat the ball-milled polymorphs using a variety of precursors e.g. sucrose, resulted in reduction of Li\(_2\)CoSiO\(_4\) and the production of Co metal and LiSiO\(_3\), as demonstrated by powder XRD. However, in the case of the \(\beta\)\(_b\) polymorph, we were able to coat the as-prepared particles with carbon without such reduction occurring. The difference may reflect the greater reactivity of the particle surfaces formed during ball-milling, making them more susceptible to reduction. Success so far has been restricted to the \(\beta\)\(_b\) polymorph because heating the \(\beta\)\(_b\) polymorph at high enough temperatures to induce a conductive carbon coat results in conversion to \(\beta\)\(_h\). In the case of the \(\gamma\)\(_0\) phase, to date it has proved impossible to quench the sample sufficiently rapidly in an inert atmosphere to form a single \(\gamma\)\(_0\) phase.

The “wiring” of \(\beta\)\(_b\) Li\(_2\)CoSiO\(_4\) was achieved using the resorcinol-formaldehyde approach.\(^15\) Hydrothermally prepared Li\(_2\)CoSiO\(_4\) was mixed with 15 wt\% of dried carbon-gel (pre-pyrolysis xerogel) and heated to 700 °C under flowing argon for 2 h. Electrochemical results for composite electrodes fabricated using the \(\beta\)\(_b\)/carbon composite are shown in Fig. 4. A well defined plateau is observed at around 4.25 V on the first charge. Despite the higher polarisation at the start of charging compared with the ball-milled material, a

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**Fig. 2** Fitted powder X-ray diffraction data for the three Li\(_2\)CoSiO\(_4\) polymorphs: (a) \(\beta\)\(_h\), (b) \(\beta\)\(_b\), (c) \(\gamma\)\(_0\).

The electrochemistry of all three polymorphs was investigated by forming composite electrodes as described in the notes. The capacity to extract lithium from the three polymorphs, even when charged slowly to 4.6 V, was very low. Each polymorph was mixed with Super P carbon in the ratio 8 : 2 and ball-milled (SPEX Centri-Prep 8000 M mixer/mill) for 1 h. TEM data collected after ball-milling (Jeol JEM-2011) indicated particle sizes of 50–100 nm for all three polymorphs and powder X-ray diffraction data showed peak-broadening compared with the as-prepared materials (see ESI†). Analysis of the peak widths using the Scherer formula revealed domain sizes of 10–40 nm. These are smaller than the particle sizes observed by TEM demonstrating that ball-milling introduces a domain structure/strain within the grains.

Ball-milling significantly improves the electrochemical response. Cells fabricated from the ball-milled polymorphs were subjected to charge and discharge at 50 °C, a typical temperature used for other Li\(_2\)MSiO\(_4\) materials, Fig. 3.\(^3\) The ball-milled \(\beta\)\(_b\) phase exhibits a gentle increase in potential on the first charge, corresponding to extraction of 180 mA h g\(^{-1}\) (equivalent to 1.1 Li per formula unit). Lithium removal is accompanied by oxidation of the tetrahedral Co\(^{2+}\) to Co\(^{3+}\). The first discharge capacity is much smaller at around 30 mA h g\(^{-1}\). Subsequent cycling leads to further capacity fade, such that after 10 cycles the cell capacity is negligible. Turning to the \(\beta\)\(_h\) polymorph, cycled under the same conditions, the shape of the first charge curve is similar, although with some additional structure evident. The first charge capacity is significantly lower at only 80 mA h g\(^{-1}\). The discharge capacity on the first cycle was again around 30 mA h g\(^{-1}\), although by virtue of the lower charge capacity the efficiency had improved from 14\% for \(\beta\)\(_h\) to 38\% for \(\beta\)\(_h\). Again after 10 cycles the capacity of the \(\beta\)\(_h\) polymorph was negligible, Fig. 3(b). The \(\gamma\)\(_0\) polymorph also exhibits a slow potential rise on the first charge corresponding to a capacity of 100 mA h g\(^{-1}\) and around 30 mA h g\(^{-1}\) on discharge, again with negligible capacity after 10 cycles.

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**Fig. 3** Variation of voltage with state of charge (Li content) on cycling the three Li\(_2\)CoSiO\(_4\) polymorphs at a rate of 10 mA g\(^{-1}\): (a) \(\beta\)\(_h\), (b) \(\beta\)\(_b\), (c) \(\gamma\)\(_0\).
Attention focusing on the of the presented. three exhibit electrochemical activity when ball-milled, Li$_2$CoSiO$_4$ polymorphs, a necessary prelude to studying solid such structural changes. This study has concentrated on the pure work on these materials is underway, including investigating any a significant difference between the first charge and subsequent agreement with theoretical predictions. For all polymorphs there is milled with carbon. Only one Li could be extracted up to 4.6 V in variation of discharge capacity with cycle number for the carbon-coated first discharge capacity was also improved (60 mA h g$^{-1}$) compared with 80 mA h g$^{-1}$ for ball-milled materials, with a capacity of 40 mA h g$^{-1}$ or ball-milled materials. As is evident in Fig. 4, by extending the voltage cut-off to 4.6 V, 170 mA h g$^{-1}$ is obtained to the same 4.3 V cut-off, 1 for the ball-milled material. This highlights the effectiveness of the carbon coat in "wiring" the electrode and hence the crucial role of electron transport to the particles on the electrochemical performance. This is reinforced on recalling that the bulk particles, without carbon "wiring" demonstrated almost no electrochemical activity (see inset, Fig. 4). By extending the voltage cut-off to 4.6 V, 170 mA h g$^{-1}$, corresponding to 1.1 Li per formula unit, could be extracted. The first discharge capacity was also improved (60 mA h g$^{-1}$) compared with the as-prepared or the ball-milled materials. As is evident in Fig. 4(b) capacity retention is better than for any of the as-prepared or ball-milled materials, with a capacity of 40 mA h g$^{-1}$ observed after 10 cycles. The previous theoretical study suggested extraction of the second Li (associated with the Co$^{3+}$/Co$^{4+}$ couple) would occur at ~5 V, above the stability of the electrolyte and in agreement with the results here (i.e. only 1 Li extracted to 4.6 V). 

In conclusion, the first preliminary results concerning the electrochemical performance of any Li$_2$CoSiO$_4$ materials with, attention focusing on the $\beta_1$, $\beta_2$ and $\gamma_0$ polymorphs, have all been presented. three exhibit electrochemical activity when ball-milled, although with severe capacity fading after a few cycles. In the case of the $\beta_2$ polymorph coating the as-prepared material with carbon switches on electrochemistry without the need for ball-milling and gives superior charge capacity (170 mA h g$^{-1}$ = 1.1 Li per formula unit) and cyclability, compared with the same phase when ball-milled with carbon. Only one Li could be extracted up to 4.6 V in agreement with theoretical predictions. For all polymorphs there is a significant difference between the first charge and subsequent cycling. Usually this is indicative of structural changes. Further work on these materials is underway, including investigating any such structural changes. This study has concentrated on the pure Li$_2$CoSiO$_4$ polymorphs, a necessary prelude to studying solid solutions of Li$_2$M$_{x}$Si$_{y}$O$_{4}$, M = Fe, Mn, Co. It will be interesting to see whether the performance of such solid solutions proves superior to the pure phases as observed in the case of the LiMO$_2$ cathodes e.g. Li(Co$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$)O$_2$ and therefore of technological significance.

P. G. B. is indebted to the EPSRC and the EU for financial support.

Notes and references

§ Hydrothermal synthesis of Li$_2$CoSiO$_4$ : 0.05 mol. LiOH·H$_2$O (Aldrich), was added to 0.0125 mol SiO$_2$ (Aldrich) in 20 ml of distilled water and stirred. 0.0125 mol CoCl$_2$ (Aldrich) was added to 10 ml of ethylene glycol and stirred under gentle heat until solution occurred. The two sols until dissolution occurred. The solutions were then mixed with stirring and the slurry transferred to a 40 ml Teflon-lined autoclave. The sealed autoclave was heated at 150 °C for 72 h. The product was filtered off and dried at 60 °C overnight.


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Structural Polymorphism in Li2CoSiO4 Intercalation Electrodes: A Combined Diffraction and NMR Study

A. Robert Armstrong,†,§ Christopher Lyness,†,§ Michel Ménetrier,†,§ and Peter G. Bruce*,†,§

1EuStCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, U.K.,
2ICMCB-CNRS, 87 Av. Schweitzer, 33608 Pessac, France, and 3Allstore European Research Institute,
33 Rue Saint Leu, 80039 Amiens Cedex, France

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Li2CoSiO4 was prepared in three polymorphic forms. The βII (Pnn21) polymorph was obtained by hydrothermal synthesis (150 °C), and subsequent heat treatments yielded the βI (Pbn21) form (700 °C) and the γ (P21/n) form (1100 °C) then quenching from 850 °C. Rietveld refinement of X-ray and neutron powder diffraction patterns reveal considerable Li/Co mixing for βI, very moderate mixing for βII, and no mixing for γ. 1Li MAS NMR spectra have been recorded for the three forms. The mechanism of the Fermi contact interaction that leads to negatively shifted signals is as yet unexplained, but the nature and the number of signals were analyzed in relation to the site occupancies for each compound. The agreement is good for βII, although the extent of disorder leads to very poorly defined NMR signals; it is reasonable (although not fully quantitative) for βI, where well-defined NMR signals can be assigned to definite environments; finally, the γ sample surprisingly leads to a single rather broad NMR signal, whereas two well-defined and rather different environments are present in the structure deduced from diffraction.

Introduction

New batteries are needed urgently to meet the demands of modern technology and to address the challenge of Global Warming. The layered Li intercalation compound, LiCoO2, is used as the cathode in the majority of commercial rechargeable lithium-ion batteries.1,2 A number of alternative layered compounds, such as LiNiO2 or LiMnO2, have also been considered: their solid anion, such as the olivine LiFePO4, could act as lithium intercalation hosts and thus operate as cathodes in rechargeable lithium batteries, represented a significant breakthrough.6 Bonding of the oxygen to the phosphorus stabilizes the former with respect to evolution from the structure, an important problem on charging simple transition metal oxides. Recently, an entirely new class of lithium intercalation compounds based on silicates, Li2M2SiO4, where M = Fe, Mn, Co, has been described.7 Of these the most studied is Li2FeSiO4; it has been shown that at 60 °C, 165 mAhg−1 of charge may be extracted, equivalent to 1 lithium per formula unit; with reversible lithium cycling over the range Li1−xFeSiO4, 1.15 < x < 2, corresponding to 140 mAhg−1 when suitably carbon coated and with a particle size of <150 nm.7a In this paper we focus on Li2CoSiO4.

The Li2MSiO4 compounds (M = Fe, Mn, Co) belong to a large family of materials known as the tetrahedral structures.8 Generally the tetrahedral structures are composed of tetragonally packed oxide ions (a distorted form of hexagonal close packing) within which half the tetrahedral sites are occupied by cations, such that face sharing between the pairs of tetrahedral sites is avoided.9 These...
tetrahedral structures exhibit a rich polymorphism, with more than 8 different polymorphs known. They may be divided into two families, designated β and γ. In the case of the former all the tetrahedra point in the same direction, perpendicular to the close-packed planes, and share only corners with each other. In the case of the γ polymorphs, the tetrahedra are arranged in groups of three with the central tetrahedron pointing in the opposite direction to the outer two, with which it shares edges. Where both β and γ polymorphs exist for a given compound the latter is stable at higher temperatures, with the β to γ transformation involving inversion of half the tetrahedral sites. Several variants of both β and γ exist, involving either ordering or distortions of the parent structures; they are designated β1, γ0, γ11, etc. In many instances these phases may be quenched to room temperature, where they exhibit long-term stability. Originally the different polymorphs were distinguished only on the basis of differences in their powder X-ray diffraction patterns. More recently, the complete crystal structures of a few isolated examples have been solved.

As a result of the complex polymorphism exhibited by the tetrahedral structures it is beneficial, when studying the structures of these materials to employ techniques that probe both short- and long-range structure. Magic angle spinning NMR was chosen as a probe of the local structure since it was shown to be very powerful in assessing the purity of high-pressure treated Li2MnSiO4 (Pmn21), characterized by a well-defined single type of Li. Since Li is a weak scatterer of X-rays, neutron powder diffraction was chosen to investigate the long-range structure in three polymorphs of Li2CoSiO4.

**Experimental Section**

The βII polymorph was prepared by hydrothermal synthesis. LiOH·H2O (0.05 mol) (Aldrich) was added to 0.0125 mol of SiO2 (Aldrich) in 20 mL of distilled water and stirred. CoCl2 (0.0125 mol) (Aldrich) was added to 10 mL of ethylene glycol and stirred under gentle heat until dissolution occurred. The two solutions were then mixed with stirring, and the slurry was transferred to a 40 mL Teflon-lined autoclave. The remaining volume was topped up with distilled water. The sealed autoclave was heated at 150 °C for 2 h and then lowering the temperature to 850 °C for 2 h and then lowering the temperature to 850 °C whereupon the material was quenched to room temperature.

Powder X-ray diffraction data were collected on a Stoe STADI/P diffractometer operating in transmission mode with FeKα radiation (λ = 1.936 Å) to eliminate Co fluorescence.

**Results**

Powder X-ray diffraction patterns of the three Li2CoSiO4 polymorphs βII, βI and γ0, prepared as described in the Experimental Section are presented in Figure 1.

**Neutron Diffraction.** Powder diffraction data for the as-prepared product of hydrothermal synthesis could be indexed on the basis of a primitive orthorhombic unit cell, space group Pmn21. According to the notation of West and Glasser this represents the βII polymorph. Rietveld refinement of the powder neutron diffraction data using this space group gave an excellent fit with Rwp of 1.63%. However, instead of the ideal βII cation arrangement with all the Co in the 2a tetrahedral sites and Li in 4b sites, pronounced disorder was observed. The transition metal 2a site is effectively exclusively occupied by lithium, while the 4b site is approximately equally occupied by lithium and cobalt. This gives a site in which the average neutron scattering length is close to zero, giving poor definition of the cation position. Accordingly, a combined X-ray and neutron refinement was carried out to give better characterization of this 4b site. Final refined parameters are shown in Table 1, and the fit to the neutron data is shown in Figure 2a. The final refined composition corresponds to Li1.96Co1.04SiO4, within 2 e.s. d.s of the ideal stoichiometry. As indicated above the β polymorphs all exhibit corner shared tetrahedra, aligned such that the vertices point along the c direction. In βII Li2CoSiO4 chains of the Li/Co tetrahedra run along the a direction parallel to chains of alternating...

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Table 1. Refined Crystallographic Parameters for $\beta_{II}$ Li$_2$CoSiO$_4$, Space Group Pmn2$_1$\(^a\)

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyckoff symbol</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>B$_{iso}$</th>
<th>occupancy</th>
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<td>Li1</td>
<td>2a</td>
<td>0</td>
<td>0.1515(18)</td>
<td>-0.0121(19)</td>
<td>0.94(19)</td>
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<tr>
<td>Si1</td>
<td>2a</td>
<td>0.5</td>
<td>0.1743(7)</td>
<td>0</td>
<td>0.50(3)</td>
<td>1</td>
</tr>
<tr>
<td>Li2/Co1</td>
<td>4b</td>
<td>0.264(4)</td>
<td>0.293(4)</td>
<td>0.442(6)</td>
<td>0.48/0.52(1)</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4b</td>
<td>0.2839(3)</td>
<td>0.3180(4)</td>
<td>0.9070(8)</td>
<td>0.60(2)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>2a</td>
<td>0</td>
<td>0.1164(4)</td>
<td>0.4004(11)</td>
<td>0.47(3)</td>
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<tr>
<td>O3</td>
<td>2a</td>
<td>0.5</td>
<td>0.1789(6)</td>
<td>0.3362(8)</td>
<td>0.74(3)</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ R$_e$ = 1.46%, R$_{wp}$ = 1.63%, R$_p$ = 2.70%, a = 6.2558(2) Å, b = 5.3584(2) Å, c = 4.9357(2) Å.

LiO$_4$ and SiO$_4$ tetrahedra. Bond lengths and angles are shown in Table 4.

By heating the as-prepared material to 700 °C for 2 h a polymorph with double the lattice parameter along the b direction is obtained. Powder diffraction data for this phase could be indexed in space group Pbnm. A Li$_2$CoSiO$_4$ phase adopting this space group was previously reported by Yamaguchi et al., who described it as the $\beta_{II}$ polymorph.\(^{11a}\) However, using the notation of West and Glasser, this should more properly be designated $\beta_1$.

Rietveld refinement of the powder neutron diffraction data, using starting coordinates from Yamaguchi et al., gave an excellent fit with R$_{wp}$ of 1.77%. A small degree of site disorder was observed with 2.4(16)% Li on the Co site and 8.6(14)% Co on one of the two Li sites. Final refined parameters are shown in Table 2, and the fit to the data is shown in Figure 2b. Again the final refined composition corresponds to Li$_{1.94}$Co$_{1.06}$SiO$_4$, within 2 e. s.d.s of the ideal stoichiometry. While the tetrahedra are again all aligned along the c direction, they are ordered in a different manner. There are chains of alternating LiO$_4$ and CoO$_4$ tetrahedra along a, parallel to chains of alternating LiO$_4$ and SiO$_4$ tetrahedra. Bond lengths and angles are given in Table 5.

The product of heating the $\beta_{II}$ polymorph to 1100 °C with quenching from 850 °C generated a third polymorph (7). This is also characterized by a lattice doubling along the b direction and can be indexed in the monoclinic space group P2$_1$/n. Once more Rietveld refinement of the powder neutron diffraction data gave an excellent fit with R$_{wp}$ of 1.62%. No site disorder was observed for this polymorph.

Final refined parameters are shown in Table 3, and the fit to the data is shown in Figure 2c. In the $\gamma$ polymorphs the tetrahedra are arranged in groups of 3 with the central tetrahedron pointing in the opposite direction to the outer 2, with which it shares edges. In the $\gamma$ Li$_2$CoSiO$_4$ group this structure of 3 edge-sharing tetrahedra consists of Li–Li–Co. Bond lengths and angles are given in Table 6.

Figure 3 shows schematic representations of the structures of the 3 polymorphs revealing the different connectivity.

NMR. The full $^7$Li MAS NMR spectra for the three polymorphs are shown in Figure 4. Integration of the whole signal (including the spinning sidebands) leads to very similar amounts of Li per mass of sample for the three polymorphs. Although one cannot exclude the possibility that the T2 relaxation time could be different for the three polymorphs, this suggests that all the Li are observed in the three cases. Most isotropic signals are strongly negatively shifted due to Fermi contact interaction from the paramagnetic Co$^{3+}$ ions present in the structure.

NMR Shifts – Background. $^7$Li NMR Fermi contact shifts are due to the transfer of some density of electron spins to the site of the Li nucleus from the orbitals of a neighboring ion carrying unpaired electrons. Based on earlier Li NMR characterization of Li-transition metal oxides and DFT modeling of the electron spin distribution, the transfer mechanisms elucidated so far can be described as follows.\(^{14}\)

If a orbital carries an unpaired electron spin, it aligns with the applied field. If this orbital can overlap with the 2s orbital of Li, either directly 2s-nd (like a spin in a t$_{2g}$ orbital of an octahedral transition metal ion with a Li in an edge-sharing octahedron) or via p orbitals of O 2s-2p-nd (like a spin in an e$_g$ orbital of an octahedral transition metal ion with a Li in a corner-sharing octahedron), a delocalization mechanism operates, and Li receives a density of unpaired spin with the same polarization. This leads to a positive Fermi contact shift.

A fully occupied d orbital (therefore carrying no unpaired spin) can be polarized by unpaired spins in another (higher energy) d orbital of the same transition metal ion that carries unpaired spins (parallel to the applied field). This polarization consists in a separation (in space and in energy) of the two otherwise paired spins. The spin (from the pair) with the same orientation as that of the unpaired spin in the other orbital is attracted by this unpaired spin. Therefore, the spin (from the pair) with the opposite orientation is more spread out in the orbital. If this polarized orbital overlaps with the 2s of Li, again either directly or via oxygen, Li receives a density of spin with opposite orientation to the applied field. This leads to a negative Fermi contact shift. One such case is e$_g$ spins for an octahedral transition metal ion that polarize full t$_{2g}$ orbitals; the latter can overlap with an edge sharing octahedral Li. Another case is electron spins in a (nonbonding) t$_{2g}$ orbital that polarize the bonding counterpart of an empty antibonding e$_g$ (that should actually be called e$_g^*$). This polarized bonding e$_g$ orbital can overlap via O with a Li in a corner-sharing octahedron.

This is relatively straightforward in octahedral coordination where the e$_g$ orbitals point to the oxygens and the t$_{2g}$ orbitals point to the edges, and the Li in edge or corner sharing octahedra are ideally placed to interact with these.

orbitals. However, in tetrahedral coordination for the transition metal ion and for Li, the e and t₂ orbitals point, respectively, toward the edges (perpendicularly) and to the faces (not perpendicular to a face but parallel to two of the opposite edges) of the tetrahedron, and the Li in adjacent tetrahedra are not in obvious positions to overlap with these orbitals.

Following these rules of thumb, the shifts expected for the Li₂CoSiO₄ polymorphs can nevertheless be tentatively discussed as follows.

Cobalt has an oxidation state +2 in these compounds, and its electronic configuration in a tetrahedron is therefore e⁴ t₂³ (the e orbitals are fully occupied, while each t₂ orbital contains one unpaired spin).

In the β polymorphs, the nature of the connection of any tetrahedral Li site with the surrounding ones containing Co is represented in Figure 5. The Co tetrahedra present either face-to-face, face-to-edge, or edge-to-face connection relative to the Li tetrahedron. Following the rules just expressed, a Co²⁺ ion with a face-to-face connection would have t₂ orbital lobes pointing toward this Li through the facing faces of the tetrahedra (face-to-face geometry); and one would expect the transfer of an electron spin density aligned with the applied field, leading to a positive Fermi contact shift. A similar situation arises for the face-to-edge connection (the orbital exiting from the face now points to Li through the edge of its tetrahedron). Finally, for the edge-to-face connection the fully occupied but polarized e orbital points from the edge but perpendicularly, in such a way that it is not directed toward the Li tetrahedron, and the latter should not receive significant electron spin density with polarization opposite to the applied field.

The experimental shifts in these polymorphs are however clearly negative (Figure 4). There is therefore a polarization mechanism not taken into account in our discussion. This most probably operates via the oxygens, through bonding counterparts of the e and t₂ orbitals discussed so far. If these bonding (mostly of O character) orbitals are polarized by the spin-carrying t₂ orbital, they must transfer an electron spin density leading to a negative Fermi contact shift via the O, superseding the direct overlap of the t₂ orbital through the faces. The precise interplay and respective geometries of the t₂ orbital and of the bonding ones remains to be studied in detail in a tetrahedral coordination.

As concerns the γ₀ polymorph, the same type of connection between the tetrahedra occurs (although with considerable distortion in the alignment of the tetrahedral) (Figure 6), but edge-sharing also occurs in addition, as discussed in the Introduction and shown in Figure 6. In this configuration, a polarized e orbital from Co should point directly to Li through the common edge, contributing a negative Fermi contact shift that could explain the negative shift for one of the Li sites.

Despite this lack of global understanding of the spin transfer mechanism, we can still analyze the NMR signals in terms of number of signals with respect to the possible local environments due to the actual Li/Co site distribution deduced from the Rietveld analyses.

β₁ Polymorph. The Li (2a) site (Figure 6) is surrounded by 4 (0.52Co/0.48Li) tetrahedra with a face-to-face geometry; this should lead to a distribution of 5 resonances, out of which 3 have significant magnitudes ((1:2:3 Co) with probabilities (0.23:0.37:0.27)). The remaining two have probabilities much lower than 0.10. In addition, the
same Li is also surrounded (Figure 7) by two (0.52Co/0.48Li) tetrahedra with a face-to-edge-geometry and two with an edge-to-face geometry. This should lead to a further splitting of each of the resonance just mentioned into 9 resonances with rather similar magnitudes (probabilities ranging from 0.05 to 0.19).

The Li/Co site (0.48Li/0.52Co) (Figure 8) is surrounded by 4 (0.52Co/0.48Li) tetrahedra (2 face-to-face, 1 face-to-edge, 1 edge-to-face). This should lead to a distribution of 12 resonances with rather similar magnitudes (probabilities from 0.05 to 0.13). Altogether, the distribution of resonances for the two crystallographic types of Li is therefore expected to be very broad.

The experimental pattern (Figure 9) is in good agreement with this. It shows a set of at least two broad resonances, but, not knowing the value of the shift caused by each Co in each possible environment, one cannot infer that these two apparent signals correspond to the two crystallographic sites. It is more likely that for a given crystallographic site the very broad distribution in the possible number of Co leads to a set of signals contributing within the whole ppm range. For both types of Li, among all the possibilities is the one having zero adjacent Co; such a configuration occurs statistically for 5% of the Li in 2a and for 5% of the 0.48 Li in Li/Co site. It is reasonable to assume that these environments lead to the contribution observed around 0 ppm in the spectrum. Besides, it is interesting to note that contributions with positive shifts are also present in the overall spectrum. These may correspond to cases where the delocalization mechanisms mentioned above are not overtaken by a polarization via O. Improvement of the modeling of these interaction mechanisms is clearly needed in this respect.

**β** Polymorph. The Li site (containing 0.91Li) is surrounded as in Figure 4 by four tetrahedra containing 0.98 Co: two with a face-to-face geometry, one with a face-to-edge geometry, and one with an edge-to-face geometry. This should lead to a distribution of 12 signals

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyckoff symbol</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>occupancy</th>
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<tr>
<td>Co1</td>
<td>4a</td>
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<td>0.1652(9)</td>
<td>0.253(3)</td>
<td>0.61(11)</td>
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<td>4a</td>
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<td>0.1638(13)</td>
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<td>Li2</td>
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<td>0.2402(13)</td>
<td>0.77(9)</td>
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<tr>
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<td>0.33(6)</td>
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<td>4a</td>
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<td>0.5578(14)</td>
<td>0.1459(6)</td>
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\[ a = 6.25990(10) \text{ Å}, \ b = 10.6892(2) \text{ Å}, \ c = 4.92866(8) \text{ Å}. \]

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<td>-0.0047(10)</td>
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<td>Li2</td>
<td>4e</td>
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<td>0.3400(2)</td>
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<td>0.34(2)</td>
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\[ a = 6.27433(10) \text{ Å}, \ b = 10.6854(2) \text{ Å}, \ c = 5.01631(9) \text{ Å}, \ \beta = 90.600^\circ. \]

**Table 2. Refined Crystallographic Parameters for β**<sub>1</sub>**Li<sub>2</sub>CoSiO<sub>4</sub>, Space Group Pbn2<sub>1</sub>**

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<td>122.4(5)</td>
<td>103.7(3)</td>
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<td>2.044(11)</td>
<td>107.7(5)</td>
<td>1.922(10)</td>
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<td>SiO4</td>
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<td>1.622(3)</td>
<td>112.9(3)</td>
<td>111.6(2)</td>
<td>106.0(2)</td>
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<td></td>
<td>O1</td>
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<td>106.0(2)</td>
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<tr>
<td></td>
<td>O2</td>
<td>1.635(5)</td>
<td>1.660(4)</td>
<td>1</td>
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<tr>
<td>(Li/Co)O4</td>
<td>O1</td>
<td>2.113(2)</td>
<td>91.8(9)</td>
<td>111.0(11)</td>
<td>117.2(13)</td>
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<tr>
<td></td>
<td>O1</td>
<td>2.305(3)</td>
<td>100.5(11)</td>
<td>106.3(12)</td>
<td>123.1(13)</td>
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<td></td>
<td>O2</td>
<td>1.912(2)</td>
<td>1.682(2)</td>
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corresponding to Li with different numbers of Co neighbors in different positions, but one signal (the one with 4 Co) should dominate (92% of total magnitude, the others representing less than 4%).

The Li2 site, with a Li occupancy of 1, is similarly surrounded by 0.98 Co sites, leading to a similar distribution of signals. In addition, this Li2 site also is similarly surrounded by 0.09 Co (Li1) sites that further splits each of these 12 resonances into a distribution of 12, of which the major one is 0 Co and corresponds to 69% of the total (the rest less than 14%).

The 0.02 Li present in the 0.98 Co site do not have any connection with a Co-rich site. However, again they have the same type of surrounding as shown in Figure 4 with the 0.09 Co tetrahedra. This again leads to a distribution of 12 resonances for this 0.02 Li, the major one being the one with 0 Co corresponding to 69% of the total (the others are less than 14%). These 0.02 × 0.69 Li should resonate at 0 ppm since they do not have any connection to a Co tetrahedron.

The NMR spectrum of the βI polymorph (Figure 10) exhibits three well-defined signals; following the analysis described above, they can tentatively be assigned as shown in the figure. The other resonances would be too distributed to be identified, although they should account for 25% of the total amount of Li. In addition, a very weak narrow signal close to −1.5 ppm most probably corresponds to an unidentified diamagnetic impurity.

| Table 5. Refined Bond Lengths and Angles for βI Li2CoSiO4, Space Group Pbn21 |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| CoO4 | O1 | O2 | O3 | O4 |
| O1 | 1.957(16) | 108.5(6) | 109.7(6) | 109.4(6) |
| O2 | 2.036(12) | 105.7(6) | 112.2(6) | 111.3(6) |
| O3 | 1.928(13) | 1.980(11) |

| SiO4 | O1 | O2 | O3 | O4 |
| O1 | 1.625(8) | 111.0(4) | 106.9(4) | 111.5(3) |
| O2 | 1.631(3) | 109.2(2) | 109.6(4) | 108.6(4) |
| O3 | 1.632(2) | 1.650(8) |
| O4 | 1.650(8) |

| Li1O4 | O1 | O2 | O3 | O4 |
| O1 | 2.004(16) | 109.0(8) | 114.8(9) | 107.0(8) |
| O2 | 2.074(16) | 106.6(8) | 105.9(8) | 113.3(9) |
| O3 | 1.876(18) | 1.916(22) |
| O4 | 1.928(9) |

| Li2O4 | O1 | O2 | O3 | O4 |
| O1 | 2.062(17) | 104.8(7) | 104.6(7) | 122.5(4) |
| O2 | 2.012(7) | 107.3(3) | 107.7(7) | 109.2(7) |
| O3 | 1.958(7) | 1.992(17) |
| O4 | 1.992(17) |

| Table 6. Refined Bond Lengths and Angles for γ0 Li2CoSiO4, Space Group P21/n |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| CoO4 | O1 | O2 | O3 | O4 |
| O1 | 1.955(5) | 112.8(2) | 109.4(2) | 111.9(2) |
| O2 | 1.960(5) | 95.7(2) | 118.0(2) | 118.0(2) |
| O3 | 2.022(4) | 107.3(4) | 107.5(2) | 1.942(5) |
| O4 | 2.022(4) | 1.942(5) |

| SiO4 | O1 | O2 | O3 | O4 |
| O1 | 1.629(2) | 110.25(12) | 107.72(14) | 108.98(14) |
| O2 | 1.629(2) | 110.25(12) | 110.94(16) | 108.61(16) |
| O3 | 1.632(3) | 1.632(3) | 1.633(3) | 1.633(3) |
| O4 | 1.633(3) |

| Li1O4 | O1 | O2 | O3 | O4 |
| O1 | 1.926(6) | 113.4(3) | 112.0(3) | 109.6(3) |
| O2 | 1.946(6) | 117.0(3) | 117.0(3) | 97.1(3) |
| O3 | 1.979(7) | 106.3(3) | 106.3(3) | 2.025(6) |
| O4 | 1.979(7) | 106.3(3) |

| Li2O4 | O1 | O2 | O3 | O4 |
| O1 | 1.930(5) | 106.8(2) | 111.6(3) | 117.7(3) |
| O2 | 1.946(6) | 89.9(2) | 93.3(23) | 93.3(23) |
| O3 | 2.053(6) | 127.1(2) | 1.962(7) |
| O4 | 2.053(6) | 1.962(7) |
assignment, is shown in Table 7. The 0 ppm signal is clearly too intense for this assignment, which would imply more Li in the Co site (or less Co in the adjacent 0.91Li/0.09Co site). This might however also partly be due to difficulties in subtracting the narrow additional component in the spectral decomposition for integration and to the influence of the additional unresolved distribution of signals representing 25% of the total amount of Li.

$\gamma_0$ Polymorph. In the $\gamma_0$ polymorph there is no Li/Co mixing according to the Rietveld results reported in this paper, so that only one resonance is expected for each Li site.

The Li in the Li1 site (Figure 6) is connected to four Co tetrahedra with globally the same geometry as in the other two polymorphs (2 face-to-face, 1 face-to-edge, 1 edge-to-face). However, the arrangement of the tetrahedra is so distorted that one can hardly expect the t$_2$ or the polarized e orbitals of Co to point toward this Li.

The Li in the Li2 site (Figure 6) has a quite different environment, since, in addition to “face-to-face” connection with two Co tetrahedra, it also shares one edge with a Co tetrahedron. Following the mechanisms discussed in this paper, this is an ideal situation
for a negative shift due to transfer of electron spin density from the polarized e orbital, although Li2 appears quite off-centered in its tetrahedron (Figure 11).

The $^7$Li NMR spectrum of the $\gamma_0$ polymorph (Figure 12) however shows a single resonance with a 58\% Gaussian – 42\% Lorentzian line shape. Variable temperature (cooling to about 250 K), $^6$Li resonance at 44.2 MHz, or $^7$Li resonance at 38.9 MHz with a 30 kHz spinning did not lead to any sign of splitting of this signal. Not knowing the shift mechanisms in this system, we cannot exclude the possibility that the shifts for the two types of Li happen to coincide, although this appears somewhat unlikely for such different environments. Besides, the width of the line (as compared to the other 2 polymorphs) would rather suggest a distribution of signals that should result from some kind of Li/Co exchange.
Conclusion

Li$_2$CoSiO$_4$ was prepared in three pure polymorphic forms ($\beta_{II}$, $\beta_{I}$, and $\gamma_{0}$) as described previously.$^{7g}$ Rietveld refinement of X-ray and neutron powder diffraction patterns demonstrated a considerable Li/Co mixing for $\beta_{II}$ with close to 50/50 occupation in the 4b site. Very moderate mixing in the Co site (2.4% Li) and one of the Li sites (8.6% Co) was observed for the $\beta_{I}$ polymorph, and no mixing was found for $\gamma_{0}$. $^7$Li MAS NMR spectra were recorded for all 3 polymorphs. The mechanism of the Fermi contact interaction that leads to the observed negatively shifted signals cannot be explained based on our present understanding. A polarization-type mechanism involving bonding orbitals with O character seems to overwhelm the expected delocalization mechanism from the t$_2$ orbitals of tetrahedral Co$^{2+}$ ions that carry the unpaired spins. However, the nature and the number of signals were analyzed in relation with the site occupancies for each compound. Very poorly defined signals are obtained for $\beta_{II}$, in good agreement with the considerable extent of disorder expected from the diffraction results. For $\beta_{I}$, well-defined NMR signals can be assigned to definite environments, in reasonable (although not fully quantitative) agreement with the expected structure and site occupancies. Finally, the $\gamma_{0}$ sample surprisingly leads to a single rather broad NMR signal, whereas two well-defined and rather different environments are present in the structure deduced from diffraction.

Acknowledgment. We thank Dany Carlier for fruitful discussions. Peter G. Bruce is indebted to EPSRC for financial support.

Table 7. Relative Magnitude of the $^7$Li NMR Signals in the $\beta_{I}$ Polymorph Compared to the Values Expected Based on the Analysis Described in the Text

<table>
<thead>
<tr>
<th>signal</th>
<th>0 ppm</th>
<th>-68 ppm</th>
<th>-105 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>expected magnitude %</td>
<td>0.9</td>
<td>56.3</td>
<td>42.7</td>
</tr>
<tr>
<td>integration %</td>
<td>5.8</td>
<td>48.43</td>
<td>45.53</td>
</tr>
</tbody>
</table>

Figure 10. $^7$Li MAS NMR spectrum (isotropic signals) of the $\beta_{I}$ polymorph (116 MHz, 30 kHz spinning, Hahn echo).

Figure 11. Open view of the Li(2)O$_4$ tetrahedron.

Figure 12. $^7$Li MAS NMR spectrum (isotropic signal) of the $\gamma_{0}$ polymorph (116 MHz, 30 kHz spinning, Hahn echo).
Appendix iii: X-ray diffraction pattern of the Li$_2$CoSiO$_4$ solid state precursor

Appendix iv: Galvanostatic profile of 1$^{st}$ charge of $\beta$$_1$ Li$_2$CoSiO$_4$ with different electrolytes. A) 1M Lithium bis(oxalate)borate (LiBOB) in polycarbonate(PC), B)1M Sulfane in polycarbonate(PC), C) LP31, 1M LiPF$_6$ in 2:1 ethylene carbonate(EC):dimethyl carbonate(DMC), D) LP30, 1M LiPF$_6$ 1:1 ethylene carbonate(EC): dimethyl carbonate(DMC)
Appendix v: DC voltage vs. Current plot for ball-milled $\beta_0 \text{Li}_2\text{CoSiO}_4$ material
Appendix vi: Galvanostatic profile of 1st discharge of $Li_{1.08}V_{0.92}O_2$ with different electrolytes. 
A) 1M LiPF$_6$ ethylene carbonate(EC):polycarbonate(PC), B) 1M LiClO$_4$ in polycarbonate(PC), 
C) 1M LiAsF$_6$ in polycarbonate, D) LP31 LP31, 1M LiPF$_6$ in 2:1 ethylene carbonate(EC):dimethyl carbonate(DMC), 
E) LP30, 1M LiPF$_6$ 1:1 ethylene carbonate(EC): dimethyl carbonate(DMC)
Appendix

Published Paper:

The lithium intercalation process in Li$_{1+x}$V$_{1-x}$O$_2$: a low voltage anode for lithium batteries

AR Armstrong, C Lyness, P Panchmatia, MS Islam, PG Bruce – Nature Materials
The lithium intercalation process in the low-voltage lithium battery anode Li$_{1+x}$V$_{1-x}$O$_2$

A. Robert Armstrong$^1$, Christopher Lyness$^1$, Pooja M. Panchmatia$^2$, M. Saiful Islam$^2$*
and Peter G. Bruce$^1$*

Lithium can be reversibly intercalated into layered Li$_{1+x}$V$_{1-x}$O$_2$ (LiCoO$_2$ structure) at $\sim$0.1 V, but only if $x > 0$. The low voltage combined with a higher density than graphite results in a higher theoretical volumetric energy density; important for future applications in portable electronics and electric vehicles. Here we investigate the crucial question, why Li cannot intercalate into LiVO$_2$ but Li-rich compositions switch on intercalation at an unprecedented low voltage for an oxide? We show that Li$^+$ intercalated into tetrahedral sites are energetically more stable for Li-rich compositions, as they share a face with Li$^+$. We also show that Li$^+$ in the transition metal layers triggers a change in the structure of the oxide layers from cubic to hexagonal packing because the Li$_x$VO$_2$ structure can accommodate two Li per formula unit in tetrahedral sites without face sharing. Such understanding is important for the future design and optimization of low-voltage intercalation anodes for lithium batteries.

**Initial characterization**

Li$_{1+x}$V$_{1-x}$O$_2$ was prepared by solid state reaction as described in the Methods section. Powder X-ray diffraction patterns for $x = 0$, 0.03 and 0.07 are shown in Fig. 1a. All peaks may be indexed on the basis of the $\alpha$-FeO$_2$ (LiCoO$_2$) crystal structure, space group $\bar{R}3m$. The materials are highly crystalline, exhibiting sharp diffraction peaks (FWHM = 0.11° in 2θ for the (104) reflection of $x = 0.07$). These results are consistent with the particle sizes observed by electron microscopy, Fig. 1b, which are typically 100–200 nm and with Brunauer–Emmett–Teller (BET) surface areas of 1–5 m$^2$/g. Compositions were confirmed by structure refinement, inductively coupled plasma (ICP) and vanadium oxidation state analysis, as discussed later.

**Structures of the as-prepared materials**

To understand the intercalation process, and in particular why extra Li in the structure is necessary to facilitate intercalation, it is first necessary to establish the structures of the as-prepared materials. Rietveld refinement, employing combined X-ray and neutron diffraction data, because Li is insensitive to X-rays and V is insensitivity to neutrons, was carried out on LiVO$_2$ and Li$_{0.07}$V$_{0.93}$O$_2$, based on a structural model derived from LiCoO$_2$ ($\alpha$-FeO$_2$) in which Co was replaced by V. The only positional parameter constrained by symmetry is the $z$ coordinate of O; this was allowed to vary freely. In view of the insensitivity of V to neutrons the temperature factor for the transition metal site was fixed in the course of the refinements; those of all other sites were varied independently. The cation distribution was investigated by refining Li and V on the transition metal, 3a, and alkali metal, 3b, sites of the $\bar{R}3m$ space group. In the case of the stoichiometric material, no occupancy of V on the alkali metal sites was observed; therefore, in the final refinements only Li was located on the alkali metal sites. The occupancy of the transition metal sites was 0.99/0.01(1) V/Li. The final refined composition was LiVO$_2$ within one standard deviation. For Li$_{0.07}$V$_{0.93}$O$_2$, again no occupancy of the alkali metal sites by V was detected, only Li. The Li and V

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1 EastChem, School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK.
2 Department of Chemistry, University of Bath, Bath, BA2 7AY, UK.
3e-mail: m.s.islam@bath.ac.uk; p.g.bruce@st-and.ac.uk.
occupancy on the transition metal sites were varied independently, giving values of 0.92(1) and 0.08(1) and a composition Li$_{1.08}$V$_{0.92}$O$_2$. The final parameters are presented in Supplementary Table S1 along with the corresponding R-factors, which indicate excellent fits. The fitted profiles are available as Supplementary Fig. S1. Chemical analysis was carried out by ICP, following the procedure described in the Methods section. Compositions of Li$_{1.01}$V$_{0.99}$O$_2$ and Li$_{1.07}$V$_{0.93}$O$_2$, ±0.02 were obtained. Oxidation state analysis by redox titration, also described in the Methods section, gave values of +3.03 and +3.16 ± 0.05 respectively. The compositions derived from the ICP and oxidation state analyses are, within errors, in accord with those derived from the refined data, Supplementary Table S1.

**The intercalation process**

Considering first stoichiometric LiVO$_2$, the load curve, Fig. 2, exhibits a short plateau at 0.8 V corresponding to the potential of electrolyte reduction observed previously for graphite and other low voltage anodes.$^{27-29}$ The low voltage plateau is very short (~40 mA h g$^{-1}$), occurs at 0 V; there is no corresponding plateau on charge and no cycling. No change in the X-ray or neutron diffraction patterns was observed up to the end of discharge, hence understand the process taking place in these early stages of the load curve, whereas the focus of the present paper is the two-phase nature of the intercalation reaction; the combination of which leads to strain at the interface between the two phases. However, the composite electrode structure (for example distribution of conducting matrix) may also play a role. Better capacity retention has been reported.$^{31,32}$ The extent of the low voltage plateau increases markedly with increasing lithium content up to $x = 0.07$, more lithium-rich compositions do not exhibit higher discharge capacities. The load curves are similar to previous reports.$^{2-4}$

Turning to Li$_{1.07}$V$_{0.93}$O$_2$, it also exhibits a short plateau at 0.8 V, Fig. 2. However, in contrast to LiVO$_2$, the low voltage plateau is extensive, commences at ~0.1 V with a slight downward slope, possesses a corresponding plateau on charge (lithium extraction) and the material can be cycled (inset Fig. 2). The observed fading of capacity on cycling may be due to the volume change (~25%) and to the two-phase nature of the intercalation reaction; the combination of which leads to strain at the interface between the two phases. Further detailed studies are required to fully explore and understand the process taking place in these early stages of the load curve.
Neutron counts

\[ d \text{-spacing (Å)} \]

Figure 3 | Expanded regions of the powder neutron diffraction patterns collected at various states of charge for Li_{1.07}V_{0.93}O_2. P1 and P2 are prominent peaks of the host structure and Li_2VO_2 respectively whilst T represents an intermediate phase containing tetrahedral lithium ions. The asymmetry of the peak at 2.4 Å in the charged material may be due to a small amount of residual Li_2VO_2 phase. Note that neutron counts are in arbitrary units.

Two phase refinements were carried out using combined powder X-ray and neutron diffraction data collected on the \( x = 0.07 \) material at 160 mA h g\(^{-1}\) and full discharge. The fitted profiles are available as supplementary data, Supplementary Fig. S2, and demonstrate that the fit is good. Crystallographic parameters for the new, Li_2VO_2 phase are presented in Supplementary Table S2. The structure of Li_2VO_2 is composed of hexagonal close packed oxide ions with vanadium ions occupying alternate sheets of octahedral sites between the oxide ion layers and lithium ions occupying all of the tetrahedral sites in the intervening layers, Fig. 4. On charging the cell to 2 V, the Li_2VO_2 phase converts back to the original structure. High-resolution transmission electron microscopy data collected on samples discharged to 160 mA h g\(^{-1}\), Supplementary Fig S3, are consistent with the presence of two phases in the material. Overall the combined X-ray and neutron refinements confirm that Li intercalation occurs via a 2-phase mechanism between LiVO_2 and Li_2VO_2 (refs 1,2).

On the basis of the ratios of the two phases extracted from fitting the powder diffraction data at 160 mA h g\(^{-1}\) and at the end of discharge, the amount of lithium intercalated as the discharge proceeds along the plateau has been calculated. The analysis indicates that the amount of intercalated lithium corresponds to charges of 65 and 166 mA h g\(^{-1}\) respectively, compared with the actual charges passed along the plateau of 90 and 240 mA h g\(^{-1}\). Clearly, the charge passed on progressing along the discharge plateau exceeds the amount of lithium inserted into the structure, and this discrepancy increases with increasing depth of discharge, the difference being 25 mA h g\(^{-1}\) and 74 mA h g\(^{-1}\) respectively.

A reduction process in addition to Li intercalation is taking place along the plateau. This may involve more SEI layer formation or the formation of soluble products from electrolyte reduction. The difference between the lengths of the charge and discharge plateaux for the \( x = 0.07 \) composition is similar to the discrepancy between the lithium content and charge passed along the first discharge plateau. This is consistent with the excess capacity on the first discharge plateau being associated with an irreversible process, such that the magnitude of the subsequent charging plateau is less than discharge. It is noteworthy that the efficiency on subsequent cycles is

Figure 4 | Schematic representation of the structure of Li_2VO_2, LiO_4 tetrahedra (red), VO_6 octahedra (blue).
much closer to 100%, further indicating that the irreversible process occurs mainly on the first discharge. The incomplete conversion of ccp to hcp on the first discharge may be due to polarization; the greater the polarization the earlier the low voltage cut-off will be reached. We have observed small variations in the polarization between cells, with conversions of up to 70%. Detailed work on optimizing the composite electrode structure should help to maximize the conversion. In the case of x = 0.03 material, the discharge plateau is shorter than that for x = 0.07 and the difference between the charge and discharge plateaux is correspondingly less.

The role of non-stoichiometry

Why is it that Li cannot intercalate into stoichiometric LiVO₂, yet a relatively small amount of excess lithium can switch on a large capacity to intercalate lithium at low voltages? Given the low rate used in Fig. 2, it is unlikely to be the result of differences in transport properties between the stoichiometric and lithium-rich compositions, that is to differences in ionic or electronic transport. This view is supported by galvanostatic intermittent titration technique (GITT) pseudo-equilibrium measurements, which show the same behaviour as in Fig. 2. The 2-phase intercalation process involves shearing of the close packed oxide ion layers from cubic to hexagonal stacking. The structure of stoichiometric LiVO₂ shows no evidence of V in the Li layers (site exchange), so the inability to intercalate Li into stoichiometric LiVO₂ is not due to V pinning the alkali metal layers together and inhibiting shearing.

To investigate the difference between stoichiometric and non-stoichiometric materials further, atomistic modelling methods were employed, being well-established tools in the study of defect structures in complex oxides. First, the crystal structures of LiVO₂, Li₁.07V₀.93O₂ and Li₂VO₃ were reproduced and exhibit good agreement with the experimental structures (see Supplementary Table S3). Simulations of intrinsic defects in stoichiometric LiVO₂ find an unfavourable formation energy of more than 3 eV for Li/V site exchange (comprised of isolated Li⁺ on the V sites, Li⁺, and isolated V⁴⁺ on the Li⁺ sites, V⁴⁺); this is clearly in accord with the above observation from Rietveld refinement that there is no V in the Li layers.

Formation of the solid solution Li₁+xV₁−xO₂ involves the mechanism 3V⁴⁺ + Li⁺ = 2V⁴⁺ + Li⁺, that is substitution of V⁴⁺ by Li⁺ on the octahedral V site and charge compensation by oxidation of two other V⁴⁺ to V⁴⁺. Effective charges are expected to favour the two V⁴⁺ occupying the nearest neighbour (nn) sites that each share an edge with the Li⁺ site. Modelling studies have investigated the energetics of several configurations of the 2V⁴⁺ and Li⁺ in the V layer of Li₁.07V₀.93O₂ (shown in Fig. 5); the energies listed in Supplementary Table S4 confirm the stability of the (2V⁴⁺/Li⁺) trimer cluster compared with isolated defects. Although the small energy differences do not allow us to distinguish between the three trimer configurations, Fig. 5a–c (the energy differences are small compared with kT at the temperature of synthesis, 850 °C), the results clearly indicate a non-random distribution of V⁴⁺ and Li⁺ in the vanadium layers.

There is scope for the trimer clusters to coalesce into larger clusters. Each Li⁺ site is surrounded by six edge-sharing V sites. We therefore explored how the V⁴⁺ could be distributed around the Li⁺ to form larger clusters, which included a dodecamer (or ‘flower-like’) arrangement in which all six of the edge-sharing sites surrounding Li⁺ are V⁴⁺. However, the most stable configurations (shown in Supplementary Figs S4 and S5) are still less favourable than the trimer clusters by more than 350 meV. In general, the calculations on the Li₁.07V₀.93O₂ composition indicate that the (2V⁴⁺/Li⁺) trimer is the most favourable arrangement compared to larger, more complex, clusters.

Turning to the intercalation of Li into LiVO₂ and Li₁.07V₀.93O₂, Li⁺ must first be inserted into a tetrahedral site, as all the octahedral sites are already occupied. In the case of LiVO₂, the most favourable empty tetrahedral site is located in the alkali metal layers, and shares one face with a V⁴⁺ ion in an octahedral site in the transition metal layers. Fig. 6a. In contrast, in Li₁.07V₀.93O₂ the intercalated Li⁺ can occupy a tetrahedral site in the alkali metal layer that shares a face with the Li⁺ in the Li⁺ site, Fig. 6b. Atomistic modelling calculations have probed the energies for lithium ion occupancy at these two sites (Table 1); note that the lowest energy trimer structure was used for the calculations on Li₁.07V₀.93O₂. The relative energies clearly indicate that the intercalated Li⁺ at the site sharing a face with Li⁺ in Li₁.07V₀.93O₂ is about 620 meV lower in energy than for Li⁺ in LiVO₂, rendering the intercalation of Li into the lithium-rich Li₁.07V₀.93O₂ much more favourable.

Previous density functional theory (DFT) studies on a variety of oxide electrode materials have shown that such methods

**Figure 5** | Configurations of 2V⁴⁺ and Li⁺ in the vanadium layer of Li₁.07V₀.93O₂. Configurations a–c are trimer clusters of nearest-neighbour ions, and configuration d shows isolated species (yellow: Li⁺; blue: V⁴⁺; purple: V⁴⁺).
are well suited to probing lithium insertion properties and to predicting precise trends in cell voltages. Here we derived cell voltages for lithium intercalation into the stoichiometric LiVO$_2$ and Li$_{1.07}$V$_{0.93}$O$_2$ systems using the total energies from a series of structural optimizations. Table 1 indicates a negative cell voltage of $-2.98$ V for Li$_{1.07}$V$_{0.93}$O$_2$, confirming that the intercalation of lithium into the stoichiometric oxide is unfavourable; lithium plating would occur, at 0 V, before the voltage for intercalation was reached. This result is consistent with the above experimental data, which show no evidence of intercalation into stoichiometric LiVO$_2$, and with previous reports. In contrast, for Li intercalation into Li$_{1.07}$V$_{0.93}$O$_2$ a cell voltage of $+0.58$ V is derived, indicating intercalation into this phase is possible. This is consistent with the neutron diffraction data, discussed above, where evidence for Li intercalation into the tetrahedral sites in the ccp structure was observed; although the calculated voltage is somewhat greater than the average for the sloping region of the discharge curve.

The simulations also produce valuable local structural information, which can be difficult to extract from diffraction experiments alone. Figure 6 indicates that the inserted Li$^+$ in Li$_{1.07}$V$_{0.93}$O$_2$ is displaced slightly from the centre of the tetrahedron towards the shared face with Li$_{V}^{IV}$, leading to three Li$^+$–O distances of 1.8 Å and one of 2.1 Å. Owing to Li$^+$–Li$^+$ repulsions the adjacent Li$_{V}^{IV}$ ion is also displaced away from the inserted lithium, leading to a separation of 2.1 Å between the two lithium ions. Interestingly, the Li$_{V}^{IV}$ ion now sits in a distorted coordination environment of three short Li$^+$–O and three long Li$^+$–O distances of about 1.91 Å and 2.45 Å respectively (comparable to the initial octahedral coordination of 6 × 1.99 Å). Li insertion has also perturbed the local anion sublattice with lengthening of several O–O distances from 2.93 Å to more than 3.0 Å. The inserted lithium therefore causes large distortions to the local structure of Li$_{1.07}$V$_{0.93}$O$_2$, which could be viewed as precursors to the shearing of oxide layers for cubic to hexagonal packing.

Although the tetrahedral site in the Li layer of Li$_{1.07}$V$_{0.93}$O$_2$ is more stable than in LiVO$_2$ it does share all four faces with Li$^+$ ions in octahedral sites (3 in the alkali metal layers and the V site substituted by Li, Li$_{V}^{IV}$). The resultant Li$^+$–Li$^+$ repulsions trigger the shearing of the close packed oxide ion layers from ABC to the AB stacking of the hexagonal close packed Li$_{V}$VO$_2$ structure. AB stacking can accommodate all of the original Li plus one extra Li per formula unit in the tetrahedral sites of the alkali metal layers (there are twice the number of tetrahedral sites to octahedral sites per alkali metal layer), Fig. 4. The tetrahedral sites share faces with empty tetrahedral sites in the transition metal layers and empty octahedral sites in the alkali metal layers, that is there is no face sharing of occupied sites, leading to a stable structure. By this mechanism it is possible to understand why a small degree of vanadium substitution by lithium can trigger a marked capacity to insert lithium via a 2-phase mechanism.

DFT studies have been extended to calculate the voltage expected for the 2-phase reaction, and give a value of $+0.23$ V, Table 1, in good accord with the low voltage plateau commencing at $\sim 0.1$ V. As with previous DFT studies, there are small quantitative differences with experimental values, which have been attributed largely to the overestimation of the calculated binding energy for lithium metal. In any case, our calculated trend in cell voltages as a function of structure and stoichiometry confirms the important role that the lithium-rich composition plays in initiating lithium intercalation, and accords well with the electrochemical measurements.

It is interesting to consider the implications of the present work for other layered LiMO$_2$ compounds. The results presented here indicate that the presence of Li on the transition metal sites should favour Li intercalation and transformation of ccp to hcp in layered compounds. It is noteworthy that compounds such as Li(Li$_{0.82}$Mn$_{0.18}$)$_2$Ni$_{3.46}$Ti$_{10.65}$O$_2$, with Li on the transition metal sites, can readily intercalate Li with a marked capacity associated with the ccp to hcp transformation. In contrast, Li cannot be

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**Table 1 | Calculated energies for intercalated Li$^+$ and cell voltages for stoichiometric and Li-rich structures.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Insertion site</th>
<th>$E$(Li$^+$) (meV)</th>
<th>$\Delta E^*$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric LiVO$_2$</td>
<td>Li$^+$ adjacent to V$_{V}^{IV}$</td>
<td>$-3552$</td>
<td>$+618$</td>
</tr>
<tr>
<td>Li-rich Li$<em>{1.07}$V$</em>{0.93}$O$_2$</td>
<td>Li$^+$ adjacent to Li$_{V}^{IV}$</td>
<td>$-4170$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

**Average cell voltages**

<table>
<thead>
<tr>
<th>Composition/range</th>
<th>Cell voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric Li$_{1+y}$V$_2$O$_x$ ($0.0&lt;y&lt;0.07$)</td>
<td>$-2.98$</td>
</tr>
<tr>
<td>Li-rich Li$<em>{1.07+y}$V$</em>{0.93}$O$_2$ ($0.0&lt;y&lt;0.07$)</td>
<td>$+0.58$</td>
</tr>
<tr>
<td>Li-rich Li$<em>{1.07+y}$V$</em>{0.93}$O$_2$ ($0.0&lt;y&lt;0.93$)</td>
<td>$+0.23$</td>
</tr>
</tbody>
</table>

*Energy difference between these sites with reference to the most stable site.*

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**Figure 6 | Calculated local structures around an inserted Li$^+$ ion in LiVO$_2$ and Li$_{1.07}$V$_{0.93}$O$_2$.** Dotted lines highlight its local coordination: a, Li$^+$ at a tetrahedral site in an alkali metal layer of the LiVO$_2$ structure and sharing a face with a V ion in an octahedral site in the layer below (the other three faces of the tetrahedron are shared with Li in octahedral sites in the alkali metal layers); b, Li$^+$ at a tetrahedral site in an alkali metal layer of the Li$_{0.07}$V$_{0.93}$O$_2$ structure and sharing a face with a Li ion in an octahedral site in the layer below (the other three faces of the tetrahedron are shared with Li in octahedral sites in the alkali metal layers). The inserted Li$^+$ in Li$_{0.07}$V$_{0.93}$O$_2$ is displaced by $\sim 0.3$ Å from the centre of the tetrahedron towards the shared face with Li$_{V}^{IV}$. The adjacent Li$_{V}^{IV}$ ion is also displaced away by $\sim 0.6$ Å from the inserted lithium leading to a distorted coordination environment.
intercalated into LiCoO₂. However, further work is required to corroborate this trend.

In this work, the process of lithium intercalation into Li1+xV1-xO2 (x = 0.1) has been investigated by a combination of computational methods along with powder X-ray and neutron diffraction, focusing in particular on the role that excess lithium plays on switching on intercalation. Whereas Li cannot be intercalated into stoichiometric Li2O, substituting as little as 3% of the V on the transition metal sites by Li is sufficient to promote a 2-phase intercalation process between cubic close packed Li2O and hexagonal close packed Li2V2O5 at potentials of ~0.1 V. The process may be reversed on charging (Li extraction). The results show that the inability to intercalate into stoichiometric Li2O2 is not due to the presence of site-exchange disorder involving V ions in the alkali metal layers pinning them together, as might have been thought. Instead, we show that substitution of Li for V on the octahedral transition metal sites renders tetrahedral sites in the alkali metal layers energetically accessible by Li, which in turn triggers the shearing of the cubic close-packed oxide ion layers to hexagonal close packing such that two Li per formula unit can be accommodated without face sharing.

Given the importance that Li intercalation into Li1+xV1-xO2 at ~0.1 V has for lithium battery anodes, and that this occurs only for the Li-rich compositions, the results presented in this paper provide a framework not only for understanding the intercalation process but also for the future design and optimization of low voltage intercalation oxides as anodes for rechargeable lithium batteries.

Methods

Li1+xV1-xO2 was synthesized from lithium carbonate and vanadium oxide using a solid state method. Appropriate ratios of dried V2O5 (Aldrich, 99%) and Li2CO3 (Aldrich, 99% +) powders were mixed together, placed in a gas-tight container and subsequently ball-milled for 60 min (SPEX Centri-Prep 8,000 M mixer/mill). The mixture was then heated in a crucible crucible, covered with a lid and heated at 800 °C for 10 h under flowing argon. The compound was allowed to cool to room temperature, then heated to 850 °C for 12 h under a flowing gas mixture of 95% argon/5% hydrogen to complete the reaction and obtain a single phase product.

Chemical analysis was carried out by ICP using a Perkin-Elmer Optima 7300DV ICP-OES. The samples of lithium vanadium oxide were carefully weighed out, dissolved in hot aqua regia and then diluted before analysis for Li and V. ICP analysis was carried out by an external company (Butterworths Ltd.). Vanadium oxidation state analysis was performed by double titration following the method described in ref. 45. After dissolution in H2SO4, the V(V) and V(IV) content in the sample was determined by titration (V1) with aqueous KMnO4 (0.01 M). An aqueous solution of FeO(NH4)2·H2O was then added to reduce all the V(V) to the V(IV). The solution was cooled in an ice bath and an excess of (NH4)2S2O8 was added to oxidize Fe(II) to Fe(III). Finally, V2O5 was titrated (V2) with KMnO4 (0.01 M) to measure the total vanadium content of the sample. The average oxidation state of vanadium was given by S = V(V)/V(II). Errors, based on the above volumetric analysis are estimated to be ±5%.

Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺. Composite electrodes were fabricated using the active material, super S carbon and Kynar Flex 2801 (a co-polymer based on PVDF) binder in a mass ratio of 80:15:5. The mixture was then transferred to an argon-filled glove box before opening and active material was added to oxidize Fe²⁺ to Fe³⁺.


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Author contributions

A.R.A. and C.L. carried out the experimental work and data analysis, P.M.P. the modelling, M.S.I. and P.G.B. conceived and directed the project.

Additional information

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