Atomistic Simulation of Polyanion Cathode Materials for Lithium Batteries

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Abstract

Rechargeable lithium-ion batteries are attractive candidates for implementation into new large-scale energy storage applications, such as hybrid and electric vehicles, due to their high energy density. Modern atomistic modelling techniques can provide valuable insights into the fundamental defect and ion transport properties of electrode materials at the atomic scale, which are essential for a full understanding of lithium battery function. In this thesis, three types of polyanion materials, for use as alternative cathodes in lithium batteries, are examined using such computational techniques. Firstly, the mixed-metal phosphate material LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ is investigated. The intrinsic defect type in this olivine-structured material with the lowest energy is the cation antisite defect, in which Li$^+$ and Fe$^{2+}$/Mn$^{2+}$ ions exchange positions. Lithium ion diffusion occurs down one-dimensional $b$-axis channels following a curved path in accord with experiment. Migration energies for Fe$^{2+}$ and Mn$^{2+}$ antisite cations on Li$^+$ sites suggest that such defects will impede bulk Li$^+$ mobility in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$. Secondly, ion conduction paths through the tavorite structures of recently discovered LiFeSO$_4$F and NaFeSO$_4$F are investigated by a combination of static lattice and molecular dynamics simulation techniques. The results indicate that LiFeSO$_4$F is effectively a three-dimensional (3D) lithium-ion conductor with an activation energy of $\sim$ 0.4 eV for long-range diffusion, which involves a combination of zigzag paths through [100], [010], and [111] tunnels in the open tavorite lattice. In contrast, for Na$^+$ migration in NaFeSO$_4$F, only one direction ([101]) is found to have a relatively low activation energy (0.6 eV). This leads to a diffusion coefficient that is more than six orders of magnitude lower than in any other direction, suggesting that NaFeSO$_4$F is a one-dimensional (1D) Na-ion conductor. Finally, the defect and diffusion properties of LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F, which exhibits a complex triplite structure in which the cation ($M$) sites are shared by Li$^+$, Fe$^{2+}$ and Mn$^{2+}$ ions, are examined. Low activation energies ($\leq$ 0.45 eV) are found for several nearest-neighbour jumps between lithium sites which make up a 3D network of long-range migration pathways. However, due to cation site sharing, coherent long-range diffusion may be blocked by Fe$^{2+}$ and Mn$^{2+}$ ions which would affect the rate capability of this material.
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List of Publications and Presentations

Publications

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   Times cited: [16]

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Oral Presentations

Sep 2011  CCP5 Annual Conference, Bath
“Defects and Ion Transport in Phosphate and Fluorosulphate Materials for Lithium Batteries.”

May 2011  Chemistry Postgraduate Symposium, University of Bath
“Simulation Studies of New Lithium Battery Materials.”

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“Atomistic Study of Anti-Site and Ion Migration in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$.”

Jan 2010  Chemistry Postgraduate Seminar, University of Bath
“Atomistic Simulation Studies of the LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ Lithium Battery Material.”

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Poster Presentations

July 2011  Lithium Battery Discussion, Arcachon, France
“Anti-Site Defects and Clustering in Mixed-Metal LiFe$_{0.5}$M$_{0.5}$PO$_4$
($M = Mn, Ni, Co$) Materials.”

Dec 2010  RSC Solid State Group, UCL
“Defects and Ion Migration in Phosphate and Fluorosulphate Materials for Lithium Batteries.”
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Dec 2009  RSC Solid State Meeting, Open University
“Phosphate-Based Lithium Battery Materials: Anti-Site Defects and Lithium Transport.”

“Atomic-Scale Insight into Phosphate-Based Lithium Battery Materials.”

May 2009  Chemistry Postgraduate Symposium, Bath
“Atomic-Scale Insight into Phosphate-Based Lithium Battery Materials.”
(Prize Winner)
Chapter 1

Introduction

1.1 Background: Energy Storage

Development of clean sustainable energy sources is one of the most important global challenges. There is a widespread effort to reduce the usage of fossil fuels because of their limited supply, and concern over the implications of global warming driven by CO\textsubscript{2} emissions. Approximately 25% of CO\textsubscript{2} emissions in developed countries arise from road transport [1]. It is widely acknowledged that addressing this problem requires the electrification of transport. The main barrier is the storage of electrical energy, which lies at the heart of such hybrid and electric vehicles. Energy storage will also play a vital role in large scale applications such as grid energy storage, particularly with a growing need to move towards renewable energy sources, which are inherently intermittent in nature [2].

Rechargeable lithium ion batteries have dominated the portable electronics market in recent years and are widely regarded as excellent candidates for implementation into larger scale applications (see Figure 1.1), because they have the highest energy density of any rechargeable battery (see Figure 1.2). Although current Li battery technologies have been successfully implemented into a number of hybrid-electric and fully electric vehicles, there are a number of technological hurdles to overcome before they can be integrated sustainably. The main barrier to progress is a lack of good electrode materials and electrolytes, which can present problems with regard to safety, cost and cycle life particularly when scaled up to meet the demands of powering vehicles. Innovation is therefore required from materials chemists to produce more efficient and sustainable electrode materials.

Often an atomic-scale understanding of the structural, defect and transport properties which underpin these complex lithium battery materials is lacking. Computer modelling techniques and experimental techniques can be combined to this end to improve existing systems and develop newer, more efficient materials. This thesis details the computational modelling studies of several promising new cathode mate-
Figure 1.1: Lithium battery applications: (top) portable electronics; (middle) current electric cars (Nissan Leaf left and Tesla right); (bottom) hybrid-electric helicopter currently in development; possibly a step towards fully electric vehicles for flight in the future.
1.2 Lithium Batteries

Lithium was first used as an anode material in batteries in the 1970’s. It is both the most electro-positive and the lightest metal in the periodic table, which enables production of cells with high energy density. Originally lithium cells were primary, and were ideally suited to low power applications which required long operating times, such as watches, calculators and a selection of small medical devices. However, around the same time several intercalation materials were discovered, which allowed reversible insertion and extraction of Li ions; this focused research towards the development of secondary (rechargeable) lithium batteries [3, 4].

The first example was the TiS$_2$ cell, which was comprised of a LiTiS$_2$ cathode and lithium metal anode. TiS$_2$ was an excellent Li ion intercalation compound, facilitating reversible Li ion insertion with minimal structural change. Unfortunately the lithium anode posed a number of problems with regard to safety [3]. Li metal reacts violently with water, so cells needed to be constructed in a dry atmosphere and built water tight, which increased production costs [4]. During operation Li ions are shuttled back and forth between the anode and cathode; this requires the lithium anode to be repeatedly stripped and re-plated during operation, causing the formation of dendrites (branch like growths) at the anode. The dendrites would
eventually extend across to the cathode resulting in a short circuit [3, 4]. A number of strategies were developed to solve these problems, the most successful of them replaced lithium metal with an intercalation material. These Li-ion cells did not contain any lithium metal and were therefore inherently safer. This is the same strategy currently employed by modern day lithium cells.

Like all batteries, lithium ion batteries are comprised of two electrodes, the anode and cathode, separated by an electrolyte which must be a good ionic conductor but an electronic insulator. The anode and cathode have different chemical potentials, which depend on the chemistry that occurs at each. A schematic of Li-ion battery operation is provided in Figure 1.3, highlighting the highly successful Sony cell, consisting of a LiCoO$_2$ cathode and graphite anode, as an example.

![Figure 1.3: Schematic of a lithium ion cell.](image)

Once the electrodes are connected via an external circuit, the redox reactions at the electrodes proceed spontaneously. Electrons flow from the anode, round the external circuit to the cathode, whilst an equivalent number of Li ions are transported across the electrolyte before inserting into the cathode, thus maintaining the charge balance [3–6]. Charging the cell requires applying a larger external potential in the opposite direction, forcing the reverse process.

The introduction of Li-ion batteries has solved many of the safety issues associated with lithium batteries. The Sony cell in particular has been an incredible success with global sales now comfortably into the billions. However, there are still many improvements that can be made if this technology is going to continue sustainably into the future. It is important that as we aim to reduce cost by searching for cheaper more abundant materials, the reliability performance and safety be maintained.
1.2.1 Overview of Lithium Battery Materials

For the remainder of this chapter the historical developments of lithium ion battery materials will be discussed, before examining current materials of interest. The three main component materials will be introduced and their roles within the cell will be explained. Because the research presented here is focussed on cathode materials, this area will be covered in much greater detail.

Electrolyte

To prevent a short circuit both electrodes must be separated, so a thin porous material is inserted between them to keep them apart [7]. The electrolyte has the crucial job of facilitating transport of Li ions between the anode and cathode through this porous separator. It must be an excellent ionic conductor but an electronic insulator, otherwise the cell would short circuit.

The electrolyte is typically a lithium salt LiPF$_6$ dissolved in an organic solvent. Current electrolytes are thermodynamically stable up to 3.5 V; at voltages higher than this the electrolytes decompose via oxidation reactions. Fortunately current electrolytes have high kinetic stability so are able to operate well outside of this stability window, at voltages as high as 5.5 V [3]. However, although electrolyte decomposition is slow, it still happens continuously throughout the lifetime of the cell causing a gradual decline in performance. Ideally we would like electrolytes with much higher thermodynamic stability, which do not degrade at all, even in very high voltage cells.

For electric vehicles batteries will need to be scaled up in order to meet performance demands. Scale up of our current technology would require storage of much larger volumes of volatile solvents containing electrolyte within the cell. This presents an increased risk of fires and explosions, particularly under the abusive conditions of a car engine. For this reason there has been much interest in development of polymer electrolytes, which would provide a fully plastic cell. These liquid free electrolytes would not only be safer, but also provide weight, volume and packing advantages too. Unfortunately they currently only operate efficiently at temperatures around 80°C, providing poor ionic conduction at lower temperatures [3].

Attempts to improve polymer electrolytes lead to development of liquid polymer gels, which should in theory contain the advantages of both solid state and liquid electrolytes, i.e. high ion mobility without safety issues. Hard gels containing 10-25% liquid electrolyte, increase ionic conductivity by an order of magnitude compared to solid polymer electrolytes. The softer gels which can contain up to 95% liquid can be as little as 2 times less conductive than fully liquid electrolyte. However, adding more liquid electrolyte does reduce safety; the harder gels can accommodate a lithium metal anode but moving towards softer gels requires a lithium ion cell [3].
The electrodes

Whilst finding cheap sustainable materials is very important, a huge amount of effort is devoted primarily to improving the energy density of lithium batteries. As mentioned previously there are two ways of doing this, increasing the potential difference between the electrodes and increasing the capacity per unit volume or weight. Figure 1.4 is a voltage verses capacity graph, showing a number of anode and cathode materials of current use or interest. Ideally the cathode would be situated at the top right and the anode at the bottom right of the graph, ensuring both electrodes have high capacity, and there is a large potential difference between them. Currently the relatively low thermodynamic stability of the electrolyte is an important limiting factor, so maximising the cell voltage can lead to a drop in cycling performance. As improvements in the electrolyte are made we should be able to pick pairs of anodes and cathodes which provide higher voltages without a loss in performance.

Anode

It is important that the anode material has a low potential vs Li/Li$^+$ and that Li ions can be reliably inserted and extracted from the material during cycling. As mentioned previously, Li metal was originally used as the anode material, but dendritic growth due, to continuous re-plating of its surface during cycling, caused serious safety issues. This was unfortunate as Li metal has a higher capacity than any of its possible replacements (see Figure 1.4), and for this reason research into Li metal anodes is still active [5]. The most successful approach to solve these problems involved replacing Li metal with an intercalation material, although it took almost 10 years before a successful lithium ion cell was developed. The failures were attributed to a lack of suitable materials for the anode and failure of the electrolytes to meet safety, cost and performance requirements. The current anode material is graphite, which allows lithium to be inserted between the carbon layers [3]. Graphite has many advantages, being cheap, readily available and an excellent electronic conductor. However, there have been on going research efforts focussed on developing anodes with higher capacities [3, 8, 9].

Transition metal nitrides initially showed great potential, with the cobalt member offering a large stable and reversible capacity 600 mAhg$^{-1}$ (nearly double that of graphite). Unfortunately all other members showed inferior electrochemical performance. Furthermore cobalt is associated with toxicity and cost issues. Various attempts were made to create alloys of Li with a variety of metallic and semi-metallic elements such as Bi, Pb, Sn and Cd, but cycling these materials results in severe changes in volume (up to 200%) causing the material to disintegrate. A series of metal oxides were also investigated because of their large capacities (double that of graphite). However, poor long term cyclability and large irreversible capacity loss during the first cycle, as a result of large volume changes, initially ruled them out.
Figure 1.4: Voltage vs capacity for anode and cathode materials, either in current use or under development. Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] [3], copyright (2001)
as an alternative [3, 8].

Over the last decade there have been huge advances in nano-science which have prompted researchers to re-visit previously dismissed anode materials such as alloys and metal oxides. nano-structured materials have been shown to overcome previous problems such as large volume changes and poor electrochemical performance, by reducing diffusion lengths for lithium ions and providing greater structural flexibility [8].

Nano-structured anatase TiO$_2$ has attracted considerable interest due to its low voltage and fast lithium diffusion kinetics compared to other titanate polymorphs such as rutile and TiO$_2$-B [8]. The ease of modification of its nano-scale structure provides enhanced stability thus increasing its cycle life. Unfortunately, TiO$_2$ based anodes in general offer a poor capacity in comparison to other developing technologies. SnO$_2$ however, has a theoretical capacity (993 mAhg$^{-1}$) over double that of graphite (372 mAhg$^{-1}$) [9], but further developments are required to improve cycling stability; one of the most popular strategies to achieve this involves nano-sizing [8, 9].

Both of these oxide materials would currently provide lower overall cell voltages due to their discharge potentials, which are higher than graphite; this would increase safety and electrolyte stability but ultimately results in reduced energy density. In order to improve upon energy densities of current materials, higher voltage cathode materials would need to be used [9]. Nano-structured silicon however, could potentially provide a high capacity (theoretically an order of magnitude higher than graphite) as well as comparable cell voltages to current materials [10].

**Cathode**

The cathode material is currently the bottleneck for battery development, because cathode materials typically have much lower capacities than the anodes. From Figure 1.4 it is clear that all the cathodes congregate on the left hand side, at the low capacity end. For this reason our research has focused on this area.

The main goal is to find new materials which can uptake more active mass into smaller volumes, whilst maintaining safety and performance. The following text will provide a more detailed insight into the historic developments of these materials (summarised in Figure 1.5), before introducing a selection of promising new materials which are currently in development.

As noted a series of dichalcogenides were first investigated, and they were shown to be good intercalation hosts, which could perform well as cathodes in an electrochemical cell [11]. LiTiS$_2$ was the most appealing of these for use in an energy storage device for several reasons: it was the lightest material [12]; it showed semi-metallic behaviour, so there was no need for a conductive coating [7]; there was no phase changes during cycling, allowing for deep, and highly reversible extraction of lithium
Figure 1.5: Timeline summarising cathode development.
This is in contrast with more recent materials, for which two phase intercalation behaviour results in limited lithium extraction [13, 14]. Although the heavier dichalcogenides provided many desirable properties for lithium batteries, research activity moved towards the lighter oxides in an effort to increase energy density [3].

Initial movement away from TiS\(_2\) focused on the layered oxides of vanadium and molybdenum [15]. Interest in MoO\(_3\) diminished quickly due to its low rate of reaction with lithium [7]. V\(_2\)O\(_5\) showed good intercalation results allowing insertion of up to three Li ions per formula unit. Unfortunately intercalation of Li ions above one per formula unit caused permanent structural changes, resulting in a phase that was able to cycle over all 3 Li ions, but would rapidly lose capacity upon cycling [7]. Throughout the 1980’s layered oxides were extensively studied. Variation in the stacking of MO\(_2\) layers was found; this was shown to be related to the lithium content, so lithium insertion/extraction provoked structural changes. Such structural changes during cycling reduced the electrochemical performance of these materials. Despite these issues, LiCoO\(_2\), first studied by Goodenough [13] in 1980, was found to perform excellently as a cathode [7].

The first commercial rechargeable lithium ion cell was released by Sony in 1990; it combined the LiCoO\(_2\) cathode material with a graphite anode (shown in Figure 1.3) [16]. It was coined the “rocking chair” cell because lithium ions are shuttled back and forth between the electrodes during cycling. The cell is built in the discharged state, so LiCoO\(_2\) is the source of lithium ions. It offers a cell potential of approximately 4 V with a moderate cell capacity of 130 mAh g\(^{-1}\) which is about 50% of its theoretical capacity. Delithiation beyond 50% results in phase changes which reduce reaction rates and cause capacity loss [7]. In the highly charged state, i.e. at low lithium concentration, there are safety concerns due to the high concentration of Co\(^{4+}\), which is highly oxidising and tends to oxidise the electrolyte reverting to a more stable 3+ state [17]. The heat generated from this reaction, coupled with the volatility of the electrolyte presents a fire/explosion risk [17]; this is also an important mechanism through which cell capacity is lost [6]. Cobalt is expensive due to its low natural abundance, and would also be limited to small scale applications. In order to sustainably power electric vehicles, materials made from cheaper more abundant elements are required [3, 7]. Finally cobalt is environmentally hazardous. All of the reasons above present a good argument for finding viable cathode alternatives.

There are two main cathode structures which dominate in commercial lithium cells: these are LiMO\(_2\) layered and LiMn\(_2\)O\(_4\) spinel.

LiMO\(_2\) Layered: Modern layered structures take the general form LiMO\(_2\) (where \(M = V, Cr, Mn, Fe, Co, Ni\)). The oxide ions adopt a cubic close packed arrangement in which \(M\) ions occupy edge-sharing octahedral sites in alternate layers (shown in Figure 1.6); lithium ions reside in edge sharing octahedral sites in the remaining layers.
Figure 1.6: The layered structure of LiCoO₂, which consists of layers of edge sharing CoO₆ octahedra, with lithium ions residing in edge-sharing LiO₆ octahedra between the layers.

The structure has a distorted rhombohedral symmetry with space group R3m. This layered structure accommodates two dimensional diffusion of lithium within the lithium layers [6]. This is an important aspect, as there will be significant focus on lithium diffusion pathways throughout this thesis because they are such an integral part of the function of the battery. As mentioned previously LiCoO₂ has been the main player for this class of material. However several other transition metal oxides have also been examined.

LiNiO₂ would in principle offer a cheaper cell with higher capacity [6, 17], but it has not been pursued for a number of reasons. Many reports suggest that stoichiometric LiNiO₂ cannot be synthesised, and that there is a nickel excess which resides in the lithium layers. This ultimately results in poorer ionic conductivity due to obstruction of lithium diffusion pathways [7]. LiNiO₂ also suffers from similar drawbacks to those in LiCoO₂; several structural changes occur during cycling, and Ni⁴⁺ much like Co⁴⁺ is highly oxidising so there are safety concerns, particularly in the highly charged state when there is high Ni⁴⁺ content [6, 17]. Various solid solutions have been investigated to overcome these problems. It has been shown that substitution of 30% of nickel with cobalt helps maintain site order by preventing nickel from moving into the lithium layer [6, 7, 17]. Introduction of small amounts of redox inactive species such as aluminium or magnesium prevents complete delithiation, thus stabilising the material in the highly charged state [6, 7, 17]. This is a typical example of how modifications at the atomic level can enhance the properties of a material, creating a solid solution which performs better than its end members.

Fe based materials would be ideal on the basis of toxicity. However the cell voltage that can be achieved with LiFeO₂ is too low to be considered for commercial application [17]. LiMnO₂ is also an attractive prospect because Mn⁴⁺ is more stable than Co⁴⁺, so could offer utilisation of its full capacity, as opposed to half in LiCoO₂ [6]. Unfortunately, LiMnO₂ does not form a stable layered phase, reverting to the
more stable spinel structure during cycling [6, 7, 17]. Solid solutions of Mn, Ni and Co, such as LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and LiNi$_{0.4}$Mn$_{0.4}$Co$_{0.2}$O$_2$, have been extensively studied. Ni is the electrochemically active ion, Mn acts to stabilise the structure, and Co prevents Ni migration into Li sites and is also electrochemically active at low lithium content. Small amounts of Ni are however required in the lithium layer to prevent structural changes from occurring during delithiation. These phase changes would ultimately reduce cathode performance, so Co content is tuned accordingly. Unfortunately, the electrical conductivity of these solid solutions is low, and the optimum composition is yet to be determined [7].

**Figure 1.7:** The spinel structure of LiMn$_2$O$_4$. Lithium ions reside tetrahedral sites within a 3-dimensional network of channels formed by edge-sharing MnO$_6$ octahedra.

**LiMn$_2$O$_4$ Spinel:** The spinel structure has space group Fd3m and consists of an array of cubic close-packed oxide ions with Mn ions in half of the octahedral sites and Li ions in an eighth of the tetrahedral sites (shown in Figure 1.7). The Mn$_2$O$_4$ framework provides a series of tunnels which intersect in all three dimensions, facilitating fast lithium migration [6]. In contrast to the layered materials site disorder is unseen in LiMn$_2$O$_4$; this is due to its greater structural rigidity which makes its tunnels more selective to the small lithium ions [6]. LiMn$_2$O$_4$ was first reported in 1983 [18], and by 1996 it was implemented, by Nipon Moli [19] in Japan, into the first commercial cell to replace the LiCoO$_2$ cathode. The main motivation for this was that manganese is around 1/100th the cost of cobalt and environmentally benign.

Lithium can be inserted into the material to a maximum composition of Li$_2$Mn$_2$O$_4$. Li intercalation occurs at two different potentials in Li$_x$Mn$_2$O$_4$, one at 4 V where 0 < x < 1, with lithium insertion into tetrahedral sites, and one at 3 V where 1 < x < 2, with lithium insertion into octahedral sites. The redox couple in both cases is Mn$^{3+}$/Mn$^{4+}$ so the difference in voltage is thought to be related to the difference
in site energies [6]. The 3 V process is of limited interest in rocking chair cells, but could be important for Li metal cells if cycling issues can be resolved.

The major drawback of this material is the structural changes which occur during lithium insertion, due to an increase in Jahn Teller active high spin Mn$^{3+}$ species. These phase changes cause large volume changes (6%) during cycling resulting in a loss of contact between Li$_x$Mn$_2$O$_4$ particles. Cell capacity is lost because these, now isolated particles, can no longer store lithium effectively. Replacing small amounts of Mn by other metals (Li, Co, Ni, Cu, Be, Ga, Cr, Zn, Mg) to form solid solutions has been shown to stabilise the structure and protect against such effects. The LiMn$_{1.5}$Ni$_{0.5}$O$_4$ composition is of particular interest for high power applications such as hybrid-electric vehicles [20, 21]; it offers a high operating voltage of 4.7 V, and shows reasonable cycling stability and a high rate capability [20, 21]. However, this material still suffers from gradual structural degradation with cycling. Recent focus has therefore centred around stabilising the structure by substituting small amounts of Mn with Mg to form LiMg$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$ solid solutions [22]. The most attractive solution to these structural issues would simply involve creating a lithium excess because no extra synthesis steps would be required. However, substitution with any redox inactive species would inevitably decrease the cell capacity [6, 17].

Before introducing some materials currently in use or in development, it is instructive to summarise the key criteria which make up a high performance cathode material:

- Made from cheap, environmentally friendly and abundant materials.
- An excellent intercalation host, whereby the structure remains intact with Lithium insertion and removal.
- High capacity.
- High voltage, (currently limited by electrolyte stability).
- Good electronic conductivity, thus removing the need for carbon coating.
- Fast ionic conductivity, particularly for high power applications, where large amounts of energy are required over short bursts.

The current commercial batteries fulfil many of the criteria presented. However, none of them are strong in every aspect.

### 1.3 Polyanion Cathode Materials

In 1997 Goodenough [14] discovered that using poly-anions, such as phosphates and sulphates, rather than traditional anions, like oxides, the Fe$^{2+}$/Fe$^{3+}$ potential could be raised to a commercially attractive level (3.5 V). This is caused by an inductive effect which acts to destabilise the Fe$^{3+}$ state [17, 23]. As mentioned previously, the
use of Fe based materials is ideal on the basis of cost and toxicity, so this sparked a huge amount of interest in polyanion materials. The properties of several of these materials will be summarised in the following paragraphs.

![Diagram of olivine structure](image)

**Figure 1.8:** Olivine structure: lithium ions reside in edge sharing octahedral positions within 1D channels formed by corner sharing FeO$_6$ octahedra and PO$_4$ tetrahedra.

**LiMPO$_4$ Olivines:** The olivine structure (shown in Figure 1.8) crystallises in the $Pnma$ space group; it consists of an hcp array of oxygen, with an eighth of the tetrahedral holes occupied by phosphorus, and half of the octahedral holes occupied by $M$ where ($M = Fe, Mn, Co, Ni$) or lithium. This provides layers of corner sharing $MO_6$ octahedra linked by PO$_4$ tetrahedra, forming a one dimensional channel structure. Li ions sit in edge sharing octahedral positions within the channels [24–27]. The phosphates, in general show good thermal stability with high voltages vs the Li$^+$/Li couple [28].

In contrast to LiCoO$_2$ and LiMn$_2$O$_4$, lithium diffusion in the olivine phosphates is limited to 1D channels and therefore diffusion rates are comparatively low [27]. Fortunately, by altering the crystal morphology it is possible to create plate-like particles where the short dimension is parallel to the lithium channels, thus reducing the diffusion lengths and improving conduction rates [27]. However, 1D channels can easily be blocked by defects and impurities which can reduce the usable cell capacity and hinder lithium mobility. Both atomic-scale simulation [25] and experimental [29] studies have shown antisite defects, where Fe ions occupy Li sites, to be favourable in LiFePO$_4$. More recent results suggest that although antisite defects are an intrinsic feature, it may be possible to control their distribution within the structure, thus limiting their impact on lithium mobility [27, 30].

The majority of research has focused on LiFePO$_4$, which has a high operating voltage, for the Fe$^{3+}$/Fe$^{2+}$ couple, of 3.4 V vs lithium, and a high theoretical capacity of 170mAhg$^{-1}$ [3, 5, 14]. LiFePO$_4$ based cells are the most recent lithium battery success story and have been commercialised by A123 [31] and Phostech [32], predominantly for use in mobile phones and power tools. Attention continues to be
paid to the Mn system due to the ideal position of the Mn$^{3+}$/Mn$^{2+}$ couple (4.1V vs Li$^+$/Li) which is compatible with current Li-ion cathode systems [33]. Unfortunately LiMnPO$_4$ suffers from similar structural issues to the LiMn$_2$O$_4$ spinel upon cycling [26]. Olivines in general show low intrinsic electronic conductivity and a variety of attempts have been made to overcome this problem, including: cation doping; carbon coating; and reducing the particle size during synthesis [5, 7, 24, 26]. However, consistent improvement has yet to be demonstrated.

Fluorophosphates: It was initially thought that the inclusion of electron withdrawing F$^-$ combined with the inductive effect of the phosphate groups could raise cell voltages above those achieved by the olivine phosphates. This sparked significant research activity into fluorophosphates, which unlike many other classes of cathode material crystallise into several different structures [26]. LiVPO$_4$F, the first successful material of this kind, was reported by Barker et al in 2003 [34]. This material utilises the V$^{4+}$/V$^{3+}$ redox couple which has a high potential of 4.2 V vs Li. Its theoretical capacity is 156 mAh$^{-1}$ which is comparable to that of LiCoO$_2$.

In 2005, a new sodium based cathode, Na$_3$V$_2$(PO$_4$)$_2$F$_2$, was investigated [35]. Although its performance was not competitive with current lithium cells, it showed good stability with respect to the Li based electrolyte and anode materials [26]. Research in this area continued, and in 2007 competitive sodium/lithium fluorophosphate cathode materials of the form A$_2$FePO$_4$F (where A = Na, Li), were introduced [36, 37]. Although comprised of the same components, the structures of the lithium and sodium analogues differ considerably. Li$_2$FePO$_4$F crystallises in the tavorite structure which is described in more detail in section 1.3.1 (see Figure 1.12). Na$_2$FePO$_4$F has a layered structure (shown in Figure 1.9) which consists of chains...
of face-sharing dimers of Fe$^{2+}$ octahedra which are linked by phosphate tetrahedra to form layers. The sodium ions sit in two unique seven-coordinate crystallographic sites between the layers.

Li$_2$FePO$_4$F and Na$_2$FePO$_4$F have moderate theoretical capacities of 152 mAh$^{-1}$ and 135 mAh$^{-1}$ respectively [26, 36]. The sodium analogues also offer a high cell voltage of 3.5 V, which is comparable to LiFePO$_4$; unfortunately, Li$_2$FePO$_4$F is less competitive at 3 V. Both structures offer multidimensional Li diffusion capabilities; the open tavorite structure of Li$_2$FePO$_4$F provides a 3D network of Li channels, and Na$_2$FePO$_4$F shows 2D diffusion within its sodium layers. This can be a huge advantage in lithium battery materials because access to different routes can be crucial to allow lithium to move around blockages caused by crystal defects.

The fluorophosphates in general suffer from poor conductivity much like the olivine phosphates, so nano-scaling and carbon coating would be required in order for them to compete with current materials. Nevertheless, the successful demonstration of Na-based cathode materials is an important step in battery technology, especially with concerns over global lithium supply.

**Figure 1.10:** Li$_2$FeSiO$_4$ structure: lithium ions are situated between layers comprised of FeO$_4$ and SiO$_4$ tetrahedra.

**Li$_2$MSiO$_4$ (M = Fe, Mn) silicates:** Li$_2$FeSiO$_4$ is the most promising material on the grounds of cost and sustainability, as both iron and silicon are highly abundant resources. The Li$_2$FeSiO$_4$ structure consists of a tetragonally packed oxide ion lattice in which half the tetrahedral sites are occupied by cations. The geometry of the tetrahedra as well as the cation ordering between tetrahedral sites can vary giving rise to several polymorphs. The first reported structure ($\beta_{II}$) [38] is shown in Figure 1.10, and comprises of chains of corner sharing LiO$_4$ tetrahedra running along the $a$ direction, parallel to chains of alternating corner sharing FeO$_4$ and SiO$_4$ tetrahedra; all of the tetrahedra point in the same direction. Depending on synthesis conditions, Li$_2$FeSiO$_4$ can crystallise in two other structures: $\gamma_s$; and $\gamma_{II}$ [39, 40].
Generally $\beta$ structures show exclusive corner sharing and all of the tetrahedra have the same orientation. $\gamma$ structures show both edge sharing and corner sharing, and the tetrahedra alternate in orientation [26, 39].

Li$_2$FeSiO$_4$ has a high reversible capacity of 140 mAh$^{-1}$, which is 80% of its theoretical limit. Due to the changes in structure described above, the cell potential achieved with the three as-prepared structures ($\beta_{II}$, $\gamma_s$ and $\gamma_{II}$) differs slightly, but in all cases is above 3 V. Li$_2$FeSiO$_4$ is found to undergo a first charge of $\sim$ 3.1 V, but subsequent charges, regardless of the starting structure, are all at 2.8 V. This voltage drop is caused by a change in structure to the cycled structure (inverse-$\beta_{II}$) [39, 40]. The connectivity and orientation of the tetrahedra in the inverse-$\beta_{II}$ is the same as the as-prepared $\beta_{II}$ structure. However, the tetrahedral sites usually occupied by Fe are occupied exclusively by Li, and the remaining Li ions share the conventional Li site with Fe ions [39, 40]. The electronic conductivity of the Li$_2$FeSiO$_4$ is far lower than in LiFePO$_4$; this coupled with its lower cell potentials prevents this material from becoming commercially competitive. However this is still an area of active research and improvements will continue to be made.

The Mn analogue could in principle offer a much more attractive cell potential (4 V) and an excellent theoretical capacity ($\sim$300 mAh$^{-1}$) by utilising a two electron, two lithium ion, redox process, spanning the Mn$^{4+}$/Mn$^{3+}$/Mn$^{2+}$ potential range [39]. Unfortunately, Li$_2$MnSiO$_4$ suffers from severe irreversible capacity loss after the first cycle, as result of Jahn Teller distortions [26, 39]. There are currently investigations into Fe and Mn solid solutions of the form Li$_2$Fe$_{1-y}$Mn$_y$SiO$_4$ to combat this [39].

1.3.1 New Polyanion Cathode Materials

This thesis examines three novel materials which have shown great promise as alternative cathodes. Over the following sections each material is introduced with a brief summary, as well as an outline of the objectives of our computational studies (which are detailed in later chapters).

LiFe$_{0.5}$Mn$_{0.5}$PO$_4$: A mixed-metal olivine phosphate material

To increase the energy density of current olivine phosphate based cells, it would be hugely beneficial to provide a means of utilising the 4.1 V Mn$^{3+}$/Mn$^{2+}$ couple exhibited by LiMnPO$_4$. Unfortunately in early work by Padhi et al [14], delithiation of pure LiMnPO$_4$ proved largely unsuccessful. However, it was shown that solid solutions of Li(Mn$_y$Fe$_{1-y}$)PO$_4$ allowed access to the Mn couple, where Fe acts to stabilise the structure, and is also redox active. The optimum Fe/Mn composition is yet to be determined, although it is clear Mn content above $y=0.75$ is detrimental to cell performance [33, 41]. For our investigation the 50/50 composition (LiFe$_{0.5}$Mn$_{0.5}$PO$_4$) shown in Figure 1.11 was chosen.
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Figure 1.11: LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ unit cell: corner-sharing FeO$_6$ and MnO$_6$ octahedra linked by PO$_4$ tetrahedra forming isolated 1D channels parallel to the $b$-axis; lithium ions are situated in edge sharing octahedral sites which run along these channels.

Although there have been many computational studies on LiFePO$_4$ [24, 25], the solid solutions have not been examined. Our study is detailed in chapter 3 in which we investigate intrinsic disorder, ion migration, and defect association. Anti-site defects where Fe and Li swap sites are found to be prevalent in the olivine phosphates and could affect lithium diffusion [25, 29]. We have carried out a detailed examination of the energetics of anti-site disorder and clustering in this material.

LiFeSO$_4$F and NaFeSO$_4$F: Tavorite-structured fluorosulphates

A new family of fluorosulphates has attracted considerable attention as alternative positive electrode materials for rechargeable lithium batteries. The discovery of this family originates from structural modifications of the related fluorophosphate materials discussed previously [42]. By replacing the the PO$_4^{3-}$ moiety with SO$_4^{2-}$ the operating cell voltage was shown to increase by $\sim$ 0.6 - 0.8 V to a more competitive level [43, 44]. LiFeSO$_4$F therefore exhibits an operating cell voltage of 3.6 V compared to 3.0 V for Li$_2$FePO$_4$F.

LiFeSO$_4$F exhibits the same tavorite structure as Li$_2$FePO$_4$F (shown in Figure 1.12), consisting of layers of corner-sharing FeO$_4$F$_2$ octahedra which alternate in orientation. The fluorine ions sit trans to each other forming the link between adjacent FeO$_4$F$_2$ octahedra. Tetrahedral SO$_4$ units join the layers together forming a 3D network of open tunnels. Li ions sit opposite each other in sites located at the periphery of these tunnels [44].
Figure 1.12: The experimentally determined unit cell of LiFeSO$_4$F showing the tavorite structure: layers of corner-sharing FeO$_6$F$_2$ octahedra which alternate in orientation, are connected by tetrahedral SO$_4$ units forming a 3D network of open channels; lithium ions reside in sites at the periphery of these channels.

Possibly due to the presence of this 3D network of lithium tunnels, the ionic conductivity of the material has been found to be better than its olivine phosphate analogue (LiFePO$_4$) [44]. However, apart from basic conductivity studies, there has been little attempt so far to understand the atomistic migration pathways or activation energies which govern the Li ion conduction within the structure.

It is equally important to examine Na-ion mobility in tavorite type NaFeSO$_4$F on the grounds of abundance and cost [36]. NaFeSO$_4$F also crystallises in a tavorite framework, although initial attempts to extract Na$^+$ ions from this structure have given very disappointing results. This is puzzling, given the presence of a similar open 3D network of ion transport channels [36, 45].

To fully understand the local structural and transport features influencing the electrochemical behaviour of AFeSO$_4$F (A = Li or Na) materials, it is important to further our fundamental understanding of defects and ion transport at the atomic scale. Our study detailed in chapter 4 provides a systematic investigation of structure, defects and ion transport in LiFeSO$_4$F, using atomistic modelling techniques, for the first time.

LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F: A triplite-structured fluorosulphate

The discovery of the triplite phase stems from initial investigations into fluorosulphate materials, where it was found that unlike LiFeSO$_4$F which crystallises in the tavorite structure, LiMnSO$_4$F crystallised in the triplite structure (shown in Figure 1.13) [46]. LiMnSO$_4$F shows no electrochemical activity, which is in contrast to
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![Figure 1.13: Triplite structured LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F unit cell: two crystallographically unique edge sharing chains of $MO_4F_2$ octahedra run along the [101] and [010] and are linked by corner sharing $SO_4$ tetrahedra; Li does not have a unique site, instead sharing the $M$ sites with Fe and Mn.](image)

the majority of polyanionic cathode materials where Mn based analogues tend to provide much greater cell voltages than the Fe members [14, 47].

This lead to research into Fe/Mn solid solutions where it was found that formation of the triplite structure can be achieved by substituting as little as 5% Mn for Fe in LiFeSO$_4$F. The resultant material LiFe$_{1-y}$Mn$_y$SO$_4$F provides an Fe$^{3+}$/Fe$^{2+}$ redox potential of 3.9 V which is the highest ever reported [46].

Although built from the same octahedral and tetrahedral units, the triplite and tavorite structures differ considerably. Unlike the tavorite structure, the triplite has no unique Li site, instead lithium shares the transition metal sites, as shown in Figure 1.13. X-ray crystallography experiments [46, 48] suggest there is no distinct long range Li/M order within the structure, so there are no long-range chains of connected Li$_2$F$_2$O$_4$ octahedra to form open channels along which Li may diffuse; this could suggest poor rate capability as a result. However, triplite LiFe$_{1-y}$Mn$_y$SO$_4$F shows excellent cycling performance despite the lack of coherent long-range lithium diffusion channels.

Our simulation study, detailed in chapter 5, provides atomic scale insight into the complex Li migration mechanisms required for net Li diffusion in triplite-structured LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F.
Chapter 2

Methods

2.1 Introduction

Computer modelling techniques are now well-established tools in the field of solid state materials chemistry. They provide a powerful means of investigating fundamental structural, defect and transport processes at the atomic (or nano) scale. This chapter outlines the computational methodologies employed throughout this thesis to investigate such atomic-scale properties.

There are two main techniques used in the studies presented in this thesis: energy minimisation and molecular dynamics (MD). A description of the inter-atomic forces is required for both of these techniques; in this work the forces are described by inter-atomic potentials, which are explained in detail in section 2.5.1.

These techniques have been implemented in several software packages: energy minimisation calculations were performed using the General Utility Lattice Program (GULP) [49, 50], and MD simulations were performed using DL_POLY [51, 52]. As these techniques are described in extensive detail elsewhere [49, 53–55], a more general overview has been provided here.

2.2 Energy Minimisation

Our modelling techniques are based around the Born model of solids which essentially allows the potential energy of a chemical system to be expressed as a function of its atomic coordinates (equation 2.1):

\[ U = f(x), \]  

(2.1)

where \( U \) is the potential energy and \( x \) is a vector which contains the cartesian coordinates of all the atoms in the system; for a system of \( N \) atoms \( x \) will contain \( 3N \)
elements. This function is usually referred to as the energy surface, and each point on the surface represents a different configuration of atomic coordinates. Exploration of the energy surface for a solid state system can provide information on stable structures and the transitions between them. However due to its high dimensionality, particularly for systems containing large numbers of atoms, visualisation of the entire surface is impractical. Fortunately, chemical processes of interest only make up small localised regions on the surface.

For example, two features of the energy surface we are particularly interested in are two types of stationary point: minima and saddle points, shown in Figure 2.1a and b respectively. Minima represent stable states of chemical systems, and saddle points represent transition states. The various energy minimisation algorithms detailed throughout this section are used to search for these important features. All of these algorithms follow the same general concept, which is to adjust the atomic coordinates from an initial trial configuration until a minimum on the energy surface has been reached.

For all the minimisation techniques described here the algorithms can only go down hill on the energy surface so they can only locate the minimum which is nearest the starting point. Some chemical systems can have many stable arrangements, for example several polymorphs of the same material, each of which would represent a different local minimum on the potential energy surface. The global minimum is the local minimum of lowest energy and corresponds to the most thermodynamically stable structure. In cases like this, other techniques such as simulated annealing and genetic algorithms could be employed to explore many minima. However, employing these techniques is not necessary in the bulk structure studies presented here, because sets of atomic coordinates, which provide a reasonable first guess at a minimum of interest, are taken from experimental x-ray diffraction data.

\[
f(x) = f(x_1, x_2)
\]

\[
x_m
\]

\[
x_s
\]

\[
(a)
\]

\[
(b)
\]

**Figure 2.1:** Two important stationary points on the energy surface: (a) a minimum point, (b) a saddle point.
The energy minimisation algorithms used in this work all use derivatives of the energy surface with respect to the atomic coordinates. These algorithms can be split into two categories: first-order techniques, which utilise first derivative information; second-order techniques which utilise both first derivative and second derivative information. Derivatives in general provide useful local information about the energy surface which improves the efficiency with which a minimum can be located. The accuracy of the minimisation procedure increases with more derivative information, hence fewer minimisation steps are required. However, the simulation time per step also increases. There is a fine balance between accuracy and calculation time.

For multi-dimensional functions such as the energy surface, the gradient (first derivative) is a vector \( \mathbf{g} \) containing \( 3N \) elements, where each element is a partial derivative of the energy function with respect to a component coordinate:

\[
g = U'(x) = \begin{bmatrix}
\frac{\partial U}{\partial x_1}(x) \\
\frac{\partial U}{\partial x_2}(x) \\
\vdots \\
\frac{\partial U}{\partial x_{3N}}(x)
\end{bmatrix}
\]  (2.2)

The direction of the gradient is a useful first indication of where the minimum lies and its magnitude represents how steep the slope is. The second derivative information is stored in a \( 3N \times 3N \) matrix called the Hessian matrix or the force constant matrix, and is defined as

\[
H = U''(x) = \begin{bmatrix}
\frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 U}{\partial x_1 \partial x_{3N}} \\
\frac{\partial^2 U}{\partial x_2 \partial x_1} & \frac{\partial^2 U}{\partial x_2^2} & \cdots & \frac{\partial^2 U}{\partial x_2 \partial x_{3N}} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 U}{\partial x_{3N} \partial x_1} & \frac{\partial^2 U}{\partial x_{3N} \partial x_2} & \cdots & \frac{\partial^2 U}{\partial x_{3N}^2}
\end{bmatrix}
\]  (2.3)

The second derivative information describes the local shape of the function. For the atomistic modelling work detailed in this thesis both of these quantities are calculated analytically. However depending on type of calculation being performed this is not always practical, in which case a numerical approximation is required.

At any stationary point, the gradient, \( \mathbf{g} \), is zero and the type of feature is determined by second derivative information. At a minimum the second derivative is positive in all directions, so any displacement away from this point results in an increase in potential energy. The curvature of the surface around a minimum is therefore “bowl” shaped as shown in figure 2.1a. At a saddle point the second derivative
is negative in one or more directions. A saddle point represents a transition state between stable systems, and corresponds to a maximum along the lowest energy pathways between these systems. The energy difference between the saddle point and the stable systems represents the activation barrier for the transition.

For derivative-based energy minimisation techniques it is useful to express the energy function as a Taylor series about the current position, \( x_i \), on the energy surface:

\[
U(x) = U(x_i) + \frac{(x - x_i)^T U'(x_i)}{1!} + \frac{(x - x_i)^T U''(x_i)(x - x_i)}{2!} + \ldots, \tag{2.4}
\]

where \( U' \) and \( U'' \) represent the first and second derivatives of the energy function, which are the gradient vector and the Hessian matrix. Therefore equation 2.4 can be re-written as

\[
U(x) = U(x_i) + (x - x_i)^T g_i + \frac{1}{2}(x - x_i)^T H_i (x - x_i) + \ldots \tag{2.5}
\]

It is important to note that the actual energy function is unlikely to be quadratic so the Taylor series in equation 2.5 is an approximation. However, close to a minimum a quadratic approximation is fairly valid.

Over the following sections several derivative-based energy minimisation techniques will be discussed in more detail.

### 2.2.1 Steepest Descent

The steepest descent algorithm is the simplest first derivative technique. It is a very robust technique which reduces the potential energy of the system quickly by altering the atomic positions in the direction of steepest descent, i.e. movement directly down hill on the energy surface. The direction of steepest descent is a vector \( r_i \), which points directly opposite to the gradient vector \( g_i \), such that

\[
r_i = -g_i. \tag{2.6}
\]

An example energy surface showing the direction of steepest descent \( r_i \) from a starting position \( x_i \) is provided in Figure 2.2a. The plane indicates a cross section (shown again in Figure 2.2b) of the energy function along \( r_i \). A position \( x_{i+1} \) closer to the minimum is generated from the current position \( x_i \) by minimising the energy function along this cross section (the direction of steepest descent), according to:

\[
x_{i+1} = x_i + \alpha_i r_i. \tag{2.7}
\]

The scalar \( \alpha_i \) determines how far along \( r_i \) to move to reach the minimum. The size of \( \alpha_i \) cannot be determined analytically because the energy function is likely not harmonic. Instead a line search or arbitrary step approach, where the energy
Figure 2.2: Steepest descent minimisation: (a) The energy surface, with a vector pointing in the direction of steepest descent from the current configuration $x_i$. (b) the intersecting plane from (a) which contains the energy function along the direction of steepest descent, which is minimised by a line search.

Figure 2.3: Illustration of the steepest descent algorithm: a view from above of the energy surface (shown in Figure 2.2a), showing the iterations of the steepest descent algorithm. Note the series of right-angled turns.
is monitored along \( r_i \) is used to find the value of \( \alpha_i \) which minimises the energy, as illustrated in Figure 2.2b.

By definition the gradient at the minimum of the line search \( g_{i+1} \) cannot have any component in the direction of the line search. The next iteration of the steepest descent algorithm must therefore be orthogonal to the previous search direction. This results in a series of right angled turns which gradually move closer to the minimum (see Figure 2.3).

The direction of movement at each step \( r_i \) is determined by the largest inter-atomic forces so steepest descents is good at relieving high energy configurations quickly. Also the method is very robust far from a minimum where a quadratic approximation holds less validity. However, because of all the right angled turns, the algorithm does not provide the most efficient route to the minimum, particularly in long narrow valleys where it could take many small steps to reach the minimum depending on the starting configuration.

### 2.2.2 Conjugate Gradient

The conjugate gradients algorithm is an advancement on the steepest descents algorithm which eliminates the repeated re-introduction of errors at each iteration. Conjugate gradients belongs to the conjugate directions family of algorithms, where the fundamental idea is to pick a set of orthogonal search vectors \( d_0, d_1, \ldots, d_{n-1} \), and minimise the energy in each direction only once. After each direction has been minimised the local minimum on the energy surface has been located.

Early conjugate directions algorithms were quite memory intensive because each search direction used had to be stored so as to ensure that subsequent minimisation along the energy surface would not occur along any component of a previously used direction. The conjugate gradients algorithm generates a new search vector \( d_i \) from the current gradient \( g_i \), the previous gradient \( g_{i-1} \) and the previous search vector \( d_{i-1} \) according to:

\[
d_i = -g_i + \beta_i d_{i-1}, \tag{2.8}
\]

where

\[
\beta_i = \frac{g_i \cdot g_i}{g_{i-1} \cdot g_{i-1}} \tag{2.9}
\]

A closer position to the minimum \( x_{i+1} \) is then generated by minimising the energy function in this new direction \( d_i \):

\[
x_{i+1} = x_i + \alpha d_i \tag{2.10}
\]

Because no previous gradient information exists, the initial search direction is along the direction of steepest descent \((-g_i)\) i.e. the first iteration is the same as the steepest descent algorithm. At each iteration \( \alpha \) is also determined by the same line search technique. An illustration of the conjugate gradients method is provided in Figure 2.4.
Figure 2.4: Illustration of the conjugate gradients algorithm: The first step is the same as the steepest descent, but minimisation is achieved much more efficiently in subsequent steps. This simple two variable problem is solved in two steps.

The conjugate gradients technique is more efficient than steepest descent taking fewer steps to reach the minimum; for a quadratic function of $n$ variables the minimum will be reached in $n$ steps. The calculation time at each step is also quick because it is a very simple algorithm using only first derivative information. (Note: Although the resultant algorithm is very simple, the mathematics behind why it works is fairly complex. A full and clear explanation is provided by Shewchuck [56]).

2.2.3 Newton-Raphson

The Newton-Raphson method is an extension of previous gradient techniques where second derivative information is used in conjunction with first derivative information to locate the minimum. The basis of the method is to approximate the energy surface at a point $x_i$ with the Taylor series, outlined in equation 2.5, truncated at the second derivative term:

$$U(x) = U(x_i) + (x - x_i)^T g_i + \frac{1}{2} (x - x_i)^T H_i (x - x_i).$$  \hspace{1cm} (2.11)

The first derivative of $U(x)$ gives:

$$U'(x) = g_i + (x - x_i) H_i.$$  \hspace{1cm} (2.12)

At the minimum ($x = x_m$) the gradient is zero so equation 2.12 can be set to zero and rearranged giving:

$$x_m = x_i - H_i^{-1} g_i.$$  \hspace{1cm} (2.13)
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If the potential energy surface is truly quadratic the Newton-Raphson method finds the minimum in one step. Unfortunately this is rarely the case for real systems and so the process becomes iterative; a new point closer to the minimum \( x_{i+1} \) is generated from the current position \( x_i \), gradient \( g_i \) and Hessian matrix \( H_i \) according to:

\[
x_{i+1} = x_i - H_i^{-1} g_i.
\]

(2.14)

Newton-Raphson provides rapid convergence close to the minimum where the harmonic approximation is valid. Further from the minimum it is less useful, and minimisation can become unstable. It is therefore important to choose a good starting structure for optimisation. In cases where experimental structural data is unavailable or inaccurate it can be useful to use a more robust method such as steepest descent initially, in order get near a minimum, followed by Newton-Raphson to find it more accurately.

Calculation and inversion of the Hessian matrix is very computationally expensive; fortunately it is possible to take advantage of the fact that the Hessian (local shape of the energy surface) does not change very much with each iteration. The GULP code [49] uses the Broyden-Fletcher-Goldfarb-Shanno [57] (BFGS) updating formulae to approximate changes in \( H_n \) at each iteration. The Hessian matrix is only fully recalculated after the energy has changed significantly, or a certain number of iterations have been reached since its last calculation [50].

The BFGS algorithm updates the Hessian using equation 2.15 shown below:

\[
H_{i+1} \approx H_i + \frac{(x_{i+1} - x_i) \times (x_{i+1} - x_i)}{(x_{i+1} - x_i) \cdot (g_{i+1} - g_i)} - \frac{[H_i \cdot (g_{i+1} - g_i)] \times [H_i \cdot (g_{i+1} - g_i)]}{(g_{i+1} - g_i) \cdot H_i \cdot (g_{i+1} - g_i)}
\]

\[+ [(g_{i+1} - g_i) \cdot H_i \cdot (g_{i+1} - g_i)]u \times u,
\]

(2.15)

where

\[
u = \frac{(x_{i+1} - x_i)}{(x_{i+1} - x_i) \cdot (g_{i+1} - g_i)} - \frac{[H_i \cdot (g_{i+1} - g_i)]}{(g_{i+1} - g_i) \cdot H_i \cdot (g_{i+1} - g_i)}.
\]

(2.16)

As can be seen from these expressions, the updated Hessian is approximated from the current and new positions and gradients, and the current Hessian matrix. Assuming the approximation holds, with increasing iterations the approximated Hessian becomes closer to the true Hessian matrix.

2.2.4 Finding Transition States

So far the discussion about energy minimisation has focussed on finding minima on the energy surface. However we are not only interested in the stability of various structures, but also the kinetics (the rate of conversion between stable structures. Transition states (or saddle points) represent maximum points along the minimum energy pathways between stable species. At a saddle point there are one or more
negative eigenvalues in the Hessian matrix which correspond to one or more directions which point down on the energy surface. In our simulations we typically deal with first-order transition states, where the Hessian has only one negative eigenvalue. This corresponds to the maximum along a single pathway which connect two minima. It is a minimum in all directions perpendicular to the pathway (see Figure 2.1b). There are a number of methods employed to find transition states; the two methods employed in this work involve mapping out a series of points along the minimum energy pathway, with the point of highest energy along the path an estimate of the transition state.

In the simulations presented in this thesis transition state minimisation techniques are applied to find lithium migration barriers. The lithium migration processes here, typically involve incrementally moving a lithium ion from one crystallographic site to a neighbouring vacant lithium site. Other mechanisms are possible, and are described in more detail later in section 2.5.5.

**Constrained Minimisation**

A simple method for finding lithium migration barriers is to place a lithium in an incremented series of positions between two crystallographic sites; An energy minimisation algorithm is applied at each point, but the motion of the migrating lithium ion is constrained in one direction, preferably the direction of the pathway. This will allow the mobile species to relax in directions perpendicular to the pathway, thus mapping out the lowest energy route.

Unfortunately there is an important draw back of applying this method in GULP; It is only possible to apply constraint along the cartesian axes, and for all but the simplest of systems pathways rarely lie along a cartesian axis. In such cases the resulting relaxation will not be directly perpendicular to the path direction. Therefore energy comparison between a direct linear pathway and a non-linear (relaxed) path is less trivial. This can be resolved by mapping relaxed points perpendicularly back to the linear path for direct comparison (which is described in depth in appendix B.1).

Essentially the main draw back of this method is that it requires lots of user intervention. However, it is very robust and works excellently in crystal structures with high symmetry.

**Nudged Elastic Band**

The minimum energy pathway between two minima can also be found using the nudged elastic band (NEB) method [58, 59]. A requirement of this method, as with simple constrained minimisation, is that the initial and final states (both minima) must be known.
During a typical nudged elastic band calculation a set of starting structures (or replicas) are created via linear interpolation between the initial and final structures. This set of replicas map out a direct linear path between the initial and final points, which serves as an initial guess at the minimum energy path. Each replica is linked to its neighbour by a spring force (mimicking an elastic band) which holds the replicas together and attempts to maintain an equal spacing between them. All of the replicas undergo energy minimisation simultaneously resulting in the ‘band’ lying along the minimum energy pathway.

A force projection is used to stop the spring forces interfering with the minimisation process, and the atomic forces affecting the distribution of points along the band. Only the component of the inter-atomic forces perpendicular to the band and the component of the spring force parallel to the band contribute to the energy minimisation process.

This technique is particularly useful for finding migration barriers in materials with low symmetry crystal structures (like those investigated in chapters 4 and 5), where the migration pathways are not parallel to the cartesian axes. NEB is subject to periodic boundary conditions, so it is important to ensure that the simulation cell is large enough to prevent interactions between replicas in neighbouring periodic images becoming significant.

### 2.3 Periodic Boundary Conditions

The calculation of all the interactions between atoms in large extended solids is an extremely computationally expensive task, so periodic boundary conditions are employed to reduce the simulation time. Due to their symmetry crystalline solids can be broken up into unit cells of relatively small numbers of atoms, ions or molecules which are continuously repeated in three dimensions.

![Figure 2.5: Schematic representation of periodic boundaries.](image)
For simulation the unit cell is surrounded by identical images of itself. Ions in the unit cell interact with each other and all ions contained within the images. Ions in the images only interact with those in the unit cell. Periodic boundary conditions are essentially used to make the simulation cell “feel” as if it is contained within a large extended solid.

In some cases, for example simulating an isolated defect within a crystal structure, the interaction of a species with its image requires suppression; this is achieved by increasing the size of the simulation cell to a larger “super-cell”.

### 2.4 Molecular Dynamics

The energy minimisation techniques outlined in previous sections describe systems at absolute zero and therefore contain no information about kinetic energy, focussing purely on the potential energy of the system. Although much useful information can be gained from such calculations, thermal effects are neglected.

Molecular Dynamics (MD) explicitly includes kinetic energy of atoms by assigning all the atoms a velocity. Collectively these velocities give the system temperature. One of the main disadvantages of energy minimisation techniques discussed previously is that they only travel down hill on the energy surface. The additional kinetic energy provided by molecular dynamics simulations enables the system to jump over local energy barriers, and potentially find more thermodynamically stable configurations. However, due to the short time-scale real simulated systems generally overcome small energy barriers of the order of a few $k_B T$.

In addition to exploring a larger amount of the energy surface MD simulations can provide information about diffusion processes and time averaged structures. The broad basis of these MD techniques is outlined in the following sections. Detailed information can be found in extensive reviews elsewhere [51, 52].

Simulating dynamical properties such as ion transport and crystal vibrations requires a method of calculating ion trajectories, which describe how the positions and velocities of ions vary with time. Essentially this requires integrating Newton’s laws of motion for the entire system over a finite time period. By knowing the force $\mathbf{f}$ acting on an atom we can determine its acceleration, $\mathbf{a}$, which is the second derivative of its position, $\mathbf{r}$, with time, $t$:

$$\mathbf{f} = m \frac{d^2 \mathbf{r}}{dt^2} = ma. \quad (2.17)$$

In a simple case where the force acting between ions remains constant the velocities and positions after a change in time, $dt$, can be calculated from equations 2.18 and 2.19 respectively.

$$\mathbf{v}_{t+dt} = \mathbf{v}_t + \mathbf{a}_t dt. \quad (2.18)$$
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\[ \mathbf{r}_{t+dt} = \mathbf{r}_t + \mathbf{v}_t dt + \frac{1}{2} \mathbf{a}_t dt^2. \]  \hspace{1cm} (2.19)

In real systems the forces acting on an ion will vary depending on its distance from other ions; in which case equations 2.18 and 2.19 are only accurate for infinitesimal changes in time. As this is a coupled many-body problem, describing the motion of ions over larger, more statistically relevant time-scales requires numerical integration algorithms.

2.4.1 Integration Algorithms

Integration algorithms are used to update ion trajectories over a finite time step. The integration is broken up into a series of discrete steps, each separated by a finite time, \( \Delta t \). The force acting on each ion at a given time, \( t \), is calculated from the sum of the interactions with all other ions in the system. The acceleration, determined from the force, is combined with positions and velocities at time \( t \) to generate updated positions and velocities at time \( t + \Delta t \). The force is assumed to be constant between \( t \) and \( t + \Delta t \), which is where the main source of inaccuracy in this methodology lies. This process is then repeated for the duration of the simulation time.

There are many different integration algorithms which can be used to integrate the equations of motion, all of which assume the positions, velocities, and accelerations can be approximated by a Taylor series expansion described below. The accuracy with which these properties are calculated can be improved by reducing the time step, and by including higher order terms from the Taylor expansion.

The Verlet algorithm [60], a variant of which is used in this work, is widely used in MD simulations. It can be derived by approximating the trajectory of ions as a Taylor series about the current set of ion positions, \( \mathbf{r}_t \), truncated at the third-derivative term.

\[ \mathbf{r}_{t+\Delta t} = \mathbf{r}_t + \mathbf{v}_t \Delta t + \frac{\mathbf{a}_t}{2} \Delta t^2 + \frac{\mathbf{b}_t}{6} \Delta t^3 + \Theta(\Delta t^4) \]  \hspace{1cm} (2.20)

where \( \mathbf{v}_t, \mathbf{a}_t \) and \( \mathbf{b}_t \) are the velocities, accelerations and jerks (changes in acceleration) respectively; \( \Theta \) is an error term. It is important to note that velocity, acceleration and jerk are the first, second and third derivatives of position with time.

\[ \mathbf{v}_t = \dot{\mathbf{r}}_t, \]  \hspace{1cm} (2.21)

\[ \mathbf{a}_t = \dot{\mathbf{v}}_t = \ddot{\mathbf{r}}_t, \]  \hspace{1cm} (2.22)

\[ \mathbf{b}_t = \dot{\mathbf{a}}_t = \dddot{\mathbf{r}}_t. \]  \hspace{1cm} (2.23)

the \( \mathbf{b} \) term which essentially represents change in force is difficult to compute. Fortunately Verlet was able to use a mathematical trick which takes information from
the previous time step $r_{t-\Delta t}$ allowing the third derivative information to be included implicitly.

Derived in the same way as equation 2.20, the Taylor series at $t - \Delta t$ is given by:

$$r_{t-\Delta t} = r_t - v_t \Delta t + \frac{a_t}{2} \Delta t^2 - \frac{b_t}{6} \Delta t^3 + \Theta(\Delta t^4).$$  \hfill (2.24)

The sum of equations 2.20 and 2.24 gives the Verlet algorithm,

$$r_{t+\Delta t} = 2r_t - r_{t-\Delta t} + a_t \Delta t^2 + \Theta(\Delta t^4).$$  \hfill (2.25)

By using information from the previous time step the need to calculate third-derivative information has been avoided. However, the downside of this approach is that the error increases, because the error from calculation of $r_{t-\Delta t}$ and from $r_t$ are both carried into the approximation of $r_{t+\Delta t}$.

The Verlet algorithm does not explicitly calculate the velocity as it is not necessary to generate ion trajectories. However, it is still an important quantity to compute; velocities are scaled in order to maintain a system temperature (see section 2.4.3) and computing the kinetic energy is required to calculate the total energy of the system. It is possible to recover the velocities by subtracting equation 2.20 from 2.24:

$$v_t = \frac{r_{t+\Delta t} - r_{t-\Delta t}}{2\Delta t} + \Theta(\Delta t^2).$$  \hfill (2.26)

This means that the velocities cannot be calculated until the positions have been computed at the next step. There is also a greater degree of numerical inaccuracy introduced with calculating the velocities in this manner; the error is of the order $\Delta t^2$.

There is a variant of the Verlet algorithm, Verlet-leapfrog, employed in DL_POLY_2\footnote{This is the default algorithm in DL_POLY_2, and is used for all the molecular dynamics calculations in this thesis.} which avoids some of these deficiencies. Verlet-leapfrog evaluates the velocities at half time steps:

$$v_{t-\frac{1}{2} \Delta t} = \frac{r_t - r_{t-\Delta t}}{\Delta t}$$  \hfill (2.27)

$$v_{t+\frac{1}{2} \Delta t} = \frac{r_{t+\Delta t} - r_t}{\Delta t}$$  \hfill (2.28)

An expression for calculating the new positions from the old positions and velocities at the half time step is given by:

$$r_{t+\Delta t} = r_t + v_{t+\frac{1}{2} \Delta t} \Delta t + \Theta(\Delta t^4),$$  \hfill (2.29)

and the velocities are update by:

$$v_{t+\frac{1}{2} \Delta t} = v_{t-\frac{1}{2} \Delta t} + a_t \Delta t + \Theta(\Delta t^3).$$  \hfill (2.30)
When implementing the algorithm, the accelerations at the current time step are determined by evaluating the forces, and used to update the velocities from $t - \frac{1}{2} \Delta t$ to a new set at $t + \frac{1}{2} \Delta t$ using equation 2.30. In doing so the velocities are seen to “leapfrog” over the current positions at the current time step $t$, (hence the name). Equation 2.29 is then applied to leap the positions over the velocities to their updated values at $t + \Delta t$, and the process continues.

The main advantage Verlet leapfrog holds over Verlet is that as the velocities are included explicitly, so the accuracy to which they are calculated is an order of magnitude greater. However there is a clear disadvantage in that the positions and velocities are not synchronised so the kinetic and potential energy contributions cannot be calculated accurately at the same time. In order to calculate full-step, as opposed to half-step, velocities, the average of two centred half step velocities can be taken:

$$v_t = \frac{1}{2} (v_{t+\frac{1}{2}\Delta t} + v_{t-\frac{1}{2}\Delta t}) + \Theta(\Delta t^2),$$  \hspace{1cm} (2.31)

but this carries the error of both of the half-step velocity values forward so the value of $v_t$ is less accurate.

A final point worth noting is that neither of these algorithms are self starting, that is they require information from the previous step. Initially velocities are therefore assigned. In practice, these are assigned randomly ensuring that the system starts at the desired temperature, and importantly that the system has no translational momentum. These conditions are expressed in equations 2.32 and 2.33:

$$\sum_{i=1}^{N} m_i v_i^2 = 3Nk_BT,$$  \hspace{1cm} (2.32)

$$\sum_{i=1}^{N} m_i v_i = 0,$$  \hspace{1cm} (2.33)

where $N$ is the number of atoms and $k_B$ is the Boltzmann constant.

### 2.4.2 Time Step and Equilibration

The choice of time step $\Delta t$ is important and non-trivial. If the choice is too small, the simulations take longer to move through the different states available in the system. However, too large and instabilities can arise causing atoms to move unphysical distances or collide with too much energy, resulting in failure of the simulation. The ideal choice is as large as possible, so as to cover as much “real time” as quickly as possible, but without any instability; in practice this is typically between 0.1 and 1 femto-seconds.

The initial stage of an MD simulation involves an equilibration period, which is designed to bring the system from a starting configuration with assigned velocities to
equilibrium. During this period several properties including the total energy, which is the sum of kinetic energy due to atomic motion and potential energy from the atomic arrangement, are monitored; equilibrium is achieved when these properties have settled into a steady pattern. Equilibration typically lasts tens of thousands of time steps to ensure satisfactory convergence. Once complete, the production phase starts, which is where all the desirable statistics are extracted from.

### 2.4.3 Ensembles

An ensemble is a distribution of thermally accessible states of a system subject to a set of constraints. During MD simulations the atomic coordinates change with time. Therefore, each state corresponds to a different atomic arrangement within the system. Different sets of constraints give rise to different types of ensemble.

The microcanonical ensemble ($NVE$) contains a constant number of atoms $N$, simulation cell volume $V$ and total energy $E$. Within the $NVE$ ensemble, the contributions of the potential and kinetic energy can vary, but the total energy remains constant. This conserved quantity can be represented by:

$$
\mathcal{H} = \mathcal{K} + \mathcal{V},
$$

(2.34)

where $\mathcal{H}$ is the Hamiltonian, which is an operator corresponding to the total energy, and $\mathcal{K}$ and $\mathcal{V}$ are the kinetic and potential components respectively.

The conditions of the microcanonical ensemble do not correspond to “real” conditions under which most experiments are carried out because large pressure and temperature variations are allowed [61]. The two most commonly used alternatives are the canonical (or $NVT$) and isobaric-isothermal (or $NPT$) ensembles, which allow the system to be studied as a function of temperature and pressure respectively. It is therefore important to be able to control both the temperature and pressure during simulation; this is typically done using mathematical thermostats and barostats. An added benefit of simulating under such controlled conditions is that they help to compensate for slow accumulation of rounding errors over time.

The instantaneous value of temperature is proportional to the mean kinetic energy of the constituent atoms, which is directly related to their velocities:

$$
T \propto \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2
$$

(2.35)

Therefore, a simple way to control temperature is to scale the velocities at each step, so that the system maintains a desired temperature. However, this approach does not allow for any fluctuations in temperature, which makes the model unphysical.
In this work an improved thermostat developed by Berendsen et. al. [62] is used. The simulation cell is coupled to a hypothetical external heat bath with fixed temperature $T_{\text{bath}}$. The velocities are scaled at each step such that the rate of change of temperature is proportional to the difference in temperature between the simulation cell and the heat bath:

$$\frac{dT(t)}{dt} = \frac{1}{\tau}(T_{\text{bath}} - T(t)),$$

(2.36)

where $\tau$ is an empirical parameter which determines how strongly the system and heat bath are coupled.

The value of $\tau$ should be chosen with care. At small values of $\tau$ the coupling is strong producing temperature fluctuations which are unrealistically small. At high values of coupling is weak; as $\tau \to \infty$ the thermostat is effectively removed and the simulation is sampling the $NVE$ ensemble. Values of $\tau \approx 0.1$ ps are typically used in MD simulations of condensed-phase systems [61].

The Berendsen thermostat can also be readily altered to scale simulation cell volume rather than temperature to provide a barostat. A similar principal applies where the simulation cell is connected to a hypothetical pressure bath. The rate of change of pressure is given by:

$$\frac{dP(t)}{dt} = \frac{1}{\tau}(P_{\text{bath}} - P(t)),$$

(2.37)

Where $\tau$ is the coupling parameter and $P_{\text{bath}}$ is the pressure of the bath. The positions of the atoms are simply scaled to compress or expand the simulation cell depending on the pressure difference.

### 2.4.4 MD Data Analysis

MD simulations can provide useful data about ion diffusion and time averaged structures. These data can be extracted directly from the simulated ion trajectories.

#### Radial Distribution Function

The radial distribution function (RDF) provides a useful description of the structure of a system. It describes how the density of the system varies spherically outward from a given reference atom. The RDF is defined as the probability of finding an atom at a distance $r$ from the reference atom, relative to that for an ideal gas.

An RDF is generated by sorting the neighbouring atoms around each reference atom into a series of distance “bins” or histograms. This is illustrated in Figure 2.6. Each bin is separated by a thickness $\Delta r$ and the number of neighbours in each bin is summed and then averaged over the entire ensemble.
The radial distribution function $g(r)$ is given by

$$g(r) = \left\langle \frac{V}{N^2} \sum_{i,j=1}^{N} \delta(r - r_{ij}) \right\rangle, \quad (2.38)$$

where $r_{ij}$ is the distance between atoms $i$ and $j$, $N$ is the total number of atoms, and $\delta$ is a function which is non zero only for small input values i.e. when $r_{ij}$ is close to the desired value of $r$. $V$ is the volume of a spherical shell of inner radius $r$ and thickness $\Delta r$, given by

$$V \approx 4\pi r^2 \Delta r, \quad (2.39)$$

which normalises for the number of atoms within a given shell, increasing with shell radius.

Crystalline materials, such as those detailed throughout this thesis, show RDF plots which consist of a series of sharp peaks at regular intervals; this is because the atoms in crystals are arranged in a regular ordered lattice, therefore the atomic density varies regularly with distance. An example RDF plot of a crystalline material is provided in Figure 2.7.

RDF plots can provide valuable insight into long-range (dis)order within materials. They also provide a means of “finger printing” crystal structures.

**Time-Averaged Densities**

For systems, such as lithium ion batteries, where ion migration occurs it is useful to be able to visualise the mechanisms of migration. Time-averaged atomic den-
Figure 2.7: Example of a radial distribution function between cations in a crystalline material. Note the presence of well defined peaks at large ion separations.

Density plots generated directly from the trajectory data allow us to view the various pathways which ions have taken.

Our approach to generating such plots is to split the cell into a grid of three-dimensional boxes. The positions of the specified atoms at each time step are all superimposed and then the number of atoms in each box are counted and the final data set normalised. The end result is a density image which shows all the regions the specified ion has passed through during the simulation. This technique produces similar results to experimental neutron diffraction maximum entropy method data, cross sections of which are shown in Figure 3.5c (Chapter 3).

Mean Square Displacement

The means squared displacement (MSD) is a measure of the distance atoms in the simulation cell have been moved from their initial coordinates. Examining the MSD as a function of time provides information about the diffusion rate of atoms in the system. The MSD is defined by:

$$\text{MSD}(t) = \frac{1}{N} \sum_{i=0}^{N} |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2,$$

(2.40)

where $N$ is the number of specified atoms, and $\mathbf{r}_i(0)$ and $\mathbf{r}_i(t)$ are the initial and current positions of atom $i$ respectively. $\mathbf{r}_i(0)$ can be reset as a further averaging process.

The slope of the MSD, when considered over long time scales, is related to the self-diffusion coefficient $D$ via the Einstein relation:

$$\text{MSD}(t) = 2dDt$$

(2.41)
where \( d \) is the systems dimensionality. Therefore for three dimensional systems we get

\[
D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} MSD.
\]  

(2.42)

It also possible to estimate the activation barrier for migration from an Arrhenius plot using diffusion data obtained from a set of MSD plots at several different temperatures. In this form the Arrhenius equation is

\[
\ln D = \frac{-E_a}{RT} + \ln A,
\]

(2.43)

where \( R \) is the gas constant. It is clear a plot of \( \ln D \) vs \( T^{-1} \) provides a slope proportional to the activation energy \( E_a \). Here MD simulations provide new information about migration barriers which static lattice simulations cannot access.

## 2.5 Atomistic Modelling

Both energy minimisation and MD techniques require evaluation of the forces between the atoms at each step. The description of such forces can be broken into two distinct methodologies: atomistic techniques; or ab-initio techniques.

Atomistic simulation techniques use simple empirically derived functions to describe the inter-atomic forces, whereas ab-initio techniques are based around the fundamental principles of quantum mechanics and are therefore more complex. The choice of technique to use is determined by the properties you wish to extract. Ab-initio techniques explicitly include electron density subject to the rules of quantum mechanics; they are computational expensive, and therefore more suited to small system sizes. Atomistic techniques employed in the work presented in this thesis can readily simulate large numbers (several thousand) atoms, and are frequently used for modelling relaxation around defects which can extend far into the crystal lattice.

### 2.5.1 Inter-Atomic Potentials

The starting point for atomic scale simulation is to accurately calculate the lattice energy (\( U_L \)) for the system in question. The lattice energy is defined as the energy of the crystal with respect to its component ions at infinity and it can be derived experimentally using the Born-Haber cycle. In materials modelling studies the lattice energy is calculated using a set of empirically derived, parameterised equations (or inter-atomic potentials), which collectively make up a potential model. The parameters of these potentials are altered depending on chemical factors such as atomic radius, atomic mass and bond strength; some of which vary depending on the crystal structure.
The most general expression for the lattice energy ($U_L$) is a series expansion of pairwise, three-body, and increasingly larger body terms:

$$U_L = \sum_{ij} V_{ij}(r_{ij}) + \sum_{ijk} V_{ijk}(r_{ijk}) + \ldots \quad (2.44)$$

The potential model used in this work is based around the Born model in which predominantly pairwise terms are included. These two-body terms are then subdivided into long range Coulombic interactions and short range interactions. The short range interaction include both a repulsive term which represents the overlap of electron density\(^{\dagger}\) and a small attractive term due to dispersion in semi-ionic systems:

$$U_L = \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + \sum_{ij} \Phi_{ij}(r_{ij}) \quad (2.45)$$

The short range interactions can be modelled using a number of different expressions. One of the most popular is the Buckingham potential [63] which has been used to successfully model a variety of polar solids [64–67]. The Buckingham potential, used to describe the majority of pairwise interactions in this work, takes the following form:

$$\Phi_{ij}(r_{ij}) = A \exp \left( -\frac{r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6}. \quad (2.46)$$

It is split into two parts, the first part is an exponential repulsion term containing parameters $A$ and $\rho$, which represent electron cloud repulsion between atoms. The second part is an attractive term based on van der Waals interactions parameterised by $C$.

For the studies of fluorosulphate materials (detailed in chapters 4 and 5), a Morse potential [68] was used to model S-O bonds in the SO\(_4\) units. The Morse potential takes into account the covalent nature of such bonds, where inter-atomic separations can vary significantly from the equilibrium distance, and takes the following form:

$$\Phi_{ij}(r_{ij}) = D_e \left[ (1 - \exp(-a(r_{ij} - r_0)))^2 - 1 \right], \quad (2.47)$$

Where $D_e$ is the bond dissociation energy (equivalent to the potential well depth), $r_0$ is the equilibrium bond distance and $a$ controls the width of the potential well. It is noted that the bond dissociation energy is subtracted so that that the interaction energy becomes zero at infinite separation. Pairwise interactions within the SO\(_4\) tetrahedra are also Coulomb subtracted in this work; essentially each SO\(_4^2^-\) moiety is treated as an individual molecular anion unit. This model has previously been used to successfully simulate $M_2$SO\(_4\) ($M = Na$, K, Rb, and Cs) and XSO\(_4\) ($X = Sr$, Ca, Ba) [69–72].

Finally, an additional three body term was used in this work to take into account the angle dependent nature and rigidity of O-P-O and O-S-O bonds in the PO\(_4\) and

\(^{\dagger}\)It is important to note that this term is a simplistic mathematical representation; electrons are not explicitly modelled with atomistic techniques.
SO$_4$ units. The three-body term penalises any deviation from the equilibrium bond angle, $\Theta_0$, with an increase in energy.

$$\Phi_{ijk} = \frac{1}{2} k_{ijk}(\Theta - \Theta_0)^2$$  \hspace{1cm} (2.48)

$k$ is the force constant and $\Theta_0$ is the equilibrium bond angle for a tetrahedron.

**Ewald Summation**

The summation of the Coulombic interactions presents a problem for computational modelling. The contribution of each pairwise Coulombic interaction decreases with $\frac{1}{r_{ij}}$ where $r_{ij}$ is the inter-ionic separation of ions $i$ and $j$. However, the number of ionic interactions increases with the surface area of a sphere, $4\pi r^2$ and so convergence is very slow.

![Ewald summation](image)

**Figure 2.8:** Ewald summation: The sum of a set of point charges $U_{\text{Coulombic}}$ is calculated from a set of screened charges $U_{\text{Real}}$ plus a set of compensating charges which counteract the screening $U_{\text{Reciprocal}}$.

This problem is overcome by a technique developed by Ewald [73] in which the sum is divided into two rapidly convergent series shown in Figure 2.8. In the first series $U_{\text{Real}}$ the point charges of the ions are shielded by diffuse Gaussian charge distributions of opposite sign; the total charge of the Gaussian distribution exactly cancels the point charge. The electrostatic interaction felt by a neighbouring atom
is due to the fraction which has not been screened, therefore at increasing inter-atomic separation this series rapidly converges to zero. Due to this rapid convergence behaviour, the sum of all these screened charges can be calculated in real space. The second series $U_{\text{Reciprocal}}$ is a set of compensating Gaussian charge distributions, which effectively remove the screening charges; the sum of the two series therefore leaves only the interactions due to point charges. The compensating charge distributions in this second series form a smooth periodic function which can be represented by a rapidly convergent Fourier series in reciprocal space. A correction term $U_{\text{Self}}$ is also required to account for self interactions between the point charge and its surrounding screening charge.

An important condition of the Ewald method is that the simulation cell must be charge neutral and have zero dipole moment.

### 2.5.2 Deriving Inter-Atomic Potentials

To extract useful information from atomistic calculations, the potential model needs to be derived such that it reproduces some observed properties of the material. This can be achieved by empirical fitting to experimental data or materials properties such as elastic constants and phonon frequencies calculated using ab-initio techniques. The most readily available data is usually crystal structure information derived from x-ray or neutron diffraction experiments. However, it can be useful to include other properties such as elastic constants and phonon frequencies. These additional properties provide information about the curvature of the energy surface.

The quality of the fit is judged by calculating the sum of squares

$$\sum_{i=1}^{N_{\text{obs}}} w_i (f_i^{\text{obs}} - f_i^{\text{calc}})^2,$$

where $N$ is the number of observables, $f_i^{\text{obs}}$ and $f_i^{\text{calc}}$ are the experimental and calculated values of the observable respectively, and $w_i$ is the weighting factor for the given observable. The weighting factor for each observable may be adjusted depending on its reliability and importance to the model. In the ideal situation, the sum of squares will be zero (i.e. the simulation exactly matches experiment), however this is rarely the case due to the complexity of most simulation tasks.

The fitting process involves adjusting the potential parameters to minimise the sum of squares; GULP uses the Newton-Raphson minimisation algorithm to achieve this. The process can therefore be viewed as the inverse of energy minimisation; rather than iteratively modifying the structure to minimise the energy, the interactions between the ions are adjusted to match the structure.
2.5.3 Modelling Polarisation

It is important to model polarisation effects accurately as these can affect lattice relaxation during energy minimisation, and they are used to calculate dielectric constants. This is of particular importance in defect modelling, because polarisation, caused by the electric field arising from a charged point defect, affects lattice relaxation around the defect. A simple method for modelling polarisability is to assign a point polarisability to each ion using equation 2.50.

\[ \mu = \alpha E \]  

(2.50)

Where \( \mu \) is the dipole, \( \alpha \) is the assigned polarisability and \( E \) is the applied electric field. This model performs poorly in many calculations because it fails to account for the coupling of polarisation and short range repulsion. Polarisation causes redistribution of valence electrons. However, the overlap of these electrons causes short range repulsion, which dampens polarisation effects.

![Figure 2.9: Schematic of the shell model.](image)

The shell model developed by Dick and Overhauser [74] is one of the most successful models which incorporates this coupling between short-range repulsive forces and polarisation. It is a mechanical model in which an ion is divided into a massive core of charge \( X \), and mass-less shell of charge \( Y \) (shown in Figure 2.9). The shell is connected to the core by a harmonic spring, which has a force constant \( k \). A dipole develops from the displacement of the shell from the core. The polarisability of an ion is calculated from the relationship below:

\[ \alpha = \frac{Y^2}{k} \]  

(2.51)

where \( \alpha \) is the polarisability of the ion, \( Y \) is the charge of the shell, and \( k \) is the force constant of the spring. \( k \) and \( Y \) are the variable parameters in the model. It should be noted that the shell and core do not accurately represent the nuclei and valence electrons respectively as \( Y \) values are not always negative.

2.5.4 Modelling Point Defects

Before outlining the methodology used to model defects it is necessary to first introduce defect chemistry in general, and some of the common types of defect encoun-
tered in solids. All crystal systems contain an intrinsic concentration of defects due to entropy; no crystal systems are perfect.

There are three main point defects:

**Vacancy**: A lattice site that is vacant.

**Interstitial**: An ion at a site not normally occupied.

**Substitutional**: A dopant ion on a lattice site.

Figure 2.10 provides a schematic representation of these three defect types.

The introduction of a point defect to the lattice causes significant structural relaxation of the lattice. The perturbation is mainly a long range electrostatic effect caused by the effective charge of the defect. Relaxation results in a reduction of symmetry and so the crystal can no longer be modelled as an infinite array of symmetrical unit cells.

The Mott-Littleton [75] approach is used in such circumstances, whereby the lattice is broken up into two regions (shown in Figure 2.11). In region one, which contains the defect, the effect is large and all ions are relaxed explicitly. Region two is further split into two, regions IIa and IIb. For ions in region IIb the only effect is dielectric in nature i.e. a change in polarisation of the ions but no displacement. The ions in region IIa are modelled explicitly like those in region one. Although technically relaxation in IIa is a result of all the ions in region I, an approximation is used whereby the relaxation is modelled as a result of the charge of the defect alone. Region IIa is an intermediate region between region I and IIb which are modelled in very separate ways.

For this approach to be valid it is important that the defect energy has significantly converged with respect to the radius of region IIb so that no lattice relaxation is
likely to occur in region IIb. It is suggested that a good starting point is to ensure that the radius of region I, and difference between radii of region I and region IIb are both larger than the Buckingham potential cutoff radius [50]. This may still not be adequate, due to the mainly long-range Coulombic effect of the defect, and so it is good to check whether increasing region size offers any noticeable change in defect energy.

2.5.5 Ion Migration

The migration of ions through an inorganic crystal structure takes place via mechanisms involving defects. As discussed previously this ionic mobility is integral to successful operation of lithium battery cells. There are a number of different mechanisms in which ions can migrate through crystals. The common mechanisms are the vacancy hopping mechanism and the interstitial-type mechanism shown in Figures 2.12 and 2.13 respectively.

The vacancy hopping mechanism involves exchange of an ion with a neighbouring vacancy, resulting in net migration of ions in the opposite direction to the vacancy. The interstitial-type mechanism can involve migration of interstitial ions through the lattice, either directly or via exchange with lattice ions. Both mechanisms are shown in Figure 2.13.

When modelling migration using static lattice methods, it is common to create a se-
Chapter 2. Methods

2.6 Calculation Information

2.6.1 Equipment

Several different computer systems were utilised to carry out the calculations presented in this work. The system used is dependent on the type of calculation and how computationally expensive it is. GULP is optimised for single core processing, therefore a standard desktop system is adequate.

Example desktop specification:
In this work however, primarily servers which utilise a CONDOR high throughput computing system were employed. Such systems allow a large volume of calculations to be submitted simultaneously; each individual calculation is assigned a single core as soon as one becomes available.

Example server specification:

\[2 \times \text{Quad-Core AMD Opteron 2360 SE 2.5 GHz} \]
\[32\text{GB RAM}\]

For more computationally expensive MD calculations the calculation time can be reduced by parallelism, whereby the job is broken into smaller chunks each of which is processed in parallel. The performance gains are significantly reduced when the inter-process communications start to outweigh the computational load of each individual process, therefore benchmarking is important in order to maximise efficiency. The DL_POLY calculations presented in this work were carried out using the HECToR high performance computing service, and each calculation was assigned 128 processors.

2.6.2 Calculation Speed

The time taken to complete a geometry optimisation calculation is dependent on a number of factors including: Simulation cell size; material composition; structural complexity and symmetry. Optimisation of the crystal structures presented here typically took no longer than 5 seconds. However, Optimisation of larger \((3 \times 3 \times 4)\) super cells used for NEB calculations in chapter 4 took between 20 minutes and an hour to complete.

Mott-Littleton type defect calculations are dependent on the sizes of region I and II as well as the factors mentioned above. For region I and II sizes of 12 Å and 20 Å used here, defect calculations typically took between 20 and 40 minutes.

Finally, our MD calculations, designed to simulate 1 ns of atomic motion within a \(6 \times 3 \times 4\) super cell of LiFeSO\(_4\)F, were completed within the 12 hour wall time available on HECToR.

2.6.3 Calculation Error

The inter-atomic potentials used to describe the forces between atoms are an approximation, and as such the calculations will not necessarily provide the exact energies of the various defect and migration processes examined. However, so long as the
potential model is reliable the trends in the results should still be correct. The reliability of the potential model is assessed by how accurately it reproduces known experimental observables such as the crystal structure. Here, we have also aimed to ensure precision of our calculated defect energies by testing their convergence with increasing region size.
Chapter 3

Anti-Site Defects and Ion Migration in the LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ Mixed-Metal Cathode Material

3.1 Background

LiMnPO$_4$ would in principal make an excellent cathode material for use in new lithium batteries due to the high value of the Mn$^{3+}$/Mn$^{2+}$ couple vs Li (4.1 V). Unfortunately, similarly to spinel-structured LiMn$_2$O$_4$, this material suffers from structural degradation during cycling. As with the layered-oxide cathodes (for example LiNi$_{0.5}$Mn$_{0.5}$O$_2$), there have been investigations into solid solutions or mixed-metal phosphates, especially the LiFe$_{1-y}$Mn$_y$PO$_4$ materials [14, 41, 47, 76–81], to combat these issues. These mixed-metal phosphates are isostructural with their LiFePO$_4$ and LiMnPO$_4$ end-members, adopting the same olivine-type lattice.

The early work of Padhi et al. [14] showed that solid solutions of LiFe$_{1-y}$Mn$_y$PO$_4$ allowed access to the Mn$^{3+}$/Mn$^{2+}$ couple for $y < 0.75$. Padhi concluded that increasing the Mn content above $y = 0.5$ reduced the amount of lithium that could be electrochemically extracted, so accessing the Mn$^{3+}$/Mn$^{2+}$ couple may be related to Mn having nearby Fe neighbours providing Mn-O-Fe interactions; a point later consolidated by Yamada [47].

Yamada et al [33, 47, 76] carried out extensive studies of LiFe$_{1-y}$Mn$_y$PO$_4$ and found that MnPO$_4$, the highly charged state of the LiMnPO$_4$ end-member, is an intrinsically unstable compound. The instability was attributed to Jahn-Teller distortions around trivalent Mn. For this reason solid solutions with high Mn content also show instability in the highly charged state with total capacity decreasing rapidly with $y > 0.75$. This effect is amplified because the highly charged state remains at constant volume with increasing Mn content due to Mn$^{3+}$ and Fe$^{3+}$ having matching ionic radii (0.79 Å).
In contrast, Li et al [82] has reported very good performance for LiMnPO$_4$ achieving a reversible capacity of 140 mAh$^{-1}$ at room temperature. This was achieved using a new synthetic method designed to reduce particle size and therefore reduce the diffusion length of the 1-D lithium channels. It has been suggested that the previous poor performance of LiMnPO$_4$ may be due to very low ionic conductivity rather than an unstable highly charged state. Delacourt et al [83] expanded on this argument showing that although MnPO$_4$ was unstable in air it remained stable when contained within a lithium battery cell. Electrochemical measurements show LiMnPO$_4$ has a lower conductivity, by about five orders of magnitude, than LiFePO$_4$. Delithiation was also incomplete for LiMnPO$_4$ suggesting possible blocking of the [010] channels along which Li ions migrate.

In summary, mixed systems with slightly lower Mn content have shown great promise with high capacities and good cyclability. Although increasing Fe content stabilise the highly charged state, it unfortunately does sacrifice the effective 4.1 V couple. An optimum solid solution, LiFe$_{0.4}$Mn$_{0.6}$PO$_4$, was suggested as a good trade off between stability and cell voltage. It is worth noting that the introduction of Mn content enhances the Fe$^{3+}$/Fe$^{2+}$ couple raising it from 3.4V to 3.5V, and Li conduction across the compositional range occurs via single phase mechanism unseen in the end member systems; this could have implications for improved Li diffusion [33, 41].

LiFe$_{1-y}$Mn$_y$PO$_4$ olivine-typed mixed systems are widely regarded as a promising new class of cathode material which could be put to effective use so long as the application permits both the 4.1 V and 3.5 V couples of Mn and Fe respectively. It is widely acknowledged that compositions with Mn content $y < 0.75$ provide the best electrochemical performance, balancing the higher Mn voltage with structural stability [14, 47]. However the optimum Mn/Fe composition is still yet to be determined. At the time of investigation there had been no simulation studies of such mixed-systems and for preliminary investigation the 50/50 composition, LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ was chosen.

To understand the processes and structural features influencing the electrochemical behaviour of these mixed olivine phosphates, it is clear that fundamental knowledge of the underlying defect and transport properties at the atomic scale is needed. Although such atomic level analysis is difficult to perform experimentally, atomistic simulation techniques provide a powerful means of investigating these key solid state issues.

Please note this work was published in the Journal of Materials Chemistry in 2010; a copy of this paper is provided in appendix F.
3.2 Results and Discussion

3.2.1 Crystal Structure and Potentials

Table 3.1: Inter-atomic potentials and shell model parameters for LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ taken from previous work on LiMPO$_4$ [25]

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A / eV</th>
<th>ρ / Å</th>
<th>C / eV·Å$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Buckingham</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$^+$ ... O$^{2-}$</td>
<td>632.1018</td>
<td>0.2906</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe$^{2+}$ ... O$^{2-}$</td>
<td>1105.2409</td>
<td>0.3106</td>
<td>0.0</td>
</tr>
<tr>
<td>Mn$^{2+}$ ... O$^{2-}$</td>
<td>2601.3939</td>
<td>0.278</td>
<td>0.0</td>
</tr>
<tr>
<td>O$^{2-}$ ... O$^{2-}$</td>
<td>22764.3</td>
<td>0.1490</td>
<td>44.53</td>
</tr>
<tr>
<td>P$^{5+}$ ... O$^{2-}$</td>
<td>897.2648</td>
<td>0.3577</td>
<td>0.0</td>
</tr>
<tr>
<td>(ii) Three-body</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k / eV·rad$^{-2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Θ$_0$ / °</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$^{2-}$ ... P$^{5+}$ ... O$^{2-}$</td>
<td>1.322626</td>
<td>109.47</td>
<td></td>
</tr>
<tr>
<td>(iv) Shell model</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Species</td>
<td>Y / e</td>
<td>k / eV·Å$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>2.997</td>
<td>19.26</td>
<td></td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>3.42</td>
<td>95.0</td>
<td></td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>-2.96</td>
<td>65.0</td>
<td></td>
</tr>
</tbody>
</table>

The starting point of this study was to reproduce experimentally observed crystal structure with our potential model [84, 85]. Inter-atomic potential parameters were taken from previous work on LiMPO$_4$ [25]; these are listed in table 3.1. As with LiFePO$_4$ and LiMnPO$_4$ end-members, the olivine structure exhibited by LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ is orthorhombic (space group Pnma), and consists of corner sharing FeO$_6$ and MnO$_6$ octahedra linked by PO$_4$ tetrahedra, forming isolated 1-D channels running parallel to the b axis in which the Li ions reside.

The experimental structural parameters are taken from a recent x-ray diffraction study of LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ [85]. There is an extremely large number of ways in which Fe$^{2+}$ and Mn$^{2+}$ can be ordered throughout the structure and there is no experimental evidence suggesting long range cation ordering, so the experimental data (provided in table 3.3) is representative of the ensemble average. However in order to carry out our modelling studies it is necessary to impose cation ordering.

As a starting point three different Fe/Mn ordering schemes were investigated using $1 \times 1 \times 2$ P1 super-cells (56 atoms) where 50% of Fe$^{2+}$ ions were replaced by Mn$^{2+}$. 
Figure 3.1: Olivine-type structure of LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ showing three Fe/Mn cation ordering schemes: (a) FeO$_6$ and MnO$_6$ octahedra alternating regularly; (b) separate FeO$_6$ and MnO$_6$ planes; (c) random alternation of FeO$_6$ and MnO$_6$ octahedra.
The structures of each of these ordering schemes are provided in Figure 3.1 and their lattice energies are listed in Table 3.2. Our results indicate that the lowest energy structure is ordering scheme A, showing regular alternation of FeO$_6$ and MnO$_6$ octahedra within the same plane (Figure 3.1a). However, we note that the lattice energy differences between all three ordering schemes were found to be very small (<50meV), which is consistent with current diffraction studies suggesting no significant cation ordering [14, 85].

### Table 3.2: Lattice energies for different ordering schemes

<table>
<thead>
<tr>
<th>Ordering scheme</th>
<th>Lattice energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>−250.963</td>
</tr>
<tr>
<td>B</td>
<td>−250.962</td>
</tr>
<tr>
<td>C</td>
<td>−250.958</td>
</tr>
</tbody>
</table>

Using the lowest energy structure (ordering scheme A), a comparison between the calculated and experimental crystal structures is provided in Table 3.3. The calculated unit cell parameters and cation-oxygen bond lengths for LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ deviate from experiment by at most 0.07 Å, and in most cases much less. This gives us confidence that our inter-atomic potential model can be used reliably in subsequent defect, cluster and migration calculations.

### 3.2.2 Intrinsic Atomic Defects

Defect calculations were carried out using the Mott-Littleton scheme with region sizes of 12 Å and 24 Å, for region 1 and 2a respectively. A series of point defect (vacancy and interstitial) energies were calculated, these are listed in Table 3.4. Relative energies of formation of Schottky and Frenkel defects can be calculated from the combination of the individual point defect energies. These take the following forms (using Kröger-Vink notation):

\[
\begin{align*}
\text{Li Frenkel:} & \quad \text{Li}^\times \xrightarrow{\cdot} \text{V}'^\prime_{\text{Li}} + \text{Li}^\ast_i \\
\text{Fe Frenkel:} & \quad \text{Fe}^\times_{\text{Fe}} \xrightarrow{\cdot} \text{V}''_{\text{Fe}} + \text{Fe}^\ast_i \\
\text{Mn Frenkel:} & \quad \text{Mn}^\times_{\text{Mn}} \xrightarrow{\cdot} \text{V}''_{\text{Mn}} + \text{Mn}^\ast_i \\
\text{O Frenkel:} & \quad \text{O}^\times \xrightarrow{\cdot} \text{V}''_{\text{O}} + \text{O}^\ast_i \\
\text{Full Schottky:} & \quad \text{Li}_i^{\times} + \frac{1}{2}\text{Fe}^{\times}_{\text{Fe}} + \frac{1}{2}\text{Mn}^{\times}_{\text{Mn}} + \text{P}^{\times} + 4\text{O}^{\times} \rightarrow \\
& \quad V'_{\text{Li}} + \frac{1}{2}V''_{\text{Fe}} + \frac{1}{2}V''_{\text{Mn}} + V''_{\text{P}} + 4V''_{\text{O}} + \text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4 
\end{align*}
\]
### Table 3.3: Calculated and experimental structural parameters of LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ (space group Pnma)

<table>
<thead>
<tr>
<th>(a) Unit Cell Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>parameter</td>
<td>calc/Å</td>
</tr>
<tr>
<td>a</td>
<td>10.4571</td>
</tr>
<tr>
<td>b</td>
<td>6.0556</td>
</tr>
<tr>
<td>c</td>
<td>4.6786</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b) Bond Lengths</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ion pair</td>
<td>calc/Å</td>
</tr>
<tr>
<td>P-O(1)</td>
<td>1.511</td>
</tr>
<tr>
<td>P-O(2)</td>
<td>1.554</td>
</tr>
<tr>
<td>P-O(3)</td>
<td>1.572</td>
</tr>
<tr>
<td>Li-O(1)</td>
<td>2.209</td>
</tr>
<tr>
<td>Li-O(2)</td>
<td>2.104</td>
</tr>
<tr>
<td>Li-O(3)</td>
<td>2.228</td>
</tr>
<tr>
<td>Fe-O(1)</td>
<td>2.209</td>
</tr>
<tr>
<td>Fe-O(2)</td>
<td>2.062</td>
</tr>
<tr>
<td>Fe-O(3)</td>
<td>2.055</td>
</tr>
<tr>
<td>Mn-O(1)</td>
<td>2.208</td>
</tr>
<tr>
<td>Mn-O(2)</td>
<td>2.096</td>
</tr>
<tr>
<td>Mn-O(3)</td>
<td>2.104</td>
</tr>
<tr>
<td>Mn-O(3)</td>
<td>2.262</td>
</tr>
</tbody>
</table>

$^a$ reference [85] with data transposed to Pnma

Li$_2$O Schottky like: $2 \text{Li}^\text{x}_\text{Li} + \text{O}^\text{x}_\text{O} \rightarrow 2 \text{V}^\prime\text{Li} + \text{V}^\ast\text{Li} + \text{Li}_2\text{O}$ (3.6)

FeO Schottky like: $\text{Fe}^\text{x}_\text{Fe} + \text{O}^\text{x}_\text{O} \rightarrow \text{V}^\prime\text{Fe} + \text{V}^\ast\text{O} + \text{FeO}$ (3.7)

MnO Schottky like: $\text{Mn}^\text{x}_\text{Mn} + \text{O}^\text{x}_\text{O} \rightarrow \text{V}^\prime\text{Mn} + \text{V}^\ast\text{O} + \text{MnO}$ (3.8)

Li/Fe Antisite: $\text{Li}^\text{x}_\text{Li} + \text{Fe}^\text{x}_\text{Fe} \rightarrow \text{Li}'\text{Fe} + \text{Fe}'\text{Li}$ (3.9)

Li/Mn Antisite: $\text{Li}^\text{x}_\text{Li} + \text{Mn}^\text{x}_\text{Mn} \rightarrow \text{Li}'\text{Mn} + \text{Mn}'\text{Li}$ (3.10)

Off-stoichiometry defects i.e. lithium deficiency and transition metal excess were also considered, these take the following form (where $M = \text{Fe, Mn}$).

\[
\text{Li}^\text{x}_\text{Li} + \frac{1}{4}\text{O}_2 \rightarrow \text{V}^\prime\text{Li} + \text{h}^\ast + \frac{1}{2}\text{Li}_2\text{O} \quad (3.11)
\]

\[
\text{MO} + 2\text{Li}^\text{x}_\text{Li} \rightarrow \text{M}^\ast\text{Li} + \text{V}^\prime\text{Li} + \text{Li}_2\text{O} \quad (3.12)
\]

Our approach to electronic defects follows that used for other transition-metal oxides [86, 87] in which we model the localised hole (h$^\ast$) species (small polaron) on the
transition metal ion as $M^{3+}$. Our calculations show that initial formation of Fe$^{3+}$ species is more favourable than Mn$^{3+}$ by about 2 eV. This is in agreement with electrochemical data where oxidation of Fe$^{3+}$ precedes that of Mn$^{2+}$ in a step-wise manner during charging [14, 41, 47].

Table 3.5: Intrinsic defect energies in LiFePO$_4$, LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ and LiMnPO$_4$

<table>
<thead>
<tr>
<th>Defect</th>
<th>Equation</th>
<th>LiFePO$_4$</th>
<th>LiFe$<em>{0.5}$Mn$</em>{0.5}$PO$_4$</th>
<th>LiMnPO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li Frenkel</td>
<td>3.1</td>
<td>2.15</td>
<td>2.75</td>
<td>1.97</td>
</tr>
<tr>
<td>Fe Frenkel</td>
<td>3.2</td>
<td>5.58</td>
<td>6.71</td>
<td>-</td>
</tr>
<tr>
<td>Mn Frenkel</td>
<td>3.3</td>
<td>-</td>
<td>6.84</td>
<td>6.80</td>
</tr>
<tr>
<td>O Frenkel</td>
<td>3.4</td>
<td>5.46</td>
<td>6.00</td>
<td>7.32</td>
</tr>
<tr>
<td>Full Schottky</td>
<td>3.5</td>
<td>25.30</td>
<td>28.38</td>
<td>33.58</td>
</tr>
<tr>
<td>Li$_i$O Schottky like</td>
<td>3.6</td>
<td>6.33</td>
<td>6.53</td>
<td>7.36</td>
</tr>
<tr>
<td>FeO Schottky like</td>
<td>3.7</td>
<td>5.58</td>
<td>5.98</td>
<td>-</td>
</tr>
<tr>
<td>MnO Schottky like</td>
<td>3.8</td>
<td>-</td>
<td>6.23</td>
<td>7.15</td>
</tr>
<tr>
<td>Li/Fe Antisite</td>
<td>3.9</td>
<td>1.13</td>
<td>1.22</td>
<td>-</td>
</tr>
<tr>
<td>Li/Mn Antisite</td>
<td>3.10</td>
<td>-</td>
<td>1.34</td>
<td>1.48</td>
</tr>
<tr>
<td>Li$^+$ deficiency$^b$</td>
<td>3.11</td>
<td>4.41</td>
<td>4.69</td>
<td>-</td>
</tr>
<tr>
<td>Li$^+$ deficiency$^c$</td>
<td>3.11</td>
<td>-</td>
<td>6.80</td>
<td>8.97</td>
</tr>
<tr>
<td>$M^{2+}$ excess$^b$</td>
<td>3.12</td>
<td>3.31</td>
<td>3.15</td>
<td>-</td>
</tr>
<tr>
<td>$M^{2+}$ excess$^c$</td>
<td>3.12</td>
<td>-</td>
<td>3.00</td>
<td>3.14</td>
</tr>
</tbody>
</table>

$^a$ reference [25]; $^b$ Fe energies used; $^c$ Mn energies used

Examination of results in table 3.5 reveals three main points. First, the magnitudes of the calculated energies suggests formation of Fe Frenkel, Mn Frenkel, O Frenkel and various Schottky and Schottky-like defects is unfavourable.

Second, the most favourable intrinsic defect for LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ is the Li/$M$ anti-
site pair, comparable to the end-member systems studied in our previous work [25].
This suggests that even at low synthesis temperatures there will be a very small percentage of Fe or Mn ions on Li sites and Li ions on M sites. The concentration of such defects would be temperature dependent and hence sensitive to experimental synthesis conditions. Structural analysis of hydrothermally synthesized LiFePO$_4$ suggests 3 mol % Fe on Li sites [88], whereas a recent scanning transmission electron microscopy (STEM) study [29] suggests a concentration of around 1%. Diffraction and EXAFS studies of LiMnPO$_4$ find Mn$^{2+}$ on Li sites [29, 77]. Axmann et al. [89] also find a few at.% Fe on Li sites in LiFePO$_4$ but not Li on Fe sites, however Li is very difficult to detect using traditional diffraction experiments, particularly when placed in an environment dominated by Fe and Mn ions which have much larger electron densities. Hamelet et al. [90] have found Li-Fe exchange in LiFePO$_4$ nano powders with significant amounts of structural defects.

Such cation exchange is well known in the olivine silicates such as MgFeSiO$_4$ [91] and can be rationalised in terms of the similar volumes and coordination environments of the two cation sites. In olivine-phosphate materials, however, one consequence of this exchange is that an M ion on a Li site could block the lithium diffusion pathway, a point we return to in section 3.2.5.

Finally the second lowest energy is found for the Li Frenkel defect which suggests that a minor population of such defects could be present at high synthesis temperatures. The favourable interstitial positions are located at the edges of the [010] lithium channels either side of a Li lattice site.

### 3.2.3 Defect Clustering

It is well established that the electrostatic interactions between oppositely charged point defects can lead to clustering or association. Defect association and possible association (trapping) has been discussed by Maier and Amin [92], where they noted that detail atomistic modelling is required to quantify the energies involved. Previous studies on complex oxides [53, 93] demonstrate that our simulation methods can accurately model the electrostatic, polarisation and elastic strain energies which are predominant terms in any local association process. The clusters considered in the LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ system are comprised of combinations of anti-site defects and hole species. The cluster binding energies were calculated using the following relationship,

$$E_{\text{bind}} = E_{\text{cluster}} - \Sigma E_{\text{isolated}},$$  

(3.13)

whereby energies of pairs of defects on nearby sites are compared with the sum of their isolated values $E_{\text{cluster}}$. A negative $E_{\text{bind}}$ value indicates that the cluster is stable with respect to the isolated defects.

The defect clusters considered were:

1. Li/M anti-site defects, [Li$^\prime_M$–M$^\ast_{\text{Li}}$]
Chapter 3. Anti-Site Defects and Ion Migration in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$

2. $M$ ion on an Li site and a lithium vacancy $[M^*_\text{Li} - V'_\text{Li}]$

3. $M^{3+}$ hole centre (small polaron) and a lithium vacancy, $[M^*_M - V'_\text{Li}]$

These clusters consist of defects centred only on $M$ and Li sites. There are several non-equivalent Li-$M$ distances to consider for the above clusters (shown in Figure 3.2). The shortest separation between defects gave the lowest binding energies for all cases. The binding energies for all considered pair clusters are provided in Table 3.6.

![Figure 3.2: Cation neighbours relative to an Li site, showing three pairs of non-equivalent Li-$M$ distances (Roman numerals indicate increasing distance).](image)

**Table 3.6:** Binding energies of defect pair clusters on neighbouring cation sites in LiFePO$_4$, LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ and LiMnPO$_4$

<table>
<thead>
<tr>
<th>Defect cluster</th>
<th>LiFePO$_4^a$</th>
<th>LiFe$<em>{0.5}$Mn$</em>{0.5}$PO$_4$</th>
<th>LiMnPO$_4^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Li}^<em>_\text{Fe} - \text{Fe}^</em>_\text{Li}]$</td>
<td>-0.44</td>
<td>-0.46</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Li}^<em>_\text{Mn} - \text{Mn}^</em>_\text{Li}]$</td>
<td>-</td>
<td>-0.49</td>
<td>-0.57</td>
</tr>
<tr>
<td>$[\text{Fe}^*<em>\text{Li} - V'</em>\text{Li}]$</td>
<td>-0.48</td>
<td>-0.52</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Mn}^*<em>\text{Li} - V'</em>\text{Li}]$</td>
<td>-</td>
<td>-0.54</td>
<td>-0.65</td>
</tr>
<tr>
<td>$[\text{Fe}^*<em>\text{Fe} - V'</em>\text{Li}]$</td>
<td>-0.39</td>
<td>-0.47</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Mn}^*<em>\text{Mn} - V'</em>\text{Li}]$</td>
<td>-</td>
<td>-0.46</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

$^a$ reference [25]

Three key points can be identified from the results. First all Li/Fe and Li/Mn antisite pair clusters have negative binding energies, indicating pairs of intimately
associated antisite defects are more stable than isolated ones. This opens up the possibility that anti-site defects could aggregate in the material acting as precursors to larger clusters.

Second, similar trends are found for clusters involving lithium vacancies and $M^{2+}$ cations on lithium sites. The results reveal significant $[M^*_{Li}-V^{\prime}_{Li}]$ association which could lead to trapping of lithium vacancies during migration. The presence of $M$ ions on Li sites could also hinder Li diffusion along the $b$-axis channel [24, 25, 88], by blocking the channel. Our results agree well with recent studies of Axmann et al. [89] who find that the anti-site Fe$^\ast_{Li}$ is not isolated but coupled with a Li vacancy to form an Fe$^\ast_{Li} + V^\prime_{Li}$ complex. Overall LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ has binding energy values which are between those of its end members. Less trapping and therefore higher Li conduction rates are predicted in this mixed system over LiMnPO$_4$. LiFePO$_4$ is still expected to exhibit the highest conduction rates.

Finally, we find significant binding between small polaron species (e.g. Fe$^{3+}$ or Mn$^{3+}$) and lithium vacancies, which are of relevance to the observed electronic conductivity, because Mössbauer experiments indicate that electron transport in LiFePO$_4$ occurs via small polaron hopping [94]. Our results suggest the coupling or trapping of these charge carriers in Li$_{(1-x)}$Fe$_{0.5}$Mn$_{0.5}$PO$_4$, and are compatible with GGA+U-type calculations which find a hole-vacancy binding energy in LiFePO$_4$ of greater than 500 meV [95, 96].

Aggregation of antisite Fe defects into larger clusters has been recently observed by STEM in LiFePO$_4$ [29, 30]. We have therefore carried out a detailed examination into larger cluster sizes comprised 4 and 8 defects.

In this study many configurations are possible for the combination of pairs of defect into larger sized clusters. Previously, it was found that pair defects with the shortest inter-atomic separation gave the lowest binding energies, therefore only larger clusters with the shortest inter-atomic separations have been considered. Even with a limit on inter-atomic distance there are still several configurations possible for these clusters; table 3.7 provides the lowest energy configurations which therefore have the most negative binding energies.

The results show that the binding energies per defect pair remain consistent as cluster size is increased. This suggests that antisite defects aggregate in the material forming larger clusters, which agrees strongly recent experimental observations [29, 30].

The latter of these two experimental studies [30] also suggests favourable aggregation of Fe$^\ast_{Li}$ defects along the $b$-axis channel. However the charge compensation mechanism for possible supervalent Nb doping, and the effective positive charges of Fe$^\ast_{Li}$ has not been clearly stated. A schematic detailing such 1-D clusters from this electron microscopy study is shown in Figure 3.3a.

Our calculations focused on two neutral clusters comprised of two antisite cations ($M^*_{Li}$) and two lithium vacancies at neighbouring sites along the $b$-axis channel.
Table 3.7: Binding energies of $[M'_\text{Li}-V\text{Li}]$ defect clusters of varying size in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$

<table>
<thead>
<tr>
<th>Defect</th>
<th>$E_{\text{bind}}$ (per defect pair) / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe}^\cdot_\text{Li}-\text{Li}^\cdot_{\text{Fe}}]$</td>
<td>-0.46</td>
</tr>
<tr>
<td>2$[\text{Fe}^\cdot_\text{Li}-\text{Li}^\cdot_{\text{Fe}}]$</td>
<td>-0.53</td>
</tr>
<tr>
<td>4$[\text{Fe}^\cdot_\text{Li}-\text{Li}^\cdot_{\text{Fe}}]$</td>
<td>-0.28</td>
</tr>
<tr>
<td>$[\text{Mn}^\cdot_\text{Li}-\text{Li}^\cdot_{\text{Mn}}]$</td>
<td>-0.49</td>
</tr>
<tr>
<td>2$[\text{Mn}^\cdot_\text{Li}-\text{Li}^\cdot_{\text{Mn}}]$</td>
<td>-0.52</td>
</tr>
<tr>
<td>4$[\text{Mn}^\cdot_\text{Li}-\text{Li}^\cdot_{\text{Mn}}]$</td>
<td>-0.50</td>
</tr>
<tr>
<td>$[\text{Fe}^\cdot_\text{Li}-V'_\text{Li}]$</td>
<td>-0.52</td>
</tr>
<tr>
<td>2$[\text{Fe}^\cdot_\text{Li}-V'_\text{Li}]$</td>
<td>-0.57</td>
</tr>
<tr>
<td>4$[\text{Fe}^\cdot_\text{Li}-V'_\text{Li}]$</td>
<td>-0.52</td>
</tr>
<tr>
<td>$[\text{Mn}^\cdot_\text{Li}-V'_\text{Li}]$</td>
<td>-0.54</td>
</tr>
<tr>
<td>2$[\text{Mn}^\cdot_\text{Li}-V'_\text{Li}]$</td>
<td>-0.57</td>
</tr>
<tr>
<td>4$[\text{Mn}^\cdot_\text{Li}-V'_\text{Li}]$</td>
<td>-0.57</td>
</tr>
<tr>
<td>$[\text{Fe}^\cdot_{\text{Fe}}-V'_\text{Li}]$</td>
<td>-0.47</td>
</tr>
<tr>
<td>2$[\text{Fe}^\cdot_{\text{Fe}}-V'_\text{Li}]$</td>
<td>-0.66</td>
</tr>
<tr>
<td>4$[\text{Fe}^\cdot_{\text{Fe}}-V'_\text{Li}]$</td>
<td>-0.46</td>
</tr>
<tr>
<td>$[\text{Mn}^\cdot_{\text{Mn}}-V'_\text{Li}]$</td>
<td>-0.46</td>
</tr>
<tr>
<td>2$[\text{Mn}^\cdot_{\text{Mn}}-V'_\text{Li}]$</td>
<td>-0.58</td>
</tr>
<tr>
<td>4$[\text{Mn}^\cdot_{\text{Mn}}-V'_\text{Li}]$</td>
<td>-0.68</td>
</tr>
</tbody>
</table>

Table 3.8: Binding energies of neutral clusters along the b axis channel (shown in Figure 3.3)

<table>
<thead>
<tr>
<th>cluster configuration</th>
<th>$E_{\text{bind}}$ (per defect pair) / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiFePO$_4$</td>
</tr>
<tr>
<td>$[2\text{Fe}^\cdot_\text{Li} - 2V'_\text{Li}]$</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>-0.62</td>
</tr>
<tr>
<td>b</td>
<td>-0.42</td>
</tr>
<tr>
<td>$[2\text{Mn}^\cdot_\text{Li} - 2V'_\text{Li}]$</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.3: (a) A schematic of Fe antisite cation distribution from an electron microscopy study of LiFePO$_4$ showing preferential arrangement along the $b$ axis. Reprinted by permission from John Wiley & Sons, inc.: [Angewandte Chemie] [30], copyright (2009). (b) Similar schematic of a structural plane in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ showing two neutral cluster configurations along the $b$-axis channel comprised of two antisite defects (Fe or Mn on Li sites) and two Li vacancies: (A) antisite cation and Li vacancy at alternating sites, (B) antisite cations at adjacent sites.
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The two configuration examined (shown in Figure 3.3b) have either alternating antisite and vacancy defects, or two antisite defect at adjacent sites. The binding energies for these linear clusters are listed in table 3.8.

The linear cluster configuration with the strongest binding energy ($> -0.6$ eV) is found for cluster (A) shown in Figure 3.3b. This arrangement seems to minimise the repulsive interactions between like charged antisite cations.

In general, these results suggest aggregation or clustering of defects (rather than a random distribution), which may be important as precursors to local ordering and nano-domain formation, and warrants further investigation. Such clustering may inhibit Li extraction because defect cluster regions are more likely to retain lithium. However, preferential 1-D aggregation of these defects along the $b$-axis channels could have positive implications for lithium extraction. If antisite defects are distributed in large clusters, confined to a small selection of Li migration channels, the majority of the channels will remain unblocked.

### 3.2.4 Li Ion Migration

Our atomistic simulation techniques can be used to examine the energetics of various possible diffusion paths. Each pathway is mapped by a series of Mott-Littleton type defect calculations, where the migrating Li ion is moved between two adjacent lithium vacancies. At each point the migrating Li ion is allowed to relax in directions orthogonal to the direct linear path. The position of highest energy along the migration path corresponds to activation energy of migration $E_{\text{mig}}$. Relaxation of the surrounding lattice (> 700 ions) is treated explicitly by these defect modelling methods.

Three Li migration paths in LiFe$_{1-y}$Mn$_y$PO$_4$ (where $y = 0.0, 0.5, 1.0$) were examined; labelled A-C in Figure 3.4 in order of shortest to longest jump distance. Path A involves migration between adjacent lithium sites in the [010] direction, with a jump distance of 2.9-3.0 Å. Path B involves migration in the [001] direction, with a jump distance of 4.6-4.7 Å, while path C involves migration between the lithium channels jump in the [101] direction, with the longest jump distance of 5.6-5.8 Å. The migration energies for the LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ system (as well as the LiFePO$_4$ and LiMnPO$_4$ systems for comparison) are listed in table 3.9.

The lowest energy path for Li ion migration is down the [010] channel, path A, as found previously for LiFePO$_4$ [24, 25]. High barriers of $> 2.8$ eV are calculated for the other pathways (B and C), indicating that lithium ions cannot readily jump between channels. This confirms the anisotropic nature of Li ion migration in the olivine phosphates. Our calculated energy of 0.59 eV for LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ agrees well with the experimental activation energy of 0.63 eV for LiFe$_{0.45}$Mn$_{0.55}$PO$_4$ [78]. LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ has a migration energy that is an average of its two end members indicating the mixed system will achieve similar conduction rates.
Figure 3.4: Paths considered for lithium ion migration in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$.

Table 3.9: Mechanisms and energies of Li migration in LiFePO$_4$, LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ and LiMnPO$_4$

<table>
<thead>
<tr>
<th>Path</th>
<th>$E_{\text{mig}}$/eV LiFePO$_4$</th>
<th>$E_{\text{mig}}$/eV LiFe$<em>{0.5}$Mn$</em>{0.5}$PO$_4$</th>
<th>$E_{\text{mig}}$/eV LiMnPO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A [010]</td>
<td>0.55</td>
<td>0.59</td>
<td>0.62</td>
</tr>
<tr>
<td>B [001]</td>
<td>2.89</td>
<td>2.86</td>
<td>2.83</td>
</tr>
<tr>
<td>C [101]</td>
<td>3.36</td>
<td>3.58</td>
<td>2.26</td>
</tr>
</tbody>
</table>

a reference [25]

Detailed structural analysis of our simulation data shows that a curved migration path is taken between adjacent lithium sites and not a direct linear path (shown in Figure 3.5), which results in a lower migration energy; energy profiles for linear vs curved paths are shown in Figure 3.6. The migrating ion deviates from the linear path by a maximum of 0.44 Å, which is very similar to the value of 0.5 Å for LiFePO$_4$. By neutron diffraction, the maximum entropy method, Yamada and co-workers [97] reproduced the one-dimensional Li$^+$ diffusion in LiFePO$_4$, with a curved pathway (provided in Figure 3.5c) in excellent agreement with present simulation results as well as our earlier prediction [25].

These results contrast with a recent report that lithium ion diffusion in single crystals of LiFePO$_4$ was two rather than one-dimensional [98]. However, two-dimensional transport with similar activation energies in b and c directions is difficult to reconcile with the distinctly anisotropic nature of the orthorhombic olivine structure; for
Figure 3.5: Visualisation of the calculated curved migration pathway for Li transport along the $b$ axis in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$. (a) Angled orientation Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] [97], copyright (2008); (b) view in the $ab$ plane; (c) experimental visualisation of Li diffusion in LiFePO$_4$ from neutron diffraction (maximum entropy method) in the $bc$ plane, where Li density is shown in blue and Fe density in red.
example, the corresponding Li-Li jump distances are highly disparate at 2.9-3.0 Å and 4.6-4.7 Å respectively. More recently, Li et al. [99] find different results on single crystal LiFePO$_4$ with lithium diffusion confined to one-dimension through the $b$-axis tunnels.

### 3.2.5 Anti-Site Cation Migration

As noted previously in section 3.2.2, our defect calculations suggest that the anti-site defects are intrinsic to these phosphates. There is experimental evidence of a low concentration of $M$ on Li sites in both LiFePO$_4$ [88] and LiMnPO$_4$ [77]. It may therefore be difficult to avoid $M$ cations on Li sites blocking diffusion pathways down [010] channels, unless these anti-site defects are also mobile. For further examination of how long range Li diffusion is affected by anti-site defects, the energy of migration of the divalent cation between Li sites was calculated. This process can be viewed as the exchange of an anti-site defect with a lithium vacancy as illustrated in Figure 3.7; the lithium vacancy could then continue to migrate in the opposite direction down the [010] channel. A similar simulation procedure to that used for Li diffusion was used here, which allows the migrating $M$ species to relax in directions orthogonal to the direct linear path.

All the calculated energies in table 3.10 are 0.15-0.35 eV greater than the corresponding Li migration values, indicating lower anti-site cation mobility compared to pure Li diffusion. This suggests that anti-site defects would impede Li diffusion to varying degrees down [010] channels. LiFePO$_4$ has the lowest anti-site migration energy, suggesting a population of anti-site defects in this system would have the
Figure 3.7: Schematic of the two stages of anti-site cation migration along a [010] channel: (a) Exchange of a lithium vacancy and an anti-site cation; (b) exchange of the lithium vacancy and a lithium ion.

Table 3.10: Energies of anti-site cation migration along the [010] direction in LiFePO$_4$, LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ and LiMnPO$_4$

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$E_{\text{mig}}$ /eV</th>
<th>LiFePO$_4^a$</th>
<th>LiFe$<em>{0.5}$Mn$</em>{0.5}$PO$_4$</th>
<th>LiMnPO$_4^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{Li}^*$ → V$</em>{Li}'$</td>
<td>0.70</td>
<td>0.79</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Mn$<em>{Li}^*$ → V$</em>{Li}'$</td>
<td>-</td>
<td>0.87</td>
<td>0.92</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ reference [25]

least affect on lithium diffusion kinetics. Although the mixed system has slightly higher energies, it still performs better than the Mn system.

At this point it is interesting to examine the overall trends in the energies of ion migration and defect association for the three systems. The energies listed in tables 3.6 - 3.10 reveal that the mixed system sits between its two end members with respect to lithium vacancy migration, binding and anti-site cation migration energies. Combined, these results suggest lithium conduction rates in LiFePO$_4$ to be superior to LiFe$_{0.5}$Mn$_{0.5}$PO$_4$. This area warrants further investigation related to recent experimental studies on the LiFe$_{1-y}$Mn$_y$PO$_4$ system [100–106].

### 3.3 Chapter Summary

This investigation of the LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ mixed-metal material has used atomistic simulation techniques to provide insights into the local defect chemistry and ion transport properties relevant to its electrochemical behaviour.

Several important points emerge from the results. The most favourable intrinsic defect is the anti-site defect, for a which a small population of Li$^+$ and Fe$^{2+}$ or...
Mn$^{2+}$ are expected to exchange sites. This would be temperature dependent and hence sensitive to experimental synthesis conditions.

As in LiFePO$_4$, lithium ion diffusion in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ follows a non-linear, curved path down the [010] channel; the migration energy (0.59 eV) agrees with experimental data, and is an intermediate between the two end members (LiFePO$_4$ and LiMnPO$_4$).

The binding energies suggest clustering of defects (rather than a random distribution), which has implications for lithium conductivity as $M^{2+}$ cations on Li sites could lead to trapping of the migrating Li vacancies. Furthermore, the binding energies per defect pair remain consistent with increasing cluster size, suggesting these defects could aggregate in the material forming larger clusters. Significant binding energies ($<-0.6$ eV) are found for neutral one-dimensional clusters along the $b$-axis channel, comprised of anti-site defects (Fe$^*_\text{Li}$ or Mn$^*_\text{Li}$) and Li vacancies. This could have positive implications for Li conductivity whereby anti-site defects are confined to clusters contained in a small selection of Li channels, leaving the majority free of any blockages.

Finally, the higher anti-site ($M^*_\text{Li}$) migration energy in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ compared to pure LiFePO$_4$, suggests that any anti-site defect in this mixed-metal system would have a greater blocking effect on lithium insertion/extraction rates.
Chapter 4

Alkali-ion Conduction Paths in Tavorite-Type AFeSO$_4$F
(A = Li, Na) Cathode Materials

4.1 Background

A new family of fluorosulphates has attracted considerable attention as alternative positive electrode materials for rechargeable lithium batteries. The discovery of this family originates from research into related fluorophosphates [44], which were first reported by Barker et al. [42], followed by detailed reports of their viability as attractive cathode materials by other groups [36, 107]. Alkali metal fluorophosphates form a large isostructural family with the chemical formula A$\text{MPO}_4\text{F}$, where A is an alkali metal and M is a transition metal. These structures are often named after their corresponding mineral member found in the Earth’s crust, either as hydroxides or as fluorides; the most important are montebrasite (LiAlPO$_4$OH) [108], amblygonite (LiAlPO$_4$F) [109], and tavorite (LiFePO$_4$OH) [110], which are all essentially isostructural. The LiFePO$_4$F material which crystallises in this framework, has been shown to be an excellent ionic conductor and a reversible host for the Li$^+$ ion [42]. It exhibits a theoretical capacity of 145 mAh$^{-1}$ at 3 V (redox couple: Fe$^{2+}$/Fe$^{3+}$), which is lower than that of LiFePO$_4$ (3.4 V), because of the difference in connectivity of the octahedral and tetrahedral moieties.

It has been shown previously that the open circuit voltage (OCV) of a material can be increased by tuning the covalency of the bonds in the polyanion [43]. In particular replacing the PO$_4^{3-}$ moiety by SO$_4^{2-}$ in a polyanionic Li$\text{M}_2\text{X}_2\text{O}_4$ compound increases the OCV by ~ 0.6 - 0.8 V [43]. Taking note from such examples, successful attempts were made to improve the low OCV in tavorite materials. LiFeSO$_4$F has been recently demonstrated to be an excellent cathode material by Tarascon and co-workers [44]. It exhibits an OCV of 3.6 V and a theoretical capacity of 151 mAh$^{-1}$. By comparison to LiFePO$_4$, the slightly lower capacity is compensated by the in-
increased OCV and higher ionic conductivity of the material [44]. The theoretical energy density is thus only 5% lower, and higher power characteristics are potentially possible. Like LiFePO$_4$, LiFeSO$_4$F can also be synthesised using abundantly available inorganic precursors in an inexpensive organic medium at low temperatures [111]. Possibly due to the presence of a 3D network of structural tunnels, the ionic conductivity of the material has been found to be higher than its phosphate analogue LiFePO$_4$. Nevertheless, apart from basic conductivity studies, there has been little attempt so far to understand the atomistic migration pathways or activation energies which govern the Li ion conduction within the structure.

The tavorite structure of LiFeSO$_4$F, which has the triclinic $P\bar{1}$ space group [44, 111], is shown in Figure 4.1. The structure consists of layers of corner-sharing FeO$_4$F$_2$ octahedra which alternate in orientation. The fluorine ions sit trans to each other forming the link between adjacent FeO$_4$F$_2$ octahedra. Tetrahedral SO$_4$ units join the layers together forming a 3D network of open tunnels. Li ions sit opposite each other in sites located at the periphery of these tunnels. There is debate over the exact location of Li ions within the cell. Two models have been proposed from x-ray diffraction: one assumes a half occupancy of two lithium sites, Li1 and Li2, located 0.8 Å apart; the other involves full occupancy of a single site.

Equally important is to examine Na-ion mobility in the tavorite type NaFeSO$_4$F [111, 112]. Intermediate-scale Li-based batteries are the clear choice to fill increasing demand to power plug-in hybrid vehicles and electric vehicles. These demands will inevitably put strain on the resource of lithium and hence on its cost effectiveness.

**Figure 4.1:** The experimentally determined unit cell of LiFeSO$_4$F from X-ray diffraction data, showing two unique, half occupancy lithium sites separated by approximately 0.8 Å.
Moreover a massive increase in demand for large scale rechargeable batteries is predicted in the immediate future in the energy sector. Sodium on the other hand is an abundantly available resource. Thus Na-based batteries where Na$^+$ ions replace Li$^+$ as the charge carrier have been proposed as a viable alternative for very large-scale storage that could couple with renewable energy sources for load-levelling the electric grid. Demonstration of fairly effective cathode and anode materials that can reversibly insert/de-insert Na$^+$ has, in recent years, led to a surge in the search of other crystalline systems with better Na$^+$ insertion rate and capacity [36]. Recent successes include tavorite-type NaVPO$_4$F and layered Na$_2$FePO$_4$F [36, 45]. The fluorosulphate NaFeSO$_4$F also crystallises in a tavorite-type structure. In contrast to Li in LiFeSO$_4$F there is little confusion over the position of Na in NaFeSO$_4$F, where Na ions have one fully occupied site located at the periphery of the tunnels. Initial attempts to extract Na$^+$ ions from this structure have given very disappointing results that are puzzling, given the presence of open ion transport channels and reportedly good ionic conductivity [36, 45].

To fully understand the local structural and transport features influencing the electrochemical behaviour of AFeSO$_4$F (A = Li or Na) materials, it is important to further our fundamental understanding of defects and ion transport at the atomic scale. Here we provide a detailed investigation into structure, defects and ion transport in AFeSO$_4$F, using atomistic modelling techniques, for the first time.

### 4.2 Results and Discussion

#### 4.2.1 Crystal Structure and Potentials

As noted, the structure of LiFeSO$_4$F belongs to the tavorite family of mineral structures, crystallising in the triclinic $P\bar{1}$ space group [44, 111]. The structure encompasses chains of alternatively oriented corner-sharing FeO$_4$F$_2$ octahedra that run along the c-axis. Corner sharing occurs through the fluorine located at opposite vertices. Each of the four oxygen atoms in the polyhedron is also bonded to a sulphur atom forming Fe-O-S-O-Fe chains that cross-link the structure (shown in Figure 4.2a).

The separation between the FeO$_4$F$_2$ octahedral chains introduced by the corner sharing SO$_4$ tetrahedra results in two primary open tunnels along the [001] and [010] directions in the structure that house the Li ions. In NaFeSO$_4$F, the connectivity between the atoms is essentially the same, as can be seen in the structures illustrated in Figures 4.2c and d. However, the lattice adopts a higher symmetry space group ($P\bar{2}_1/c$), compared to that of LiFeSO$_4$F ($P\bar{1}$) [36]; thus there are subtle differences. Most importantly, the corresponding crystallographic directions between the two structures are different. They can be correlated by noting that the primary tunnels
Figure 4.2: Depiction of the tavorite unit cells: (a) LiFeSO$_4$F, modelled in a $P1$ supercell with alternate occupation of two Li sites, where Li$_A$ and Li$_B$ represent the alternate full occupancy of the Li$_1$ and Li$_2$ sites respectively; (b) a view into the tunnel along the [100] direction (a similar geometry also exists for the tunnel along the [010] direction); (c) NaFeSO$_4$F, modelled in the same unit cell as experimentally obtained ($P2_1/c$); and (d) a view into the tunnel along the [110] direction (a similar geometry also exists for the tunnel along the [110] direction).
Chapter 4. Alkali-ion Conduction Paths in AFeSO$_4$F (A = Li, Na)

along the [100], [010] and [101] directions in LiFeSO$_4$F correspond to the [110], [110] and [101] directions in NaFeSO$_4$F.

As mentioned previously, the exact positioning of the lithium site(s) is not clear from X-ray diffraction studies. Two models have been proposed, one assumes a single Li site, and the other assumes split occupancy of two closely neighbouring sites. The starting structural parameters of the current simulation study were the observed crystal structure, in which the LiFeSO$_4$F structure has been refined experimentally with two half-occupied Li sites [111] (shown in Figure 4.1). For our modelling study we created a $1 \times 2 \times 1 P1$ supercell with alternating occupation of these two sites, where Li$_a$ and Li$_b$ represent alternate full occupation of the Li1 and Li2 sites respectively (shown in Figure 4.2a). We find that during structural optimisation the Li1 and Li2 ions both relax to the same local environment (Appendix, table D.1).

Table 4.1: Inter-atomic potentials and shell model parameters for LiFeSO$_4$F and NaFeSO$_4$F

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A / eV</th>
<th>$\rho$ / Å</th>
<th>C / eV·Å$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$ ... O$^{0.84-}$</td>
<td>4787.6</td>
<td>0.19998</td>
<td>0.0</td>
</tr>
<tr>
<td>* Li$^+$ ... F$^-$</td>
<td>400.6</td>
<td>0.2736</td>
<td>0.0</td>
</tr>
<tr>
<td>* Na$^+$ ... O$^{0.84-}$</td>
<td>9150.6</td>
<td>0.2219</td>
<td>0.0</td>
</tr>
<tr>
<td>* Na$^+$ ... F$^-$</td>
<td>4000.6</td>
<td>0.2200</td>
<td>0.0</td>
</tr>
<tr>
<td>* Fe$^{2+}$ ... O$^{0.84-}$</td>
<td>7500.0</td>
<td>0.22</td>
<td>0.0</td>
</tr>
<tr>
<td>* Fe$^{2+}$ ... F$^-$</td>
<td>5609.2542</td>
<td>0.227</td>
<td>0.0</td>
</tr>
<tr>
<td>O$^{0.84-}$ ... O$^{0.84-}$</td>
<td>103585.030</td>
<td>0.20</td>
<td>25.93</td>
</tr>
<tr>
<td>* O$^{0.84-}$ ... F$^-$</td>
<td>200.0</td>
<td>0.30</td>
<td>8.99955</td>
</tr>
<tr>
<td>* F$^-$ ... F$^-$</td>
<td>1153.0</td>
<td>0.1365</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$D_e$ / eV</th>
<th>$a$ / Å$^{-1}$</th>
<th>$r_0$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$^{0.84-}$ ... S$^{1.36+}$</td>
<td>5.0</td>
<td>1.20</td>
<td>1.505</td>
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</table>

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$k$ / eV·rad$^{-2}$</th>
<th>$\Theta_0$ / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$^{0.84-}$ ... S$^{1.36+}$ ... O$^{0.84+}$</td>
<td>15.0</td>
<td>109.47</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Y / e</th>
<th>k / eV·Å$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$</td>
<td>2.997</td>
<td>19.26</td>
</tr>
<tr>
<td>* F$^-$</td>
<td>$-2.321$</td>
<td>63.5772</td>
</tr>
</tbody>
</table>

* Indicates potentials refined for this work
The Li-O and Fe-O potentials were refined from a recent study on LiFePO$_4$[25]. The Na-O, O-F, Fe-F and A-F (A = Li, Na) potentials were refined from parameters acquired from previous studies on fluorides and oxyfluorides [113, 114]. For the sulphate component, the inter-atomic potential model successfully formulated to simulate $M_2$SO$_4$ ($M = Na, K, Rb, and Cs$) and XSO$_4$ ($X = Sr, Ca, Ba$) [69–72] was used. This incorporates a Morse potential to describe the intramolecular bond stretching interactions between S and O ions in the sulphate group. A three body term is also used to account for the angle dependent nature of O-S-O bonds, as previously used for other sulphates [69–72] and phosphates [24] (chapter 3).

Table 4.2: Calculated and experimental structural parameters for AFeSO$_4$F (A = Li, Na)

<table>
<thead>
<tr>
<th>parameter</th>
<th>LiFeSO$_4$F</th>
<th>NaFeSO$_4$F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ / Å</td>
<td>5.146</td>
<td>6.648</td>
</tr>
<tr>
<td></td>
<td>5.175</td>
<td>6.673</td>
</tr>
<tr>
<td></td>
<td>$-0.029$</td>
<td>$-0.025$</td>
</tr>
<tr>
<td>$b$ / Å</td>
<td>10.920</td>
<td>8.676</td>
</tr>
<tr>
<td></td>
<td>10.983</td>
<td>8.699</td>
</tr>
<tr>
<td></td>
<td>$-0.063$</td>
<td>$-0.023$</td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>7.279</td>
<td>7.252</td>
</tr>
<tr>
<td></td>
<td>7.221</td>
<td>7.187</td>
</tr>
<tr>
<td></td>
<td>0.058</td>
<td>0.065</td>
</tr>
<tr>
<td>$\alpha$ / $^\circ$</td>
<td>106.286</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>106.506</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>$-0.220$</td>
<td>0.0</td>
</tr>
<tr>
<td>$\beta$ / $^\circ$</td>
<td>107.272</td>
<td>111.839</td>
</tr>
<tr>
<td></td>
<td>107.177</td>
<td>113.524</td>
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<td></td>
<td>0.095</td>
<td>$-1.685$</td>
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<tr>
<td>$\gamma$ / $^\circ$</td>
<td>96.121</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>97.866</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>$-1.745$</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$ reference [111]

The validity of this potential model is assessed by its ability to reproduce the experimental lattice parameters. Table 4.2 provides a direct comparison of experimental vs calculated structural parameters. Our unit-cell parameters $a$, $b$, and $c$ deviate from experimental values by, at most, 0.07 Å. Such successful reproduction of these complex tavorite crystal structures gives us confidence that our potential models can be used reliably for subsequent defect and migration calculations.

It is noted that the calculations for NaFeSO$_4$F were carried out by Dr Rajesh Tripathi and Prof. Linda Nazar (Waterloo, Canada) as part of the collaborative work for our paper published in 2011 [115] included in Appendix G). The results are included in this thesis for direct comparison with our LiFeSO$_4$F calculations, and provide interesting discussion.

4.2.2 Intrinsic Atomic Defects

As noted, insight into the defect properties of cathode materials is crucial for the full understanding of their electrochemical behaviour. Defect calculations were carried out using the Mott-Littleton scheme with region sizes of 12 Å and 24 Å, for region 1 and 2a respectively.
Isolated defect (vacancy and interstitial) energies were calculated for both LiFeSO$_4$F and NaFeSO$_4$F. These are listed in Appendix table D.2. By combining these isolated defect energy values the relative energies of formation of Schottky and Frenkel defects can be calculated. The following equations represent the reactions which form these defects (using Kröger-Vink notation and where A = Li or Na):

\begin{align*}
\text{A Frenkel:} & \quad A \overset{x}{\times} A \rightarrow V'_A + A^* \quad (4.1) \\
\text{Fe Frenkel:} & \quad Fe \overset{x}{\times} Fe \rightarrow V''_Fe + Fe^* \quad (4.2) \\
\text{F Frenkel:} & \quad F^x \rightarrow V^*_F + F'_i \quad (4.3) \\
\text{AF Schottky-type:} & \quad A_A^{x} + F_F^x \rightarrow V'_A + V^*_F + AF \quad (4.4) \\
\text{FeF$_2$ Schottky-type:} & \quad Fe_{Fe}^x + 2 F_F^x \rightarrow V''_Fe + 2 V^*_F + FeF$_2$ \quad (4.5)
\end{align*}

Sulphur vacancies were found to be highly unstable and hence full Schottky disorder is unlikely. We also examined the A/Fe "anti-site" pair defect involving interchange of an A$^+$ ion with an Fe$^{2+}$ ion. This is worth investigating since Li/Fe cation exchange effects have been a significant topic of discussion for LiFePO$_4$ [24, 67]. This process can be described by the following equation:

$$\text{Anti-site:} \quad A^{x}_A + Fe_{Fe}^{x} \rightarrow A'_{Fe} + Fe^*_A \quad (4.6)$$

<table>
<thead>
<tr>
<th>disorder type</th>
<th>equation</th>
<th>LiFeSO$_4$F</th>
<th>NaFeSO$_4$F</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Frenkel</td>
<td>4.1</td>
<td>3.79</td>
<td>2.99</td>
</tr>
<tr>
<td>Fe Frenkel</td>
<td>4.2</td>
<td>7.60</td>
<td>10.09</td>
</tr>
<tr>
<td>F Frenkel</td>
<td>4.3</td>
<td>4.84</td>
<td>3.10</td>
</tr>
<tr>
<td>AF Schottky-type</td>
<td>4.4</td>
<td>4.22</td>
<td>4.10</td>
</tr>
<tr>
<td>FeF$_2$ Schottky-type</td>
<td>4.5</td>
<td>8.38</td>
<td>8.23</td>
</tr>
<tr>
<td>A/Fe antisite</td>
<td>4.6</td>
<td>2.50</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Examination of the resulting defect energies listed in Table 4.3 reveal two main predictions. First, formation of all Frenkel and Schottky defects is unfavourable in both AFeSO$_4$F structures. Interestingly, the results suggest that fluoride vacancies and fluoride interstitials are unlikely to exist in the pure (undoped) materials. Second, the anti-site energies are also relatively high, which indicates that there would be no significant concentration of Fe on A sites at operating temperatures in these fluorosulphates. This is in contrast with LiFePO$_4$ which exhibits cation exchange behaviour, particularly Fe on Li sites [24, 67] (chapter 3). Therefore, these results suggest that conduction blocking effects involving Fe on Li or Na sites are much less likely in the AFeSO$_4$F cathode materials.
### 4.2.3 Li Ion Migration

Using atomistic simulation techniques, it is possible to examine various possible transport paths that are responsible for Li$^+$ (or Na$^+$) conduction, which are often difficult to probe at the atomic scale by experiment alone. Energy profiles for conduction paths, via a vacancy-hopping model, can be derived from a set of constrained minimisation calculations. With this method migration paths are mapped via series of individual Mott-Littleton type defect calculations, where the migrating Li ion is incrementally moved along the linear path between two vacant Li sites. At each step the migrating Li ion is able to relax in a 2D plane, allowing the most energetically favourable pathway to be located. The position of highest potential energy along the migration path corresponds to the activation energy of migration ($E_{\text{mig}}$). Relaxation of the surrounding lattice (> 700 ions) is treated explicitly by this method.

In our simulated LiFeSO$_4$F cell there are two Li sites (labelled Li$_A$ and Li$_B$ in Figure 4.2a). These two sites are located opposite each other at the periphery of the [100] and [010] tunnels as shown in the long-range view of the structure (Figure 4.2b). From this we have identified all of the possible migration paths between adjacent Li sites. There are three unique Li-Li jump distances along the [100] channel and three along the [010] channel, as shown in Figures 4.3a and c. These jumps (L1-L6) represent all the possible migration paths between adjacent lithium sites.

The calculated activation energies for Li-ion migration in LiFeSO$_4$F are included in Figures 4.3a-d (and are listed in table 4.4). The lowest migration energies are 0.36 - 0.46 eV for paths involving jumps L3 - L6. Such low values suggest high Li mobility in the LiFeSO$_4$F material, which is important for good electrochemical behaviour.

<table>
<thead>
<tr>
<th>net diffusion direction</th>
<th>jumps involved</th>
<th>activation energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>L3 + L4</td>
<td>0.46</td>
</tr>
<tr>
<td>[010]</td>
<td>L5 + L6</td>
<td>0.44</td>
</tr>
<tr>
<td>[001]</td>
<td>L3 + L6</td>
<td>0.46</td>
</tr>
<tr>
<td>[101]</td>
<td>L4 + L6</td>
<td>0.44</td>
</tr>
<tr>
<td>[011]</td>
<td>L3 + L5</td>
<td>0.46</td>
</tr>
<tr>
<td>[111]</td>
<td>L4 + L5</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Second, the results indicate that net Li migration requires a combination of at least two diagonal jumps. These diagonal jumps form continuous zigzag pathways through the structure allowing long range diffusion along the tunnels listed in table...
Figure 4.3: (a) Schematic illustrating the various Li distances in tavorite LiFeSO$_4$F along the primary [100] tunnel; the preferable Li-ion migration paths are shown as dashed lines, where each colour belongs to a unique hop with a distinct activation energy. (b) Corresponding long range transport within the lattice along [100]; the same colour code described in (a) is followed. (c) Similar schematic to (a) this time along [010], and (d) the corresponding long range transport within the lattice along [010].
4.4. The lowest energy path is along the [111] direction. The 3D view of the structure (Figure 4.10a) reveals that four unique jumps (L3-L6) are available for each Li ion which leads to continuous interconnecting paths and effective 3D transport of Li ions. We should note that L1 and L2 are hops between symmetry-equivalent sites (i.e. $\text{Li}_A - \text{Li}_A$), along the [100] and [010] directions respectively, and are found to have high and unfavourable activation energies (>1.0 eV); this is probably due to the migrating Li ion coming into close proximity to the $\text{FeO}_4\text{F}_2$ octahedra.

Finally, although direct comparison with Li-ion conductivity is not straightforward, our calculated value of $\sim 0.4$ eV is consistent with experimental activation energies for Li diffusion in other related cathodes or LISICON-type materials [116].

The diffusion coefficient of any ion hop, according to dilute diffusion theory can be estimated using [117]

$$D = g\Gamma a^2,$$

where $D$ is the chemical diffusion coefficient, $g$ the geometric factor and $a$ the hop distance. $\Gamma$ is the hopping frequency, as defined according to transition-state theory [118]:

$$\Gamma \approx \nu^* \exp\left(-\frac{E_a}{kT}\right),$$

In this case, $\nu$ is the attempt frequency and $E_a$ is the migration activation energy. The activation energy gives a direct estimate for the diffusion coefficient over a specific hop distance. For our calculations, $g$ is assumed to be equal to 1 and we use the typical value [118] for $\nu$ of $10^{13}$ s$^{-1}$.

Dilute diffusion theory can be assumed to be reasonably valid for fluorosulphate materials, even during the (de)lithiation process. According to previous studies [44, 111], (de)lithiation occurs via a two-phase process over most of the compositional range. In this case, the new phase formed upon (de)lithiation remains almost stoichiometric in nature, thus giving a very dilute, and therefore non-interacting, concentration of the charge-carrying defects (Li$^+$ ions or vacancies). For the favourable activation energies in $\text{LiFeSO}_4\text{F}$, the diffusion coefficients are estimated to be in the range of $10^{-10} - 10^{-8}$ cm$^2$s$^{-1}$, which is consistent with values found for the conventional $\text{LiCoO}_2$ [119–123].

Depending upon synthesis conditions, experimental values of the activation energy for Li ion mobility in fluorosulphate tavorite materials measured by impedance spectroscopy are reported to be in the range 0.77-0.99 eV for $\text{LiFeSO}_4\text{F}$ [44, 124] and 0.94 eV for $\text{LiMgSO}_4\text{F}$ [125]. An estimated diffusion coefficient using such values of the activation energy would be of the order of $\sim 10^{-19}$ cm$^2$s$^{-1}$, implying extremely limited ion mobility. These values are in contrast to the excellent electrochemical and ion conducting behaviour exhibited by these two materials. $\text{LiFeSO}_4\text{F}$ is known to have low thermal stability; therefore, as noted earlier [44], the inability to hot-press the material leads to poor particle-particle contact and could lead to high experimental activation energy values. A minimum value of 0.3 eV for $\text{LiFeSO}_4\text{F}$ has been calculated and experimentally measured activation energies have been rationalised [126].
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Figure 4.4: Visualisation of the lowest energy pathway for an individual Li jump in LiFeSO₄F. Each blue sphere represents a Li position from an optimised NEB image. The L4 jump is used in this figure, but all Li jumps show similar S-shaped trajectories.

Table 4.5: Comparison of calculated activation energies for Li migration between the mott-littleton type method and nudged elastic band (NEB)

<table>
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<tr>
<th>jump</th>
<th>mott-littleton</th>
<th>NEB</th>
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<tr>
<td>L3</td>
<td>0.46</td>
<td>0.45</td>
</tr>
<tr>
<td>L4</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>L5</td>
<td>0.36</td>
<td>0.32</td>
</tr>
<tr>
<td>L6</td>
<td>0.44</td>
<td>0.43</td>
</tr>
</tbody>
</table>

by including Li vacancy formation energy in stoichiometric LiFeSO₄F. However this is unlikely, because the thermodynamic minimum, which is guided by the entropy of the system, always exists at a certain non-zero point defect concentration. Thus, such systems will always have a finite concentration of Li vacancies.

We also calculated Li migration energies using the nudged elastic band (NEB) method described in chapter 2 (section 2.2.4). Because this method involves periodic boundary conditions, there is a concentration of Li vacancies and migrating Li ions, which is determined by the size of the supercell. This is in contrast to the conventional vacancy hopping methodology, which utilises the Mott-Littleton scheme, and is therefore at infinite dilution. It is important to make a large enough supercell to keep interactions of defects with their periodic images to a minimum. For this work we used 20 replicas of a 3 × 4 × 4 supercell, with explicit simulation of 767 ions.

Figure 4.4 reveals that the individual jumps that make up the 3D network of dif-

fusion pathways follow a curved trajectory through the tunnels. This could be rationalised by it being energetically favourable for lithium to maintain coordination with oxygen ions on nearby Fe octahedra during migration. From table 4.5 it is clear that migration energy barriers from NEB calculations closely match those from our Mott-Littleton type calculations. This gives us confidence that our visualisation of the lowest energy pathway between adjacent Li sites provided in Figure 4.4 is valid.

4.2.4 Li Ion Diffusion: Molecular Dynamics Simulations

To complement these results and to investigate the mechanism of Li ion migration in LiFeSO$_4$F in more detail, molecular dynamics (MD) simulations were carried out. Such techniques have proven to be well suited to probing ion transport mechanisms directly [127–130], thus adding to the information derived from static lattice simulations. Hence our focus here was to investigate Li transport mechanisms and the local structure.

**Simulation details:** We created a $6 \times 3 \times 4$ P1 supercell, containing 36 (12.5%) randomly distributed Li vacancies, over both Li1 and Li2 positions, to promote Li migration; a large cell of this size provides explicit simulation of 2268 ions. The same potential parameters used in the energy minimisation work (table 4.1) were used here, although for this MD study a rigid-ion model was employed. The general simulation procedure is outlined: first, the cell was run at zero Kelvin for 50 ps with a time step of 0.5 fs to relax the system. Second, the resulting relaxed system was run at both 300K and 600K for 250 ps with a time step of 0.5 fs, and equilibration period of 25 ps using an NPT ensemble, which allows for thermal expansion of the cell. Final production simulations were run at each temperature for 900 ps with a time-step of 0.5 fs and equilibration period of 100 ps using an NVT ensemble. All the statistics were extracted from these final production runs.

**Local structure:** Valuable structural information can be extracted from radial distribution functions (RDFs), which provide valuable insight into the long-range (dis)order of the crystal lattice. The Fe$^{2+}$ cation-cation RDFs are shown in Figure 4.5, and reveal a series of sharp, well ordered peaks typical of a crystalline solid. The location of the peaks correspond to successive nearest-neighbour distances between Fe ions within the crystal lattice. In contrast, the Li-O and Li-F RDFs (shown in Figure 4.6) show relatively broad structure for separations greater than the nearest-neighbour, indicating some loss of long range order, and therefore increased mobility in the lithium sub-lattice.

As noted, there is still much debate over the location of Li in LiFeSO$_4$F, related to whether there are two sites with 50/50 occupancy or just one fully occupied site. The Li-anion RDF plots (shown in Figure 4.6) provide direct comparison of the local
Figure 4.5: Radial Distribution Functions for Fe-Fe at 300K: (a) Fe1-Fe1; (b) Fe1-Fe2.

Figure 4.6: Radial Distribution Functions for Li-O and Li-F at 300K: (a) Li1-F; (b) Li2-F; (c) Li1-O; (d) Li2-O
environment around Li1 and Li2 sites. The RDF of Li1-O1 appears identical to Li2-O1, as does the RDF of Li1-F with Li2-F, which clearly suggests that Li1 and Li2 have equivalent local environments, and there is therefore just one fully occupied Li site. This is in good agreement with our analysis of the Li ion environments of the optimised structure from energy minimisation calculations detailed earlier.

Diffusion paths: Time-averaged density plots from MD trajectory data help to visualise the regions most frequently traversed by the species of interest within the simulation cell. The density plots provided in Figure 4.7, show the lattice regions lithium has occupied during the simulation time period. The larger the volume of density the greater amount of time Li has spent in a certain region. A recent DFT study [131] found that LiFeSO$_4$F showed one dimensional Li diffusion along [111], whereas an ab-initio MD study [132] found 3D behaviour, although the simulation timescale was only 1 ps. It was also suggested that activation of other higher energy pathways, between [111] channels, may be necessary if channel blocking defects such as anti-sites were present [131]. Analysis of the lithium density plots reveals that the dominant long-range migration pathway runs along the [111] direction, indicated by the yellow arrows in Figures 4.7a and b. Long-range migration consists of the repeated combination of two distinct hops between neighbouring lithium sites, which is in agreement with previous static lattice calculations. There is also considerable Li density located between these [111] chains (highlighted in blue boxes in Figures 4.7a and b) providing a 3D network of Li migration pathways. Here our simulation cell contains no anti-site defects; hence, Li diffusion between [111] channels is found to be an intrinsic process, which does not require the presence of anti-site defects.

Overall, these results suggest that Li migration in LiFeSO$_4$F is quasi-3D, where the dominant migration pathway is along the [111] direction but other pathways which combine to form a 3D network are utilised, just to a lesser extent. This is in good agreement with our energy minimisation calculations where the lowest energy pathway was found to be along [111] (0.36 eV) but other channels also showed very low activation energies ($\sim 0.4$ eV) comparable to LiCoO$_2$ [118, 133–135].

Mean square displacement (MSD) plots can be used to provide valuable quantitative insight into Li diffusion. In Figure 4.8 the MSD data is plotted as a function of time, for all ion species at 300K. After an initial equilibration period, the MSD of all Fe, S, O and F species rapidly settle to a constant value with time, indicating their motion is limited to small vibrations about lattice positions as expected. In contrast, the lithium MSD increases with time indicating appreciable ion diffusion. The diffusion coefficients at 300K can be extracted from the slope of the MSD using the Einstein relationship for three-dimensional systems,

$$\text{MSD} = 6Dt + B, \quad (4.9)$$

where $B$ is a small thermal factor arising from atomic vibrations.
Figure 4.7: Lithium density plots from MD simulations (T = 600K) of LiFeSO₄F. (a) along [010] and (b) along [001]. Lithium density is shown in green and the SO₄ and FeO₆ sub-lattice is shown in wire frame. Yellow arrows indicate net lithium migration along the [111] direction, which consists of the combination of two jumps. Inter-channel migration along directions other than [111] are highlighted in the blue boxed regions.
Our calculated diffusion coefficient is of the order $10^{-8}$ cm$^2$s$^{-1}$ at $T = 300$K, which is in good agreement with earlier estimates from our energy minimisation calculations. This is also consistent with experimental values for LiCoO$_2$ [119–123] which shows similarly high lithium mobility. However, a recent experimental diffusion study [136] reports a very low $D$ value of $10^{-14}$ cm$^2$s$^{-1}$ for LiFeSO$_4$F at $T = 298$K; Tarascon and co workers [136] note that such a value is several orders of magnitude lower than those predicted by all calculations, and that there is currently no explanation for this discrepancy.

### 4.2.5 Na Ion Migration

NaFeSO$_4$F crystallises in a different space group ($P2_1/c$) to LiFeSO$_4$F ($P\bar{1}$) with only one Na$^+$ ion site in the unit cell (Figure 4.2c). The two intersecting tunnels that are inequivalent in LiFeSO$_4$F (along the [100] and [010] directions), become equivalent in NaFeSO$_4$F (along the [110] and [1\bar{1}0] directions). Therefore, only one schematic is shown in Figure 4.9a. As with LiFeSO$_4$F, we have identified the main migration paths in NaFeSO$_4$F between adjacent Na sites. The calculated activation energies for Na-ion migration in NaFeSO$_4$F are included in Figure 4.9a and (are listed in Table 4.6), indicating two key results.

First, the lowest migration energy is 0.6 eV for paths involving only jumps N4 and N5, with other paths involving jumps N3 - N5 having activation energies of $\sim 0.9$ eV. Na migration energies in NaFeSO$_4$F are higher than those for Li migration in
Table 4.6: Calculated activation energies for the most favourable net diffusion pathways for Na-ion migration in NaFeSO$_4$F (paths are shown in figures 4.9a-b)

(a) Li-Ion Migration in LiFeSO$_4$F

<table>
<thead>
<tr>
<th>net diffusion direction</th>
<th>jumps involved</th>
<th>activation energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>N3 + N4 + N5</td>
<td>0.91</td>
</tr>
<tr>
<td>[010]</td>
<td>N3 + N4 or N3 + N5</td>
<td>0.91</td>
</tr>
<tr>
<td>[001]</td>
<td>N3</td>
<td>0.91</td>
</tr>
<tr>
<td>[110]</td>
<td>N3 + N4 + N5</td>
<td>0.91</td>
</tr>
<tr>
<td>[110]</td>
<td>N3 + N4 + N5</td>
<td>0.91</td>
</tr>
<tr>
<td>[101]</td>
<td>N4 + N5</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Figure 4.9: (a) Schematic showing the various Na-Na distances in NaFeSO$_4$F along the primary tunnels [110] or [110]; the preferred Na-ion migration paths are depicted in colour, where each colour belongs to a unique path with a distinct activation energy. (b) Corresponding long-rang transport within the lattice; the same colour code as that described in (a) is followed.
LiFeSO$_4$F, which suggests lower Na mobility. However, we note that the tunnel-structured material Na$_4$TiP$_2$O$_9$ has been reported to have an activation energy as high as 1 eV, based on single crystal experiments [137].

The favourable Na migration pathways are also a combination of zigzag jumps forming continuous diffusion pathways through the structure. However diffusion coefficients for these migration paths of 0.6 and 0.9 eV are $1.2 \times 10^{-12}$ and $8 \times 10^{-18}$ cm$^2$s$^{-1}$ respectively. This large difference in magnitude indicates that Na$^+$ ion diffusion in NaFeSO$_4$F is effectively one-dimensional. The 3D view of the structure (Figure 4b) reveals that the lowest-energy paths (N4 and N5) produce a continuous Na diffusion pathway, but only through the [101] tunnel for effective 1D Na$^+$ transport. As in LiFeSO$_4$F, the highest-energy migration jump (1.9 eV) involving N1 and N2 is close to the FeO$_4$F$_2$ octahedra. In general NaFeSO$_4$F shows higher activation barriers than LiFeSO$_4$F, which is probably due to stronger steric interactions with the larger Na ion.

![Figure 4.10: Full view of the structures and ion conduction pathways: (a) 3D Li-ion conduction in LiFeSO$_4$F and (b) 1D Na-ion conduction in NaFeSO$_4$F. The same colour code as used in figures 4.3 and 4.9 has been used.](image)

Overall these simulations suggest that the ionic conductivity of NaFeSO$_4$F should be lower than LiFeSO$_4$F. It has been noted earlier [111] that split site occupancy of Li ions, as opposed to a fixed Na-ion site, may indicate higher Li-ion mobility in the structure, and this is also confirmed by comparing bond sums (0.99 in LiFeSO$_4$F vs 1.16 in NaFeSO$_4$F). However direct comparison with electrochemical behaviour is not straightforward. Indeed, electrochemical (de)insertion in any electrode is not solely dependent on the ionic conductivity [138]. The electrochemical properties of NaFeSO$_4$F may not be solely driven by low ion conductivity. These may be nested in the two-phase driven (de)intercalation process (with a 14.5% volume difference
[111] in end member phases), which adds a substantial additional phase-boundary migration energy term. These issues warrant further investigation, as well as detailed studies on the electronic structure using DFT-based methods.

4.3 Chapter Summary

This investigation of tavorite-type fluorosulphates has provided atomic-scale insight into the intrinsic defect chemistry and alkali-ion conduction paths, which are relevant to their electro-chemical behaviour as new lithium battery cathodes. The main results can be summarised as follows:

1. We have developed robust potential models which accurately reproduce the experimental crystal structures of LiFeSO$_4$F and NaFeSO$_4$F. We find that Li ions in both Li1 and Li2 sites relax to equivalent positions located at a point between the two sites. This was found from analysis of local interionic distances from energy minimisation calculations as well as comparisons of radial distribution functions from molecular dynamics simulations.

2. The defect calculations suggest that the formation of all Schottky and Frenkel defects is unfavourable. The Li/Fe and Na/Fe anti-site energies also suggest that there would be no significant intrinsic concentration of Fe on Li or Na sites at operating temperatures in these fluorosulphates. This is in contrast with the LiFePO$_4$ cathode material which has a small amount of Fe on Li sites.

3. Investigation of the transport paths in LiFeSO$_4$F indicates relatively low migration energies ($\sim 0.4$ eV), suggesting high Li mobility, which is important for good rate capability and capacity retention. The Li migration paths are a combination of diagonal jumps which from continuous diffusion pathways in the open tavorite structure. Li$^+$ transport is found to be quasi three-dimensional with the lowest energy path (0.36 eV) along the [111] direction. Migration along other directions which form connections between the [111] pathways are also low in energy ($\sim 0.4$ eV), giving rise to a 3D network of favourable Li migration pathways. Molecular dynamics simulations of LiFeSO$_4$F also show quasi 3D lithium diffusion in the structure. The most dominant pathway from Li density plots is found to be along [111], with clear migration along other directions providing a 3D diffusion network. In terms of rate capability in cathodes, such 3D behaviour is an advantage over lower dimensional transport in other materials e.g. 1D Li$^+$ pathways in LiFePO$_4$ [24, 25].

4. Na-ion transport in monoclinic NaFeSO$_4$F is also mediated by a combination of zigzag jumps, but with higher activation energies (0.6 - 0.9 eV), than those for Li-ion migration in LiFeSO$_4$F. The estimated diffusion coefficient for the most favourable migration path along the [101] direction is at least six orders of magnitude higher than that in any other direction, suggesting that NaFeSO$_4$F is a one-dimensional Na-ion conductor.
Such differences in intrinsic alkali-ion mobility would influence the ability to extract Li and Na from the LiFeSO$_4$F and NaFeSO$_4$F structures and, hence, lead to contrasting capacity retention and rate capability as rechargeable electrodes. These transport properties, coupled with the two-phase behaviour of (de)intercalation of alkali ions and a large volume difference between end members, helps to rationalize the difference in the observed electrochemical behavior of the Li and Na fluorosulphates.
Chapter 5

Intrinsic Defects and Lithium Diffusion in Triplite-Structured LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F

5.1 Background

From initial investigations into fluorosulphate materials, it was found that unlike LiFeSO$_4$F which crystallises in the tavorite structure, LiMnSO$_4$F is isostructural with the mineral triplite, Mn$_2$PO$_4$F [139]. The Mn-based system LiMnSO$_4$F shows no electrochemical activity, which is in contrast to the olivine-phosphate materials where Mn based analogues provide larger cell voltages than the Fe members [14, 47]. This led to research into Fe/Mn solid solutions where a very recent exciting breakthrough by Tarascon and co workers [46] found that formation of the triplite structure can be achieved by substituting as little as 5% Mn for Fe in LiFeSO$_4$F. The resultant material LiFe$_{1-y}$Mn$_y$SO$_4$F provides an Fe$^{3+}$/Fe$^{2+}$ redox potential of 3.9 V which is the highest ever reported for Fe-based polyanion cathode materials, and is higher than the tavorite phase making it a higher energy density cathode material. The energetic stability of the tavorite and triplite phases is very finely balanced, so subtle changes in reaction conditions can result in the formation of one phase over the other. It was observed that “electrodes with the best performances tend to be those on the verge of structural instability”[46].

Although built from the same octahedral and tetrahedral units, the triplite and tavorite structures differ considerably. Triplite LiFe$_{1-y}$Mn$_y$SO$_4$F crystallises in the monoclinic space group $C2/c$, in contrast to the triclinic $P1$ cell exhibited by the tavorite material. Both structures generally comprise of octahedral transition metal ($M$) sites and tetrahedral $SO_4$ groups. Triplite has two crystallographically unique edge sharing chains of (M1)O$_4$F$_2$ and (M2)O$_4$F$_2$ and octahedra running along the [101] and [010] directions respectively (shown in Figure 5.1). Tavorite LiFeSO$_4$F forms single corner sharing chains which are comprised of both transition metal
Figure 5.1: The triplite crystal structure of LiFe$_{1-y}$Mn$_y$SO$_4$F. The blue and green octahedra depict $MF_2O_4$ units where $M = \{Fe, Mn \text{ and Li}\}$. (a) shows both M1 and M2 octahedra; (b) the M2 octahedra have been removed to allow the M1 chains along the [101] direction to be viewed more clearly; (c) the M1 octahedra have been removed to view the M2 chains which run along the [010] direction.
Chapter 5. Defects and Lithium Diffusion in LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F

sites. The fluorine atoms in the triplite structure sit in cis positions on the octahedra, whereas they lie trans to each other in the tavorite structure. Finally, Li does not have a unique site in the triplite, instead sharing the two $M$ sites ($M1$ and $M2$) evenly with Mn and Fe.

X-ray diffraction experiments [46, 48] suggest there is no distinct Li/$M$ order throughout the structure, so there are no long range chains of connected Li$_2$F$_2$O$_4$ octahedra to form open channels along which Li may diffuse; this could suggest poor rate capability as a result. However, cycling performance at low rates ($C/20$) is excellent, and LiFe$_{0.9}$Mn$_{0.1}$SO$_4$F offers a reversible capacity of $\sim$120 mAh g$^{-1}$ [46]. It should also be noted that Mn is electrochemically inactive in these solid solutions, so increasing Mn content will reduce the capacity. Furthermore at high Mn content (Mn > 0.6) the capacity fades to zero indicating a possible phase change [46, 48]. More recently LiFeSO$_4$F was synthesised in the triplite framework offering potential full utilisation of the cell capacity [48, 140]. However, this pure iron triplite phase shows poorer electrochemical performance than substituted phases containing small fractions of Mn content [48, 140].

Since triplite LiFe$_{1-y}$Mn$_y$SO$_4$F is such a recent discovery, the fundamental solid-state chemistry behind many of its advantageous properties is not fully understood. It is thought that the remarkably high Fe$^{3+}$/Fe$^{2+}$ redox couple is a result of several factors: a change in the connectivity of the ions compared to the tavorite structure [46, 48]; fluorine sitting cis rather than trans in the octahedral $M$ sites [46]; Mn content enhancing the potential, as seen in the olivine phosphate materials [46, 47]. The excellent cycling performance, despite there being no channel structures for lithium diffusion, presents a far greater mystery. It has been suggested that diffusion in this material may be similar to the silicates [141, 142], where net migration of lithium ions does not occur along a single direction, instead several changes in direction are required. A recent DFT study [143] finds a 3D network of Li mobility in the material, however cation ordering and site sharing is neglected. The original study of Tarascon and co workers openly calls for simulation studies to help investigate these key questions, stating: “To definitively identify the real Li conduction pathway, atomistic modelling is absolutely necessary” [46].

Here we use well established inter-atomic potential based techniques to provide a detailed investigation into intrinsic disorder and ion migration at the atomic level of triplite-structured LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F, which clearly extends our successful simulation work on related tavorite materials [111] (Chapter 4).
5.2 Results and Discussion

5.2.1 Crystal Structure and Potentials

As noted, the triplite structure consists of crystallographically unique edge-sharing chains of \((M1)O_4F_2\) and \((M2)O_4F_2\) and octahedra, which are linked via corner sharing of \(SO_4\) tetrahedra; Li has no unique site, so shares the \(M\) sites with Mn and Fe. For this work a symmetry removed (P1) cell was devised from lattice parameters and ion positions from a recent x-ray diffraction study [48]. Triplite \(\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{SO}_4\text{F}\) shows full cation mixing whereby lithium ions share two octahedral \(M\) sites, \(M1\) and \(M2\), with Fe and Mn. Experimentally there is no evidence of long-range cation ordering, so the experimental data provided in table 5.2 is representative of the ensemble average. However, in order to carry out modelling studies it is necessary to impose some cation ordering. As a starting point, an ordering scheme where no like cations are in adjacent positions was chosen (shown in Figure 5.2).

![Figure 5.2: Triplite structured LiFe\(_{0.5}\)Mn\(_{0.5}\)SO\(_4\)F unit cell with imposed cation ordering, in which no like cations are adjacent. (Oxygen ions = red; fluoride ions = grey)](image_url)

The first step in simulating any solid-state material is to produce a reliable potential model which reproduces its experimental crystal structure. In this case all the pair potentials apart from Mn-F and Mn-O where transferred directly from our recent study on the closely related \(\text{LiFeSO}_4\text{F}\) tavorite material [111] (chapter 4). The Mn-O potential was taken from our previous studies of olivine phosphate materials [25, 67].
and the Mn-F potential was refined for this work. All potential parameters used in this work are provided in Table 5.1.

**Table 5.1: Potential and shell model parameters for LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F**

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$A$ / eV</th>
<th>$\rho$ / Å</th>
<th>$C$ / eV·Å$^6$</th>
</tr>
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<tr>
<td>Li$^+$ ... O$_{0.84}^-$</td>
<td>4787.6</td>
<td>0.19998</td>
<td>0</td>
</tr>
<tr>
<td>Li$^+$ ... F$^-$</td>
<td>400.6</td>
<td>0.2736</td>
<td>0</td>
</tr>
<tr>
<td>Fe$^{2+}$ ... O$_{0.84}^-$</td>
<td>7500.0</td>
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<tr>
<td>Fe$^{2+}$ ... F$^-$</td>
<td>5609.2542</td>
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<td>0</td>
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<tr>
<td>Mn$^{2+}$ ... O$_{0.84}^-$</td>
<td>2601.3939</td>
<td>0.278</td>
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</tr>
<tr>
<td>Mn$^{2+}$ ... F$^-$</td>
<td>7287.7032</td>
<td>0.229522</td>
<td>0</td>
</tr>
</tbody>
</table>

* Indicates potentials refined for this study

Table 5.2 provides a comparison of the experimental lattice parameters vs our calculated values; the calculated values are all within 1% of experiment, which is excellent considering the complexity of the structure. Due to the site disorder, all $M$-O and $M$-F bond lengths observed experimentally are a weighted average of Li, Mn and Fe, and are therefore not directly comparable to those in our ordering scheme. Using these potentials we investigated every possible cation ordering scheme within our unit cell, with the conditions that Fe, Mn and Li share the M1 and M2 sites evenly. This amounts to just over 178,000 configurations, of which there are thousands which show good agreement with experimental structural data; the lattice energies of these configurations differ only by fractions of an eV per formula unit. This is
in good agreement with experiment where a random cation distribution between M1 and M2 sites is found [46, 48]. Such successful structural reproduction gives us confidence that our potential model can be used reliably in defect and migration calculations.

We have selected four low energy ordering schemes for investigation: ordering scheme 1, shown in Figure 5.2, was used to investigate intrinsic defect processes, whereas the other three ordering schemes were required for a full analysis of lithium migration, and are described in more detail in section 5.2.3.

### 5.2.2 Intrinsic Atomic Defects

A range of isolated point defect energies, listed in Appendix table E.2, were calculated for LiFe_{0.5}Mn_{0.5}SO_{4}F. Defect calculations were carried out using the Mott-Littleton scheme with region sizes of 12 Å and 24 Å, for region 1 and 2a respectively. These point defect energies were combined to determine the relative energies of formation of Schottky and Frenkel defects. The following equations represent the reactions which form these defects (using Kröger-Vink notation):

\[
\begin{align*}
\text{Li Frenkel:} & \quad \text{Li}^\times_{\text{Li}} \rightarrow V'_{\text{Li}} + \text{Li}^\bullet_{\text{Li}} \\
\text{Fe Frenkel:} & \quad \text{Fe}^\times_{\text{Fe}} \rightarrow V''_{\text{Fe}} + \text{Fe}^\bullet_{\text{Fe}} \\
\text{Mn Frenkel:} & \quad \text{Mn}^\times_{\text{Mn}} \rightarrow V''_{\text{Mn}} + \text{Mn}^\bullet_{\text{Mn}} \\
\text{F Frenkel:} & \quad F^\times_{\text{F}} \rightarrow V'_{\text{F}} + F^\bullet_{\text{F}} \\
\text{LiF Schottky-type:} & \quad \text{Li}^\times_{\text{Li}} + F^\times_{\text{F}} \rightarrow V'_{\text{Li}} + V'_{\text{F}} + \text{LiF} \\
\text{FeF}_2 \text{ Schottky-type:} & \quad \text{Fe}^\times_{\text{Fe}} + 2 F^\times_{\text{F}} \rightarrow V''_{\text{Fe}} + 2 V'_{\text{F}} + \text{FeF}_2 \\
\text{MnF}_2 \text{ Schottky-type:} & \quad \text{Mn}^\times_{\text{Mn}} + 2 F^\times_{\text{F}} \rightarrow V''_{\text{Mn}} + 2 V'_{\text{F}} + \text{MnF}_2
\end{align*}
\]

As with the olivine andavorite structures, we also examined the Li/Fe and Li/Mn “anti-site” pair defects involving interchange of an Li\(^+\) ion with Fe\(^{2+}\) and Mn\(^{2+}\) ions.
These processes can be described by the following equations:

\[
\text{Fe Anti-site:} \quad \text{Li}^\text{Li} + \text{Fe}^\text{Fe} \rightarrow \text{Li'}^\text{Li} + \text{Fe}^\text{Fe} (5.8)
\]

\[
\text{Mn Anti-site:} \quad \text{Li}^\text{Li} + \text{Mn}^\text{Mn} \rightarrow \text{Li'}^\text{Mn} + \text{Mn}^\text{Mn} (5.9)
\]

<table>
<thead>
<tr>
<th>disorder type</th>
<th>equation</th>
<th>Energy/eV</th>
</tr>
</thead>
<tbody>
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<td>Li Frenkel</td>
<td>5.1</td>
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</tr>
<tr>
<td>Fe Frenkel</td>
<td>5.2</td>
<td>5.02</td>
</tr>
<tr>
<td>Mn Frenkel</td>
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<td>4.41</td>
</tr>
<tr>
<td>F Frenkel</td>
<td>5.4</td>
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</tr>
<tr>
<td>LiF Schottky-type</td>
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<td>2.63</td>
</tr>
<tr>
<td>FeF\textsubscript{2} Schottky-type</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Li/Fe anti-site</td>
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</tr>
<tr>
<td>Li/Mn anti-site</td>
<td>5.9</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Table 5.3 provides the formation energies of all the intrinsic defect processes we have investigated. The results reveal several interesting predictions. First, the most favourable defect is the Li/Mn anti-site pair, although the Li/Fe pair is also very low in energy. This may be expected because from our previous structural calculations we find numerous different cation ordering schemes which show very small differences in lattice energy, and experimentally [46, 48] full cation mixing is also observed. One consequence of such exchange is that Fe ions could block favourable diffusion pathways. Therefore, these results suggest that conduction “blocking” effects involving Fe and Mn on Li sites will be more prevalent in triplite structured LiFe\textsubscript{0.5}Mn\textsubscript{0.5}SO\textsubscript{4}F than the related tavorite material, LiFeSO\textsubscript{4}F, in which intrinsic anti-site defects are found to be relatively unfavourable [111].

Second, the Li Frenkel, F Frenkel and LiF Schottky energies are all low, suggesting a minor population of such defects could be present at high synthesis temperatures. The presence of Li interstitials could enhance ionic conductivity by utilising the interstitial positions to shorten lithium hop distances. However, the presence of F interstitials could block lithium migration pathways. Such low energies associated with formation of F vacancies also suggests that fluorine could leak from the material during cycling. The most favourable Li interstitial site was at (0.75, 0.75, 0.5) in fractional units of the simulation cell, and the most favourable F interstitial site was at (0.25, 0.65, 0.75). However, both sites have very similar local environments and are located between the faces of two SO\textsubscript{4} tetrahedra. Introducing interstitial ions causes considerable local relaxation of the crystal lattice, and Fe interstitials were found to push Li ions off lattice sites into interstitial positions.

Finally, the high energies associated with the formation of Mn and Fe based Schottky
and Frenkel defects suggest that such intrinsic defects are not significant in this material.

5.2.3 Li Ion Migration

Investigating lithium migration in this triplite-structured material is not a trivial task, because lithium does not occupy a unique crystallographic site, instead sharing two metal sites M1 and M2 with Mn and Fe ions. Such cation disorder means that there are no long-range open channels for lithium diffusion.

![Diagram](image)

**Figure 5.3:** Possible Li-ion migration channels in the triplite structure (after Nazar and co-workers [48]): (a) jumps between adjacent M1 sites form a continuous network for long-range ion migration along the [101] direction; (b) zigzag jumps between adjacent M1 sites form a continuous network along the [010] direction for long-range ion migration. Both cation sites (M1 and M2) are 50% occupied by Mn and Fe ions, so long-range transport along the [101] and [010] channels will be blocked. (De)lithiation would therefore require inter-site jumps between M1 and M2 sites to avoid such blockages; a selection of possible inter-site jumps are shown as red vectors.
As noted by Nazar and co-workers [48] the chains of M1 sites which run along [101] and the chains of M2 sites which run along [010] are located in tunnels which look similar to the Li channels found in the tavorite structure. If Lithium was exclusively located on either one of these sites, net Li-ion migration could be achieved via a series of zigzag jumps along these tunnels (shown in Figure 5.3) However, the Li ions only have a 50% occupancy of each site, with Fe and Mn ions taking up the remaining 50%; long-range Li-diffusion along these tunnels will therefore be blocked. Experimentally [46, 48] triplite-structured LiFe$_{0.9}$Mn$_{0.1}$SO$_4$F shows excellent reversible cycling at low rates (C/20), which suggests that Li ions can make inter-site hops (red vectors in Figure 5.3) from M1 to M2, thus avoiding such blockages.

To thoroughly investigate the lithium diffusion pathways in triplite LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F it is necessary to examine all the nearest neighbour jumps from each M site; these include same-site jumps (M1-M1 and M2-M2) and inter-site jumps (M1-M2). Figures 5.4a and 5.4b show all the possible migration jumps between adjacent M sites when centred on M1 and M2 respectively. There are six M1-M2 jumps, two M1-M1 paths and three M2-M2 paths making eleven unique jumps between adjacent M sites in total. Due to cation site sharing, only a selection of these jumps will be available for lithium migration in a specific region of local cation site order. The focus here was not to carry out an exhaustive study of cation order effects on lithium diffusion, rather to select a representative collection of ordering schemes which allow the full range of possible Li migration jumps to be examined. Four different ordering schemes were considered, which collectively cover the full range of Li jumps, and are shown in Figure 5.5. All four structures show good agreement with the experimentally observed crystal structure with full details provided in Appendix table E.1.

Migration distances change depending on the local cation ordering; the experimental jump distances taken from x-ray diffraction are a weighted average of Fe, Mn and Li occupancy of the M sites, because they represent the ensemble average. For examination of the energetics of lithium migration, the ordering scheme which gave the closest match to the experimental jump distance, and is therefore most representative of the ensemble average, was chosen for each jump examined.

Each migration path was mapped via a series of individual Mott-Littleton type defect calculations, where the migrating Li ion is moved between two vacant Li sites. Each individual calculation represents an increment of the Li along along the path; 20 steps were used for each path. Relaxation of the surrounding lattice (> 640 ions) is treated explicitly by this defect modelling method. Table 5.4 provides the activation energies of migration ($E_{mig}$) for all 11 possible Li pathways. The energy of activation represents the difference in energy between the peak of the energy profile and its lowest point. The energy profiles for the four most energetically favourable pathways are provided in Appendix Figure E.1.
Figure 5.4: Possible migration jumps in $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{SO}_4\text{F}$: (a) all nearest-neighbour $M-M$ hops from an M1 site in $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{SO}_4\text{F}$ (b) all the nearest neighbour $M-M$ hops from an M2 site. M1 sites are in green, M2 sites are in blue and Li, Fe and Mn octahedra have been omitted for clarity.
Figure 5.5: Four ordering schemes used for lithium migration calculations: (a) is ordering scheme 1, which has the lowest lattice energy of the four, and was used for intrinsic defect calculations; (b), (c) and (d) differ from (a) by exchange of Li ions with Mn and Fe ions. Collectively these four ordering schemes enable calculation of the full range of nearest neighbour jumps shown in Figure 5.4. A comparison of the calculated vs experimental lattice parameters for all of these ordering schemes is provided in table E.1.
Table 5.4: Calculated migration energies and jump distances of possible paths in LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F.

<table>
<thead>
<tr>
<th>configuration</th>
<th>Li pathway $^a$</th>
<th>$E_a$ / eV</th>
<th>dist calc. / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M1(a) - M2(d)</td>
<td>0.95</td>
<td>3.80</td>
</tr>
<tr>
<td></td>
<td>M1(a) - M2(f)</td>
<td>0.24</td>
<td>4.13</td>
</tr>
<tr>
<td>2</td>
<td>M1(a) - M2(c)</td>
<td>1.83</td>
<td>4.92</td>
</tr>
<tr>
<td></td>
<td>M1(a) - M2(e)</td>
<td>0.42</td>
<td>3.31</td>
</tr>
<tr>
<td>3</td>
<td>M1(a) - M1(b)</td>
<td>0.42</td>
<td>3.04</td>
</tr>
<tr>
<td></td>
<td>M1(a) - M1(c)</td>
<td>0.45</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td>M2(a) - M2(d)</td>
<td>1.39</td>
<td>4.53</td>
</tr>
<tr>
<td></td>
<td>M1(a) - M2(b)</td>
<td>1.12</td>
<td>3.84</td>
</tr>
<tr>
<td>4</td>
<td>M2(a) - M2(b)</td>
<td>0.75</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>M2(a) - M2(c)</td>
<td>1.15</td>
<td>4.02</td>
</tr>
<tr>
<td></td>
<td>M1(a) - M2(a)</td>
<td>1.08</td>
<td>3.29</td>
</tr>
</tbody>
</table>

$^a$ Shown in Figure 5.4

The energy profiles (shown in Appendix Figure E.1) reveal that most of the pathways are asymmetric because there is a difference in lithium site energies at one end of the path to the other. The activation energies quoted in table 5.4 represent the highest barrier, because for net diffusion out of the bulk this barrier will need to be overcome. It is noted that the quoted $E_{\text{mig}}$ values represent the direct linear path between two lithium sites and should be treated as an upper limit. Previous work in phosphate materials has shown that the most favourable pathway is not necessarily linear [24], and migration energies can be reduced by allowing the lithium to relax onto a curved trajectory.

The results reveal a number of key points. First, there is one especially low energy pathway (M1(a) - M2(f)) with a migration energy of 0.24 eV and three other relatively low energy paths, M1(a) - M2(d), M1(a) - M1(b) and M1A - M1(c) with migration energies of 0.42 - 0.45 eV. Such low values are comparable to those found in LiCoO$_2$ [118, 133–135] and LiFeSO$_4$F [111] cathode materials, indicating high lithium mobility in this triplite material. The remaining pathways are relatively unfavourable (> 0.75 eV).

Second, as seen in the related tavorite-type LiFeSO$_4$F material, long-range migration requires a combination of at least two jumps. Figure 5.6 shows the net diffusion which is possible in this material if all of these pathways are available throughout the entirety of the structure. It is clear that combinations of these individual pathways make up a 3D network for long range diffusion. This is consistent with a recent DFT study[143] where a 3D lithium transport network is also found, although this study neglected cation ordering effects, focusing on just one specific ordering scheme.

Finally, differences in local cation ordering results in some pathways being blocked by the Fe and Mn ions, leaving only a selection of the four low energy paths available. In
Figure 5.6: Schematic illustrating the 3D-network of low energy (≤ 0.45 eV) lithium migration pathways in triplite LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F (highlighted as thick black lines). Two orientations are shown: (a) along the [010] direction; and (b) along [100]. This figure as well as all other figures containing crystal structures was produced using the Visualisation for Electronic and STructural Analysis (VESTA) program [144].
terms of the Li\(^+\) transport mechanism LiFe\(_{0.5}\)Mn\(_{0.5}\)SO\(_4\)F is therefore likely to behave similarly to Li\(_2\)FeSiO\(_4\), where net migration occurs via a series of changes in direction [40, 142]. For this reason the triplites are likely to show poorer rate capability than the related favorite materials, despite their comparable migration barriers. Local ordering also affects the lithium site energies and migration distances, which will alter the migration barriers. We stress that our calculated migration barriers are obtained from a small selection of four specific configurations, and thus do not represent the full ensemble average. We fully expect these barriers to vary with changes in local cation order, which warrants future MD simulations.

### 5.2.4 Fe and Mn Anti-Site Migration

**Table 5.5:** Energies of Fe\(^+\) and Mn\(^{2+}\) migration along the four favourable lithium migration pathways in LiFe\(_{0.5}\)Mn\(_{0.5}\)SO\(_4\)F

<table>
<thead>
<tr>
<th>Configuration</th>
<th>pathway (^a)</th>
<th>ion</th>
<th>(E_a)/ eV</th>
<th>dist calc. / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M1(a) - M2(f)</td>
<td>Fe</td>
<td>1.51</td>
<td>4.13</td>
</tr>
<tr>
<td>2</td>
<td>M1(a) - M2(e)</td>
<td>Fe</td>
<td>2.17</td>
<td>3.31</td>
</tr>
<tr>
<td>3</td>
<td>M1(a) - M1(b)</td>
<td>Fe</td>
<td>1.93</td>
<td>3.04</td>
</tr>
<tr>
<td>3</td>
<td>M1(a) - M1(c)</td>
<td>Fe</td>
<td>1.64</td>
<td>3.05</td>
</tr>
<tr>
<td>1</td>
<td>M1(a) - M2(f)</td>
<td>Mn</td>
<td>1.09</td>
<td>4.13</td>
</tr>
<tr>
<td>2</td>
<td>M1(a) - M2(e)</td>
<td>Mn</td>
<td>1.53</td>
<td>3.31</td>
</tr>
<tr>
<td>3</td>
<td>M1(a) - M1(b)</td>
<td>Mn</td>
<td>1.27</td>
<td>3.04</td>
</tr>
<tr>
<td>3</td>
<td>M1(a) - M1(c)</td>
<td>Mn</td>
<td>0.98</td>
<td>3.05</td>
</tr>
</tbody>
</table>

\(^a\) Shown in Figure 5.4

Our defect calculations suggest that Li/Fe or Li/Mn cation exchange defects are intrinsic to LiFe\(_{0.5}\)Mn\(_{0.5}\)SO\(_4\)F, which is expected as Li and \(M\) ions share the same crystallographic sites. From our lithium migration calculations it is clear that regions of local order can have a large impact on lithium mobility. Different local ordering schemes result in blocking of favourable lithium migration pathways by \(M\) ions. It is therefore important to investigate the energetics of Fe and Mn mobility, to find out if these blocking transition metal ions can migrate away into nearby vacant lithium sites.

The process of anti-site migration is shown schematically in Figure 3.7. It involves the exchange of an anti-site cation \(M'_{\text{Li}}\) with a lithium vacancy; the lithium vacancy would then continue to migrate along one of the four favourable pathways, this time exchanging with lithium ions. It is important to note that this process is different to standard transition metal migration which would involve the exchange of a transition metal cation (\(M\)) with a transition metal vacancy (\(V''_{M}\)). Formation of transition metal vacancies were found to be highly unfavourable in our intrinsic defect calculations and are therefore highly unlikely to exist in the material.
We have investigated anti-site migration of Fe and Mn along the four lowest energy pathways found from our lithium migration calculations. We followed a similar simulation procedure to that used for lithium migration. Again, the $E_{mig}$ values, represent direct linear motion between the sites, and should therefore be treated as an upper limit.

All the calculated anti-site migration energies in table 5.5 are about 1.0 eV or higher and at least 0.5 eV greater than the corresponding lithium migration values. This suggests that Fe and Mn will show far slower diffusion than Li, and that regions where Fe or Mn ions block favourable pathways, will impede long-range Li diffusion out of the bulk.

5.3 Chapter Summary

This investigation has provided atomic scale insight into the complex Li diffusion pathways and defect chemistry exhibited by triplite-structured LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F, a recently discovered cathode material. In general, the triplite structure shows an added level of complexity over the related tavorite structure due to full site sharing (of Li, Fe and Mn) across the $M$ sites. The main results of our extensive defect and migration calculations are summarised below:

(1) Our potential model has successfully reproduced this complex crystal structure for four different ordering schemes. Li/Mn and Li/Fe cation exchange defects have the lowest energy, which is expected because the triplite structure shows full sharing of the cation sites between Li, Fe and Mn ions. F Frenkel and Li Frenkel energies are low in comparison to the related LiFeSO$_4$F tavorite structured material, and the presence of Li interstitials could enhance Li diffusion by reducing the Li migration distances.

(2) Due to site sharing of M1 and M2 sites by Li, Mn and Fe, Li diffusion is very complex. We find relatively low migration energies ($\leq$ 0.5 eV) comparable to tavorite structured LiFeSO$_4$F and the LiCoO$_2$ layered oxide, indicating high Li mobility in the material. The combination of the four lowest energy lithium hops form a long-range 3D network of migration pathways. However, we find that local cation ordering is likely to result in some of the favourable pathways being blocked, which will have a large impact on lithium diffusion.

(3) Finally, Fe and Mn anti-site migration energies are found to be much higher than the corresponding Li migration energies. This suggests that any Fe or Mn ions which block favourable Li diffusion pathways will impede lithium diffusion.

In contrast to the related tavorite-structured LiFeSO$_4$F material, cation ordering effects in triplite LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F prevent the formation of long-range open channels for fast lithium diffusion. Instead, lithium diffusion occurs via a series of changes in
direction, resulting from Mn and Fe ions blocking favourable migration pathways. This will lower the rate at which lithium ions can be extracted from the material, and helps to rationalise the lower rate capability found in triplite-structured cathodes compared to their tavorite-structured analogues.
Chapter 6

Conclusions and Future Work

6.1 General Remarks

This thesis has detailed the computational modelling studies of three types of polyanion cathode material for use in lithium ion batteries. By examining their atomic-scale properties, we have attempted to provide further insight into fundamental defect and ion transport properties, which cannot be readily investigated by experiment. Furthermore, we have endeavoured to advance the materials science of lithium ion batteries by making our simulation work predictive. It is appropriate to conclude this thesis by reviewing our findings and detailing possible extensions to each study.

6.2 Anti-Site Defects and Ion Migration in the LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ Mixed-Metal Cathode Material

In chapter 3 we investigated the defect and ion transport properties of olivine-structured LiFe$_{0.5}$Mn$_{0.5}$PO$_4$. The most favourable intrinsic defect was found to be the anti-site defect, for which a small population of Li$^+$ and Fe$^{2+}$ or Mn$^{2+}$ are expected to exchange sites.

As in LiFePO$_4$, lithium ion diffusion in LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ follows a non-linear, curved path down the [010] channel; the migration energy (0.59 eV) agrees with experimental data, and is an intermediate between the two end members (LiFePO$_4$ and LiMnPO$_4$).

The energetics of binding between Li vacancies and/or antisite cations were also examined. The binding energies indicate clustering of defects (rather than a random distribution), which has implications for lithium conductivity as $M^{2+}$ cations on Li
sites could lead to trapping of the migrating Li vacancies. Furthermore, the binding energies per defect pair remain relatively constant with increasing cluster size, suggesting these defects could aggregate in the material forming larger clusters. Significant binding energies ($\leq -0.6$ eV) are found for neutral one-dimensional clusters which run along the b-axis channel, comprised of anti-site defects ($\text{Fe}^\ast_\text{Li}$ or $\text{Mn}^\ast_\text{Li}$) and Li vacancies; by limiting the distribution of anti-site defects to a small percentage of these b-axis channels, their impact on lithium mobility could be reduced.

Finally, the high migration energies associated with anti-site cation diffusion, suggest that even a small concentration of anti-site defects in this mixed-metal system would reduce lithium insertion/extraction rates.

**Future work:** In order to extend this study there are several areas of future work which could be explored. Previous work on LiFePO$_4$ [145] showed that the [010] surface had one of the lowest energies, which is of particular interest as this surface is orthogonal to the favourable lithium diffusion direction. The substitution of Fe ions with Mn ions forming solid solutions (LiFe$_{1-y}$Mn$_y$PO$_4$) could alter these surface energies, particularly in the highly charged state where Jahn-Teller active Mn$^{3+}$ ions are likely to cause structural distortions. Therefore, a full study of the surfaces and crystal morphologies of these mixed-metal phases could be valuable.

There is still much debate over the exact Li diffusion mechanism in these olivine material, with both experimental and theoretical results showing conflicting 1D and 2D mechanisms. It would be interesting to carry out MD simulations to examine such diffusion. Of particular interest, would be simulations containing a small concentration of anti-site defects, to see if this promotes any two dimensional Li motion to navigate around these blocked channels.

### 6.3 Alkali-ion Conduction Paths in Tavorite-Type AFeSO$_4$F ($A = \text{Li, Na}$) Cathode Materials

In chapter 4 the structure, intrinsic defect chemistry and alkali-ion conduction paths in LiFeSO$_4$F and NaFeSO$_4$F has been examined. We found that Li ions in both Li1 and Li2 crystallographic sites relax to symmetry equivalent sites, after structure optimisation; this result is confirmed by analysis of local inter-ionic distances from energy minimisation calculations as well as comparisons of radial distribution functions from MD simulations, and suggests that there is just one crystallographic site for lithium in LiFeSO$_4$F.

Intrinsic defect calculations suggest that the formation of all Schottky and Frenkel defects is unfavourable. The Li/Fe and Na/Fe anti-site energies also suggest that there would be no significant intrinsic concentration of Fe on Li or Na sites at operating temperatures in these fluorosulphates. This is in contrast with the LiFePO$_4$
cathode material which has a small amount of Fe on Li sites.

Investigation of the transport paths in LiFeSO$_4$F indicates relatively low migration energies ($\sim 0.4$ eV), suggesting high Li mobility, which is important for good rate capability and capacity retention. We found that Li migration occurs via a combination of diagonal jumps which form continuous diffusion pathways in the open tavorite structure. Direct linear migration along the channels was found to be highly unfavourable, which is likely due to lithium ions coming within close proximity of FeO$_4$F$_2$ octahedra. Li$^+$ transport is found to be quasi three-dimensional with the lowest energy path (0.36 eV) along the [111] direction. Migration along other directions which form connections between the [111] pathways are also low in energy ($\sim 0.4$ eV), giving rise to a 3D network of favourable Li migration pathways. This is confirmed by molecular dynamics simulations, which show dominant Li pathways running along the [111] direction, although there is clear migration between these channels providing a 3D network of favourable pathways. In terms of rate capability in cathodes, such 3D behaviour is an advantage over lower dimensional transport in other materials e.g. 1D Li$^+$ pathways in LiFePO$_4$ [24, 25].

Na-ion transport in monoclinic NaFeSO$_4$F is also mediated by a combination of zigzag jumps, but with higher activation energies (0.6 - 0.9 eV), than those for Li-ion migration in LiFeSO$_4$F. The estimated diffusion coefficient for the most favourable migration path along the [101] direction is at least six orders of magnitude higher than that in any other direction, suggesting that NaFeSO$_4$F is a one-dimensional Na-ion conductor.

Such differences in intrinsic alkali-ion mobility helps to rationalise the superior cycling performance of LiFeSO$_4$F compared with NaFeSO$_4$F.

**Future Work:** Here we have presented an extensive study of Li-ion and Na-ion mobility in the bulk structures of LiFeSO$_4$F and NaFeSO$_4$F. However, there is always added complexity at surfaces, where many properties such as voltages and conductivity differ from the bulk. It would therefore be interesting to extend this work by investigating the surface chemistry and crystal morphologies of these materials.

As noted, in previous surface studies of LiFePO$_4$ [25] it was found that the [010] surface, which is perpendicular to the favourable Li diffusion direction in this material, was lowest in energy. Here we have several low energy diffusion directions, and the surfaces which run perpendicular to all of these pathways warrant investigation. Although diffusion through the bulk has been shown to be quasi-3D, differences in surface energies could make the insertion/extraction of Li ions less isotropic. Such investigations could prove even more valuable in NaFeSO$_4$F where Na diffusion appears limited to 1D channels. Synthesis of crystal morphologies which maximise the surfaces perpendicular to these channels, combined with nano-scaling, could improve the ionic conductivity in this material dramatically.
6.4 Intrinsic Defects and Lithium Diffusion in Triplite Structured LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F

In chapter 5 the Li diffusion pathways and defect chemistry in LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F, which exhibits a complex triplite structure, were examined. In general, the triplite structure shows an added level of complexity over the related tavorite structure due to full site sharing (of Li, Fe and Mn) across the cation ($M$) sites.

Defect energy calculations reveal that Li/Mn and Li/Fe cation-exchange defects have the lowest energy, which may be expected because the triplite structure shows full cation site sharing. F Frenkel and Li Frenkel energies are low in comparison to the related LiFeSO$_4$F tavorite structured material, and the presence of Li interstitials could enhance Li diffusion by reducing the Li migration distances.

We find low migration energies (\(\leq 0.45\) eV) which are comparable to those found in tavorite structured LiFeSO$_4$F [111] and the LiCoO$_2$ layered oxide [111, 118, 133–135], and indicate high Li mobility in the material. The combination of the four lowest energy lithium hops form a 3D network of favourable migration pathways. However, local cation ordering effects act to block these pathways, thus preventing coherent long-range diffusion. Li diffusion instead occurs via a series of changes in direction, which will result in slower insertion/extraction rates.

Finally, Fe and Mn migration energies are found to be much higher than the corresponding Li migration energies. This suggests that any Fe or Mn ions which block favourable diffusion pathways will impede lithium diffusion.

Such effects on lithium diffusion caused by local cation ordering help to rationalise the lower observed rate capability of triplite-structured fluorosulphates compared to their tavorite-structured analogues.

**Future Work:** Due to the vast number of possible configurations (> 178,000) of Fe, Mn and Li ordering across the $M$ sites, even within our relatively small simulation cell (64 ions), full investigation of all configurations is impractical. However, it would be interesting to explore the effects of disorder on defect and migration properties further.

In this study we fitted our model to one particular ordering scheme, however experimentally the cation ordering is found to be random. Our calculated lattice parameters and energies for the other three configurations that we investigated are therefore biased by the potential fitting. A possible improvement would be to relax several ordering schemes using DFT, and then fit a potential model to all of these structures simultaneously.

Here, we calculated the intrinsic defect energies from just one ordering scheme (configuration 1) which had the lowest lattice energy. The migration barriers were calculated from a small collection of possible ordering schemes; the ordering scheme
which gave the closest $M$-site to $M$-site distance to the ensemble average was used in all cases. With more time it would be interesting to calculate the full range of defect and migration energies for a larger selection of ordering schemes. This would allow us to calculate the average $M$-site to $M$-site distance and $E_{mig}$ values for each pathway, which would be more representative of the ensemble average.

Finally it would also be interesting to carry out an extensive MD study to visualise the lithium migration mechanisms. We could examine several different ordering schemes, to see how the lithium migration is affected by cation ordering. It has been suggested that certain cation ordering schemes could greatly facilitate lithium transport [46]; from MD simulations we could find out if any cation rearrangement occurs to this end, particularly at higher temperatures.
References


References


Appendix A

Glossary of battery terms

**Anode:** Electrode where oxidation takes place during the electrochemical reaction.

**Capacity:** The charge stored per unit mass (specific capacity) or volume (volumetric capacity) of the electrode material, expressed in terms of mAh g\(^{-1}\) or Ah l\(^{-1}\) respectively. In a lithium cell the charge stored is equivalent to the amount of lithium which can be stored \([4, 6]\).

**Cathode:** Electrode where reduction takes place during the electrochemical reaction.

**C-rate:** Also known as the hourly rate, is the charge or discharge rate in amperes, equal to the capacity of the battery divided by 1 hour. For example 1C for a 2000 mAh battery would be 2 A, and C/20 for the same battery would be 100 mA.

**Current density:** The current which flows per unit electrode area.

**Electrode potential:** An electrode process often involves the transfer of charge across a metallic electrode/solution interface as shown in equation A.1:

\[
A_{(aq)} + e_{(m)}^- \rightleftharpoons A^-_{(aq)},
\]

where A is an ion. The chemical reaction involves electron transfer between the metallic electrode material and the solution phase, as this electron transfer reaction reaches equilibrium a net charge separation develops between the electrode and solution. This charge separation causes a potential difference at the electrode/solution interface. It is impossible to measure this potential directly and so experimentally potentials are measured with reference to the standard hydrogen electrode, which by convention is defined as having an electrode potential of zero \([146]\).

**Energy density:** The energy which can be stored per unit weight (gravimetric energy density) or volume (volumetric energy density) expressed in terms of
Whkg\(^{-1}\) or Whl\(^{-1}\) respectively, given by equation A.2:

\[
E = V_e Q, \quad (A.2)
\]

where \(E\) is the volumetric or gravimetric energy density, \(V_e\) is the electrode potential and \(Q\) is the capacity [6].

**Open Circuit Voltage:** The difference in potential of the two electrodes in the cell [4]; equivalent to the difference in fermi-level of the two electrodes, but only when they are connected in an electrochemical cell. Not the fermi-levels of the isolated electrodes [6].
Appendix B

Additional methodology

B.1 Mapping migration points onto the migration coordinate

When investigating an ion migration mechanism, it is useful to have a scalar measure how far the migrating ion has progressed. For linear migration the migration progress $\delta$ can be determined by simply dividing the displacement of the ion along the migration path $l$ by the length of the path $|a|$: 

$$\delta = \frac{l}{|a|}, \quad (B.1)$$

where $a$ is the vector between the two end points, and $l$ is the displacement along that vector. In the complex structures presented in this thesis the pathways are usually curved, which makes determining the migration progress less trivial.

The simplest way is to define a linear migration coordinate, which is a vector $a$ defined by the initial and final positions of the migrating ion ($Li(1)$ and $Li(2)$ respectively). The current location of the migrating ion is then projected onto the migration coordinate as shown schematically in figure B.1. A vector $b$ is defined by the initial position of the migrating ion $Li(1)$ and its current position $x$. We would like to find the projected point $x_p$, which is the point along $a$ from which a perpendicular line can be draw to reach $x$, and the corresponding displacement $l$ along $a$.

The angle $\alpha$ between the two vectors $a$ and $b$ can be found using the dot product:

$$\cos \alpha = \frac{a \cdot b}{|a||b|}, \quad (B.2)$$
and because $\text{Li}_1$, $\mathbf{x}$ and $\mathbf{x}_p$ form a right angled triangle,

$$l = |\mathbf{b}| \cos \alpha \quad (B.3)$$

$$= \frac{\mathbf{a} \cdot \mathbf{b}}{|\mathbf{a}|}. \quad (B.4)$$

The perpendicular deviation of the migrating ion from the linear path $d$ can also be determined using:

$$d = |\mathbf{b}| \sin \alpha. \quad (B.5)$$

This technique useful for creating energy profiles, which provide a direct comparison of the energetics of curved migration with linear. It also provides a means to determine how far the curved trajectory deviates from linear.

A particularly useful application of this methodology is during post analysis of constrained minimisation calculations. In a GULP calculation there are three possible constraint directions, $x,y$ and $z$ corresponding to the cartesian axes. Setting a constraint (in the $x$ direction for example) by using the command,

```
fix x
```

will prevent any motion of the migrating ion in the $x$ direction, but allow it to move anywhere in the $zy$ plane.

A problem arises when the migration pathway does not run parallel to one of the cartesian axes; this is shown in a 2D schematic in Figure B.2. By constraining the migrating ion in the $x$ direction, it relaxes from its initial point resting on the linear path $\mathbf{x}_i$ to its final point on the curved path $\mathbf{x}_f$. However, in doing so it has moved along the migration coordinate $\mathbf{a}$; that is, the projected point $\mathbf{x}_p$ from relaxed position $\mathbf{x}_i$ is further along $\mathbf{a}$ than the initial position $\mathbf{x}_i$. Direct comparison of the energetics at position $\mathbf{x}_i$ and $\mathbf{x}_f$ would therefore be meaningless, so the methodology, described above, is used to map relaxed positions back to the linear path for direct comparison of the energetics.
Figure B.2: A 2D schematic of constrained minimisation. The favoured migration pathway is shown in blue, the migration coordinate $\mathbf{a}$ is a vector between the start and end points of migration ($\mathbf{Li}_1$ and $\mathbf{Li}_2$ respectively). $x_i$ is the initial position of the migrating ion, $x_f$ is its relaxed position and $x_p$ is the projection of $x_f$ onto $\mathbf{a}$. 
Appendix C

LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ supplementary material

C.1 Convergence tests of defect energy with region size

Please note the region two size is double the region one size in all cases.

The defect energies have converged well by a region one size of 12 Å.
Defect energy convergence with region size
for a manganese vacancy

Defect energy convergence with region size
for an oxygen vacancy

Defect energy convergence with region size
for a phosphorus vacancy

Defect energy convergence with region size
for an iron interstitial

Defect energy convergence with region size
for a lithium interstitial

Defect energy convergence with region size
for a manganese interstitial
Defect energy convergence with region size for an oxygen interstitial.
Appendix D

Tavorite LiFeSO$_4$F and NaFeSO$_4$F supplementary material

D.1 Convergence tests of defect energy with region size

The defect energies have converged well by a region one size of 12 Å.

D.2 Local lithium environment analysis

Table D.1 shows that after energy minimisation the Li1 and Li2 ions relax to identical local environments, suggesting that there is just one lithium site in LiFeSO$_4$F.

D.3 RDF plots for lithium environments in tavorite-structured LiFeSO$_4$F

All Li1-based RDF plots appear identical to their Li2 analogues, suggesting that Li1 and Li2 relax into the same environment. There is therefore only one lithium site in LiFeSO$_4$F.

D.4 Defect calculations

Table D.2 lists the isolated point defect energies for LiFeSO$_4$F with region sizes of 12 Å and 24 Å for region one and two respectively.
<table>
<thead>
<tr>
<th>Region one size (Å)</th>
<th>Defect energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defect energy convergence with region size for a lithium vacancy</td>
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</tr>
<tr>
<td>6</td>
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<tr>
<td>8</td>
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</tr>
<tr>
<td>12</td>
<td>7.5</td>
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<tr>
<td>14</td>
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<tr>
<td>16</td>
<td>7.6</td>
</tr>
<tr>
<td>18</td>
<td>7.65</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Region one size (Å)</th>
<th>Defect energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td>8</td>
<td>23</td>
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<td>10</td>
<td>23.2</td>
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<td>23.8</td>
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<table>
<thead>
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</thead>
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<td>8</td>
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<td>-15.2</td>
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<tr>
<td>12</td>
<td>-15</td>
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<tr>
<td>14</td>
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<td>-14.4</td>
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<table>
<thead>
<tr>
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<th>Defect energy (eV)</th>
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<tr>
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<table>
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<tr>
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<th>Defect energy (eV)</th>
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<tr>
<td>12</td>
<td>-2.5</td>
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<tr>
<td>14</td>
<td>-2.45</td>
</tr>
<tr>
<td>16</td>
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</tr>
<tr>
<td>18</td>
<td>-2.35</td>
</tr>
<tr>
<td>ion pair</td>
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<td>--------</td>
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<tr>
<td>Li\textsubscript{a}-O1</td>
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<td>Li\textsubscript{b}-F</td>
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\textsuperscript{a} reference [rajesh expt data - FIND REF]
Table D.2: Isolated point defect energies for LiFeSO₄F

<table>
<thead>
<tr>
<th>Defect</th>
<th>$E$/eV</th>
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<tbody>
<tr>
<td>$V'_{Li}$</td>
<td>7.37</td>
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<tr>
<td>$V''_{Fe}$</td>
<td>22.87</td>
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<tr>
<td>$V'_{F}$</td>
<td>7.52</td>
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<tr>
<td>$Li^+_i$</td>
<td>-3.58</td>
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<tr>
<td>$Fe^+_i$</td>
<td>-15.26</td>
</tr>
<tr>
<td>$F'^+_i$</td>
<td>-2.69</td>
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</table>
Appendix E

Triplite LiFe$_{0.5}$Mn$_{0.5}$SO$_{4}$F
supplementary material

E.1 Convergence tests for defect energy with
region size

The convergence of the defect energy with region size isn’t as well defined for this
triplite structured LiFe$_{0.5}$Mn$_{0.5}$SO$_{4}$F material as with the two other materials in-
vestigated in this thesis. The calculated values of the defect energies will therefore
have larger error bars associated with them. However, the trends will still be cor-
rect.
Defect energy convergence with region size for a lithium interstitial

Defect energy convergence with region size for a manganese interstitial

Defect energy convergence with region size for a fluorine vacancy

Defect energy convergence with region size for an iron vacancy

Defect energy convergence with region size for a lithium vacancy

Defect energy convergence with region size for a manganese vacancy
E.2 Structure comparison of four triplite ordering schemes

Table E.1 shows that the four ordering schemes used for lithium migration calculations provide reasonable reproduction of the experimental lattice parameters of this complex triplite structure.

E.3 Defect calculations

Table E.2 lists the isolated point defect energies for LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F with region sizes of 12 Å and 24 Å for region one and two respectively.

E.4 Li migration energy profiles

Figure E.1 shows the migration profiles of the four lowest energy lithium migration paths in LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F. The plots are asymmetric because there are differences in the lithium site energies; also, Figure E.1a shows an interstitial position which has a lower energy than either of the two lithium sites. However, this only occurs when there are two neighbouring Li vacancies; if one of the lithium sites is occupied the interstitial Li returns to its lattice site.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>config 1</th>
<th>config 2</th>
<th>config 3</th>
<th>config 4</th>
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<th>Δ 1 / %</th>
<th>Δ 2 / %</th>
<th>Δ 3 / %</th>
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<tbody>
<tr>
<td>a / Å</td>
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<td>13.0955</td>
<td>13.0910</td>
<td>13.1960</td>
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<tr>
<td>b / Å</td>
<td>6.4147</td>
<td>6.4458</td>
<td>6.4611</td>
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<td>6.4005</td>
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<tr>
<td>c / Å</td>
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<td>9.9394</td>
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<td>89.434</td>
<td>90.738</td>
<td>90.0000</td>
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<tr>
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<tr>
<td>γ / °</td>
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<td>90.408</td>
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<td>0.45</td>
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<tr>
<td>U_{latt} / eV</td>
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<td>−481.7586</td>
<td>−482.0739</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>
Table E.2: Isolated point defect energies for LiFe$_{0.5}$Mn$_{0.5}$SO$_4$F

<table>
<thead>
<tr>
<th>Defect</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{Li}'$</td>
<td>7.30</td>
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<tr>
<td>$V_{Fe}''$</td>
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<td>$Fe_i^-$</td>
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<tr>
<td>$Mn_i^-$</td>
<td>-15.26</td>
</tr>
<tr>
<td>$F_i'$</td>
<td>-3.99</td>
</tr>
</tbody>
</table>

Figure E.1: Lithium migration energy profiles for the four lowest energy pathways: (a) M1(a) - M2(f); (b) M1(a) - M2(e); (c) M1(a) - M1(b); (d) M1(a) - M1(c). Due to structural complexity we find a few anomalous points, but the lines, which are a guide for the eye, show the lowest energy path.
Appendix F

Published paper *Chem. Mater.* 2010

“Anti-Site Defects and Ion Migration in the \( \text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4 \) Mixed-Metal Cathode Material”
Appendix G

Published paper Chem. Mater. 2011

“Alkali-ion Conduction Paths in LiFeSO$_4$F and NaFeSO$_4$F Tavorite-Type Cathode Materials”