

The Redox Chemistry of Oxygen in Cathode Materials for Rechargeable Alkali-ion Batteries

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*A thesis submitted for the degree of
Doctor of Philosophy*

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Abstract

There is a clear and urgent need for rechargeable batteries of higher energy density. Alkali-ion batteries based on Li-ions are the state-of-the-art, although Na-ion may offer a cheaper alternative. In both cases the cathode imposes the biggest limitation on overall energy density.

Alkali-rich cathode materials can store alkali-ions and electrons densely by invoking redox chemistry of both the transition metal (TM) and oxide ions in the lattice. However, O-redox is accompanied by voltage hysteresis, irreversible O-loss and complex structural changes. In this thesis, model Na-ion materials have been investigated to isolate and examine these phenomena.

Firstly, $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, with Mg^{2+} ions occupying the TM layer rather than alkali-ions, is studied and shown to exhibit O-redox. This reveals that ionic interactions between the TM layer substituent and O are the necessary precondition for O-redox.

Secondly, by comparing the O-loss behaviours of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, the critical role of the TM layer substituent is revealed; when removed from the structure, the co-ordination number around O can drop below three and O-loss is triggered. Unlike Li^+ , Mg^{2+} is retained within the structure preventing O-loss.

Thirdly, O-redox materials $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ are studied in parallel to understand why the former exhibits voltage hysteresis and the latter not. The preservation of the TM layer ordering scheme is shown to prevent hysteresis maintaining stable electron holes on O^{2-} in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. For $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, severe in-plane TM migration destroys the ordering scheme, triggered by formation of molecular O_2 gas which is directly evidenced for the first time in the bulk. Reduction of O_2 occurs on discharge at low voltage giving rise to hysteresis.

Finally, a new Li-rich oxyfluoride, $\text{Li}_2\text{MnO}_2\text{F}$, with a stable disordered rocksalt structure is presented. $\text{Li}_2\text{MnO}_2\text{F}$ stores charge utilising both Mn and O-redox with negligible O-loss demonstrating the potential of disordered rocksalts to deliver high energy densities.

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1. House, R. A. *et al.* Superstructure controls first cycle voltage hysteresis in O-redox cathodes for alkali-ion batteries. *Nature* 577, 502-508 (2020).
2. House, R. A. *et al.* What Triggers Oxygen Loss in Oxygen Redox Cathode Materials? *Chemistry of Materials* 31, 3293–3300 (2019).
3. Somerville, J. W. *et al.* Nature of the “Z”-phase in layered Na-ion battery cathodes. *Energy & Environmental Science* 12, 2223–2232 (2019).
4. Somerville, J. W. *et al.* Identification and characterisation of high energy density P2-type $\text{Na}_{2/3}[\text{Ni}_{1/3-y/2}\text{Mn}_{2/3-y/2}\text{Fe}_y]\text{O}_2$ compounds for Na-ion batteries. *Journal of Materials Chemistry A* 6, 5271–5275 (2018).
5. House, R. A. *et al.* Lithium manganese oxyfluoride as a new cathode material exhibiting oxygen redox. *Energy & Environmental Science* 11, 926–932 (2018).
6. Maitra, U., House, R. A. *et al.* Oxygen redox chemistry without excess alkali-metal ions in $\text{Na}_{2/3}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. *Nature Chemistry* 10, 288–295 (2018).

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Introduction

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1.1 Wider Context

Rechargeable batteries have become an integral part of modern life. By providing compact, portable, electric power on demand they have ushered in an electronics revolution enabling the use of devices such as laptops, smartphones, and tablets which many now cannot live without. The sustained demand for longer life, higher power, and ever more compact devices has driven intense research into rechargeable batteries which can store energy more densely and at a lower cost. Above and beyond this, as we sit on the cusp of new revolutions in renewable power and electric transportation, there is growing realisation that high specification batteries will be essential to drive growth in these industries.

Lithium-ion technology has emerged as the key player in each of these industries.^{1,2} In its simplest form, this technology is based on a controlled, reversible chemical reaction in which Li-ions and electrons shuttle back and forth between two host materials to store and release electrical energy. Early research identified graphitic carbon and layered LiCoO_2 as two highly suitable candidates for this purpose and since then only a handful of chemical substitutions to these compositions have been found which can improve upon them.^{3,4} After much optimisation of the manufacturing and engineering processes associated with incorporating these materials into a functional battery these materials are now becoming fully exploited and there is mounting pressure for completely new materials and chemistries to deliver the next-generation performance that is so fiercely demanded.

One of the greatest opportunities towards the development of cheaper, more energy dense batteries lies in the cathode whose performance lags significantly behind that of the anode.^{5,6} This material often takes the form of a layered lithium transition metal oxide (TMO) with alternating layers of Li and TM separated by oxide ions, although other crystal structures such as olivine LiFePO_4 and spinel LiMn_2O_4 have also found applications in batteries with less of a requirement for top specification energy density. Typically the best performing layered TMOs contain cobalt or nickel as the principal TM element, each of which suffer from a number of different issues including unethical sourcing practices, limited global

distribution, toxicity and cost.² Finding suitable alternative elements to replace these is a challenge. One promising candidate is manganese, which is significantly cheaper, more earth abundant and does not pose a toxicity risk.^{7,8} Mn is the principal TM component of all the materials studied in this thesis.

The push towards Li-ion batteries with higher energy density has led researchers towards so-called *Li-rich* or *Li-excess* cathode materials, in which Li is substituted for TMs in the TM layer increasing the Li:TM ratio from 1:1.^{9–12} The guiding principle here is that, in order to store energy more densely, cathode compounds need to be able to store and exchange more Li per unit mass or volume. However, this strategy necessarily decreases the amount of TM available to store and release the electrons that shuttle alongside the Li between the electrodes, a chemical process known as *reduction* and *oxidation* respectively, or *redox* collectively. Somewhat unexpectedly, Li-rich materials can in fact store many more electrons than can be accommodated solely by the TMs present prompting the discovery of a new mode of charge storage which invokes the active participation of lattice oxide ions.^{13–16} This is referred to in this thesis as oxygen redox or O-redox.

O-redox has generated an intense amount of interest from industry as it offers one of very few routes available to significantly improve the energy density of the cathode and potentially reduce dependence on cobalt and nickel.^{17,18} It is clear that a detailed knowledge of O-redox materials chemistry will be essential to guide the discovery and implementation of the next generation of materials that can harness this phenomenon. Moreover, the unusual electrochemical behaviour and structural changes that accompany O-redox make this phenomenon an interesting scientific curiosity worthy of investigation by its own merit, explaining why it is continuing to attract attention from both industry and academia.

1.2 Rechargeable Battery Fundamentals

1.2.1 Inside a Li-ion Battery

A battery is an electrochemical cell comprising three main functional components: a positive electrode, an electrolyte and a negative electrode, as shown in 1.1.^{19,20}

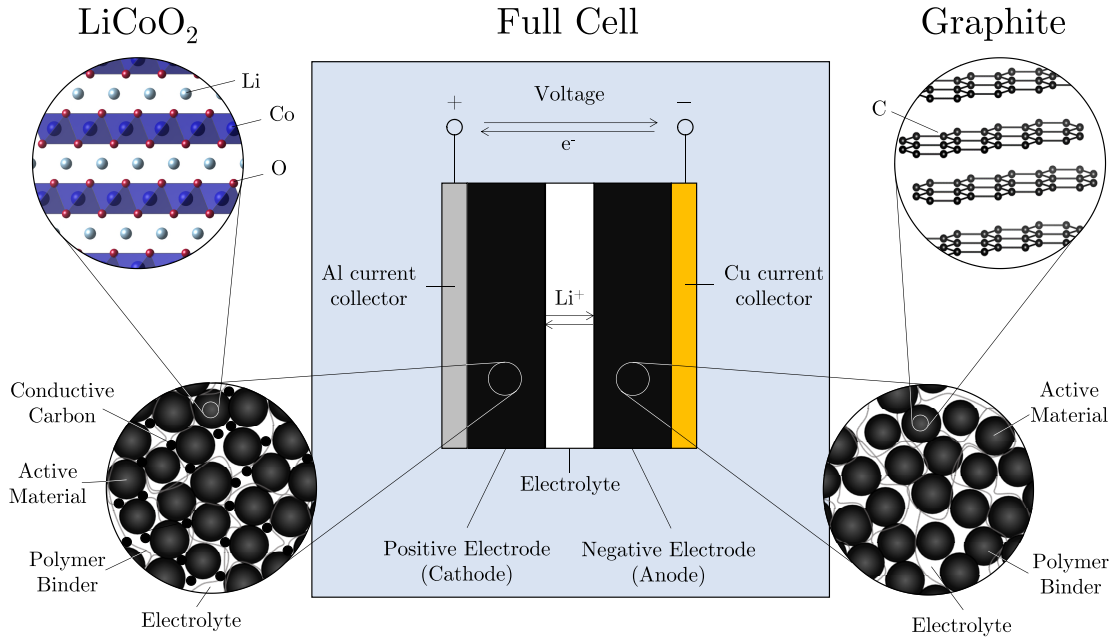


Figure 1.1: Schematic showing the key components of a Li-ion battery at macro, micro and atomic length scales.

These are arranged in a stacked configuration such that the positive and negative electrodes are physically separated from touching by an electrolyte which only allows the transmission of Li^+ ions and not electrons. Instead, the electrons must flow from the active material, to the current collector and around the external circuit to reach the other electrode, either liberating or consuming electrical energy in the process. It is this uncoupling of Li and electron mobility which allows the equilibrium position of the chemical reactions taking place in each electrode to be controlled.

The main active materials in a Li-ion cell, typically $LiCoO_2$ for the positive electrode and graphite for the negative, make up the majority of the mass and volume of commercial electrodes (upwards of 95%). Since they are both powders they must be bound together by a polymer binder to keep them immobilised and connected to the current collector. Positive electrode materials generally have pretty poor electronic conductivities and as such must also be supplemented with a small amount of finely dispersed carbon powder which acts as a conductive network for electrons between active particles.²¹ The electrolyte, which is typically a Li salt ($LiPF_6$) dissolved in a non-aqueous solvent, permeates the pores in each electrode

to ensure that the particles are wetted and that Li^+ ions can readily diffuse between each active particle and the electrolyte.

1.2.2 How Li-ion Batteries Store Energy

The two electrodes are the main reactive components of the cell and are where energy is stored in the form of chemical potential energy. Each electrode has a chemical potential associated with it which is dependent on the chemical composition of the electrode material.^{22–25} The difference between the chemical potentials of each electrode determines the equilibrium voltage of the cell, as shown in Figure 1.2, and according to the Nernst equation,

$$E = -\frac{\mu^{+ve} - \mu^{-ve}}{zF} = -\frac{\Delta G}{zF} \quad (1.1)$$

Where, E is the equilibrium cell voltage, μ^{+ve} and μ^{-ve} are the chemical potentials of the positive and negative electrodes respectively, z is the charge of the carrier ion (1 for Li^+), F is the Faraday constant and ΔG is the Gibbs free energy of the system. As Li and electrons are inserted into or extracted from an electrode, its chemical potential changes to reflect it becoming more reduced or oxidised. When a Li-ion battery is fully charged, the difference between the chemical potential of each electrode will be large and there will be a strong driving force for the reaction between the positive and negative electrodes to proceed. If current is allowed to flow between the electrodes, reduction of the positive electrode and oxidation of the negative electrode will occur spontaneously.* This is accompanied by expulsion of Li from the positive electrode and insertion of Li into the negative to maintain charge neutrality. These processes continue, discharging the cell, until either the external circuit is broken or the chemical potentials of each electrode become equal.

Beside the voltage, V , of the cell, another crucial performance metric of a Li-ion battery is its capacity. Capacity is a measure of the amount of charge that can be

*Within the battery research field the positive and negative electrodes are conventionally referred to as the cathode and anode respectively. By strict definition, the cathode and anode are where the reductive and oxidative processes occur and so the convention only holds true for discharge as the redox process in each electrode reverses on charge. This convention will be used for the remainder of the thesis.²⁰

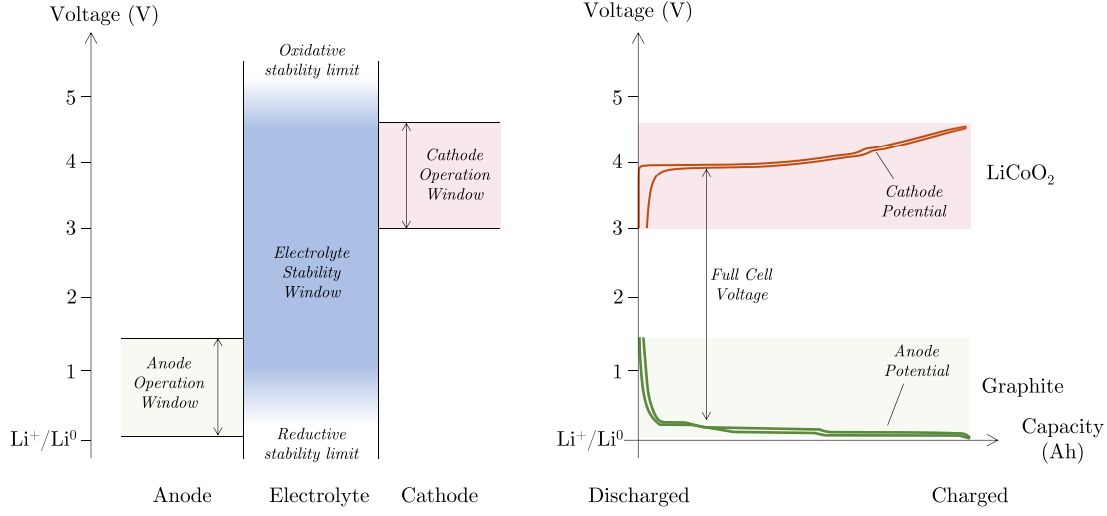


Figure 1.2: Schematic showing the operation windows of each electrode relative to the stability of the electrolyte. The potential variation of each electrode is shown as a function of capacity. The difference between the potential curves at a given capacity is the measured cell voltage. Electrodes are balanced by capacity.

stored by the cell and, for commercial cells, is often given in Ah. Together, the capacity and the voltage of the cell determine how much energy can be stored and delivered, Wh.^{25,26} To calculate the energy density of the battery as a whole, the total energy is divided either by the mass of the battery, to give gravimetric energy density, Wh kg⁻¹, or by its volume to give the volumetric energy density, Wh L⁻¹.

In battery research, when studying the properties of a specific electrode material, a more useful unit is the specific capacity, mAh g⁻¹. This is generally measured against a Li, or Na, metal anode assumed to be of constant 0 V reference potential to isolate the performance of the electrode material. The total theoretical capacity of a given material can be derived from the equation,

$$\text{Specific Capacity (mAh g}^{-1}\text{)} = \frac{zF}{3.6M_w} \quad (1.2)$$

Where, z is the number of electrons (and Li^+) transferred per formula unit, F is the Faraday constant, M_w is the molecular weight of the electrode active material. Since the transfer of electrons between the electrodes is directly related to the transfer of Li^+ ions, the specific capacity of the cell is limited by the ability of each electrode to accommodate both Li and electrons. This is determined by the

chemical compositions and the redox states of the elements in the host material that are accessible within the voltage window of the electrolyte and without incurring irreversible structural change (i.e. for Co in LiCoO_2 they are +3 and +4, although for highly delithiated states the layer stacking changes become partially irreversible).

1.2.3 The Cathode Challenge

The electrodes in commercial cells are balanced by capacity such that the potential curves for each material can be fully exploited, within chosen voltage limits as illustrated in Figure 1.2. However, the specific capacities (i.e. per unit mass) of cathode materials (typically 170-220 mAh g⁻¹) tend to be much less than those of the anode (300-500 mAh g⁻¹).⁶ This means that a higher mass of cathode than anode must be used in the cell to compensate for the poorer charge storage density of the cathode. Furthermore, the potential of the anode is already pretty close to 0 V versus Li^+/Li , which is the fundamental lower limit for Li-ion cell chemistry, whereas the cathode potential could be pushed higher in voltage. Since the voltage difference between cathode and anode and their specific capacities are the key determinants of the energy density of the battery, it becomes clear that the cathode holds back significant improvements in overall energy density.

As mentioned previously, the voltage and specific capacity of the cathode are properties directly related to the chemical composition of the cathode active material.²⁵ Conventional materials operate via the intercalation and de-intercalation of Li^+ ions compensated by the reduction and oxidation of the TM elements present in the host structure. This means that in order to improve the specific capacity, more Li must be exchanged per unit mass of material, but also more electrons must be stored. This is a challenging materials feat to realise since the host crystal structure must be able withstand very large changes in Li composition and oxidation state for many hundreds of cycles.

The chemical potential of the cathode is determined by the electronic structure of the compound and can be derived from calculation using Density Functional Theory by considering the position of the Fermi level.²⁵ Generally speaking, higher

valent TMs operate at higher voltages since the valence electrons are in deeper energy states within the atomic potential, although, in reality, the chemical bonding and crystal structure more generally are the most important factors. This means that in order to favour increasingly higher voltages, electrons must be taken from deeper electronic bonding states, increasing the possibility of incurring structural instability at high states of charge.

The change in chemical potential of a cathode with its composition determines the voltage profile, Figure 1.3. Specifically, the voltage is derived from the rate of change of chemical potential (or Gibbs free energy) with composition. A cathode undergoing a homogeneous change in composition (i.e. the Li and electrons inserted are distributed evenly throughout a single phase) will exhibit a sloping voltage profile in a plot of voltage versus capacity. In contrast, some cathodes undergo an inhomogeneous evolution in composition whereby phase segregation into two different compositions, *phase A* and *phase B*, is energetically favoured over a solid solution. As the cathode continues to charge, the relative proportion of these phases change until the transformation is complete. The voltage profile in this case is a flat plateau.²⁰

In order to provide a high energy density, battery cathodes should ideally deliver a substantial capacity at a high voltage. For constant power output throughout the discharge, which is useful for commercial applications, the voltage profile should take the form of a reversible flat plateau. Finding new materials which can satisfy both of these criteria together is a formidable challenge, but one with great reward, and as such there continues to be strong motivation for research in the battery field.

1.3 Oxygen Redox

1.3.1 Li-rich Materials

Li-rich materials have emerged as a promising candidate to potentially meet these stringent requirements.^{11,12} In general, the term *Li-rich* is used to describe a cathode compound composed of a greater fraction of Li than TM. More specifically, in relation to layered compounds, this means that Li occupies sites in both the Li and TM layers,

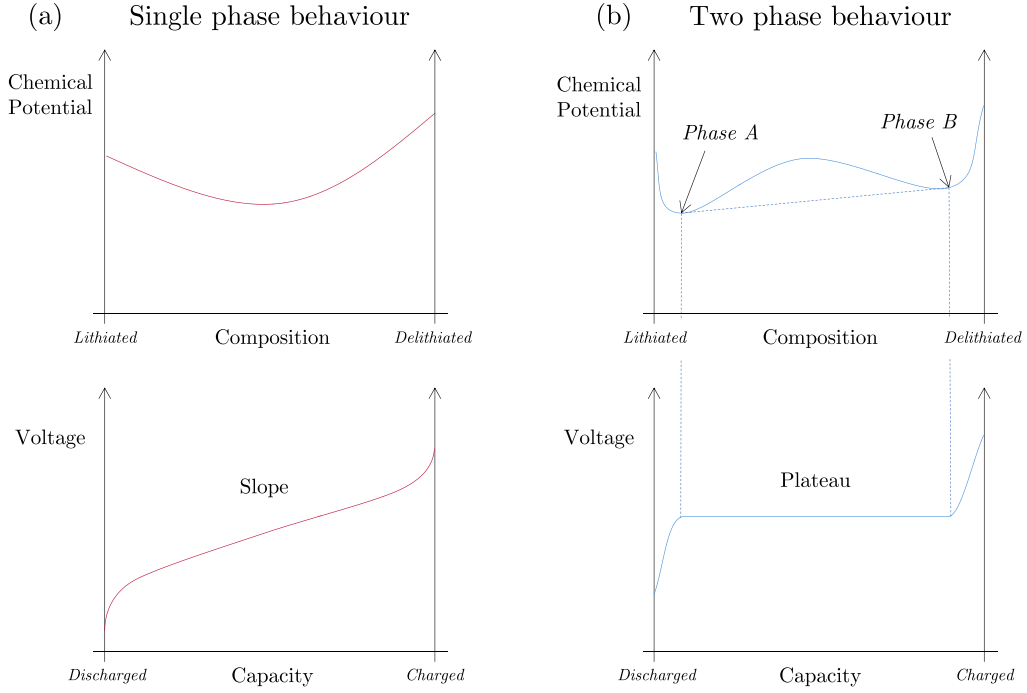


Figure 1.3: Schematic showing the dependence of voltage profile on chemical potential.

as in Figure 1.4. Within this space, the most intensely investigated materials are those based on the solid solution between Li_2MnO_3 and LiTMO_2 (where TM = Ni, Mn, Co, but also Ti and Cr) also represented as $x\text{Li}[\text{TM}]\text{O}_2 \cdot (1-x)\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ where the brackets contain the elements in the TM layer.[†] These materials are found to exhibit a peculiar voltage profile when the material is charged and discharged through one cycle. An initial sloping region corresponding to the amount of capacity expected of the TMs present (i.e. $\text{Ni}^{2+/3+/4+}$ and $\text{Co}^{3+/4+}$) is followed by an extended voltage plateau at around 4.5 V versus Li^+/Li . On discharge, the plateau is not reversed and instead a sloped S-shaped curve is observed at a lower average voltage. This is commonly referred to as first cycle voltage hysteresis.^{11,12} Following several years of debate, this *anomalous* capacity has now been largely attributed to O-redox processes by scientific consensus although the exact nature of the O-redox mechanism and origin of first cycle voltage hysteresis is still hotly debated.^{17,18}

[†]Commonly in the research field and industry these compounds are collectively referred to as Li-rich NMC since they contain Ni, Mn and Co in varying amounts.^{17,27}

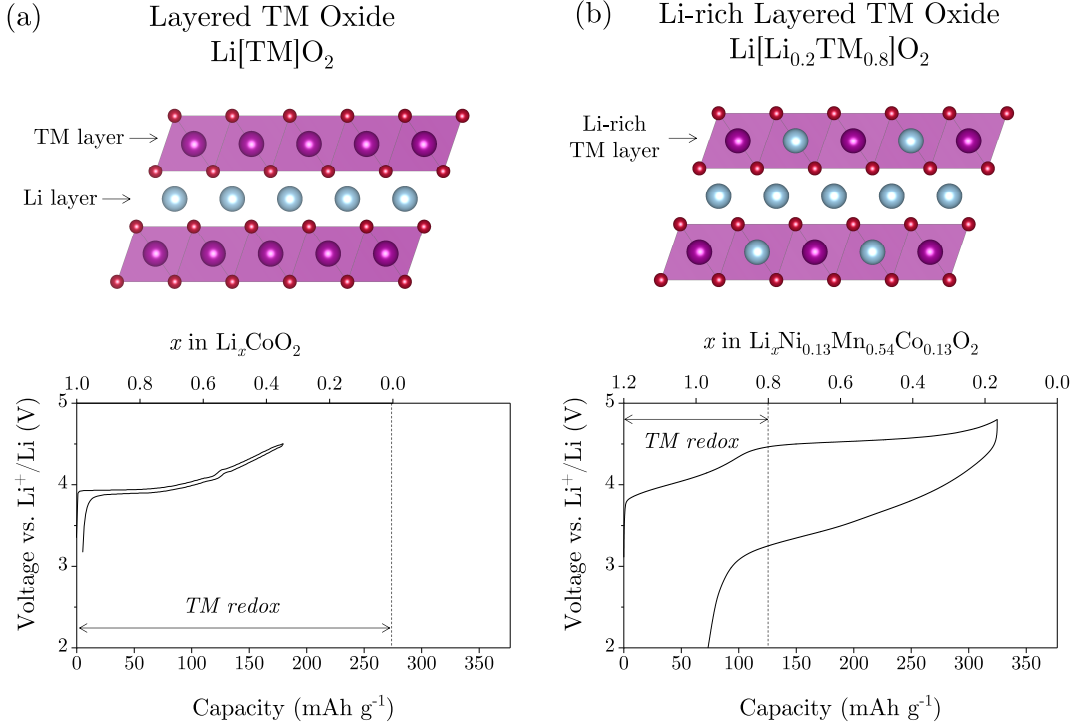


Figure 1.4: Schematic showing a conventional stoichiometric layered material and a Li-rich layered material and representative voltage versus capacity plots.

After the first cycle, Li-rich materials exhibit two other important electrochemical characteristics that have been, and continue to be, the focus of intense scrutiny. Firstly, upon the second and all subsequent cycles there exists a large voltage difference between the charge and discharge curves. This is generally what is referred to by the term *voltage hysteresis* and can be broken down into two contributions: an over-potential component which disappears when the system is rested to equilibrium either on charge or discharge; and an intrinsic difference in equilibrium potential between cells that are charged and discharged to the same nominal Li content.^{27,28} Secondly, the discharge profile gradually evolves over cycling continually dropping in average voltage and developing from a smooth curve into a two-step profile. This is known as *voltage fade*.^{27,29} While both of these phenomena are crucial impediments to the commercial implementation of these materials, for the most part, they are not the focus of this thesis.

1.3.2 A Brief History

The first reports of the anomalous capacity associated with Li-rich materials emerged in 2001 and 2002 by Lu and Dahn who studied the solid solution between Li_2MnO_3 and $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$.^{9,10} Refinements on XRD patterns of the charged materials later revealed them to be oxygen deficient leading the authors to conclude that, as Li is removed from the material across the plateau, O is lost from the structure followed by Mn reduction on discharge to account for the anomalous capacity.³⁰ Further evidence of oxygen loss came in 2006 in a study by Armstrong *et al.* who, using *operando* electrochemical mass spectrometry (OEMS) on Li-rich $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$, could detect the release of O_2 gas from the cell at the same voltage as the plateau.³¹ Further to this, from refinement of neutron data of the charged cathode material, they argued that a structural model without oxygen vacancies gave the best fit to the experimentally observed structure. This led them to claim, as initially hypothesised in a conference abstract by Delmas, that TM ions were migrating from the surface into octahedral TM layer sites (vacated by Li) in the bulk resulting in a denser material with no anion vacancies. This mechanism was later supported by others noting, in particular, the disappearance of low angle diffraction peaks arising from in plane honeycomb ordering within the TM layer, i.e. evidence of TM rearrangement.^{32,33} This process become known as *densification*.

However, there were discrepancies with this model. Mass measurements of cycled electrodes showed they did not lose enough mass to be consistent with the loss of O_2 .³⁴ Furthermore, only a slight reduction of Mn from +4 on discharge could be evidenced on discharge.³⁵ This led to the idea that oxygen might be reversibly oxidised and reduced to account for the capacity. Continuing on this theme, some proposed that O_2 released from the cathode on charge could be electrochemically reduced on discharge forming radical species that reacted with the electrolyte to be deposited as surface carbonates which could then be oxidised at lower voltage on the second charge.^{36–38} Yet this mechanism involving continuous breakdown of the electrolyte did not appear to explain how the anomalous capacity could be seen reversibly for hundreds of cycles.

In 2013, these conflicting views were reconciled. Koga *et al.* proposed that different O-redox processes were occurring at the surface and the bulk.¹³ Irreversible loss of O₂ and densification of the surface of electrode particles might explain the observed O₂ gas evolved and reversible oxidation and reduction of oxide in the bulk of the material could account for the reversibility of the anomalous capacity and lack of Mn reduction.^{14,15} Around the same time, Oishi *et al.* showed the first direct spectroscopic evidence of bulk O-redox participation using soft X-ray Absorption Spectroscopy (XAS).¹⁶ They observed an increase and decrease in intensity of the pre-edge of the O K-edge over charge and discharge which they attributed to the formation and depletion of electron holes in O 2*p* energy levels. Furthermore, by using Total Electron Yield (TEY) and Partial Fluorescence Yield (PFY) collection modes, sensitive to the surface and the bulk respectively, they could confirm the presence of different O-redox behaviours.

1.3.3 The Latest Understanding

O-redox in 3*d* Li-rich materials

More recently, research from Bruce and co-workers on Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O₂ and Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ has shown, through ¹⁸O-labelling the cathode materials, that the amount of O loss as O₂ and CO₂ arising from lattice oxygen in the cathode is only sufficient to account for a small fraction of the anomalous charging capacity. Further to this, by applying a new spectroscopic technique called Resonant Inelastic X-ray Scattering (RIXS), they were able to evidence the formation of localised electron holes on O in the bulk of each material.^{39,40} The signatures seen in RIXS, unique to O-redox, only appeared when exciting in the middle of the O pre-edge at 531 eV where an increase in intensity in the XAS is observed across the plateau. They hypothesised that only O²⁻ ions in certain local environments were likely to be oxidised, specifically those coordinated to 1 Li and 2 Mn which were the most ionic and whose electronic states were consequently placed at the top of the valence band. This, they argued, could explain why the Mn K-edge X-ray Absorption Near-Edge

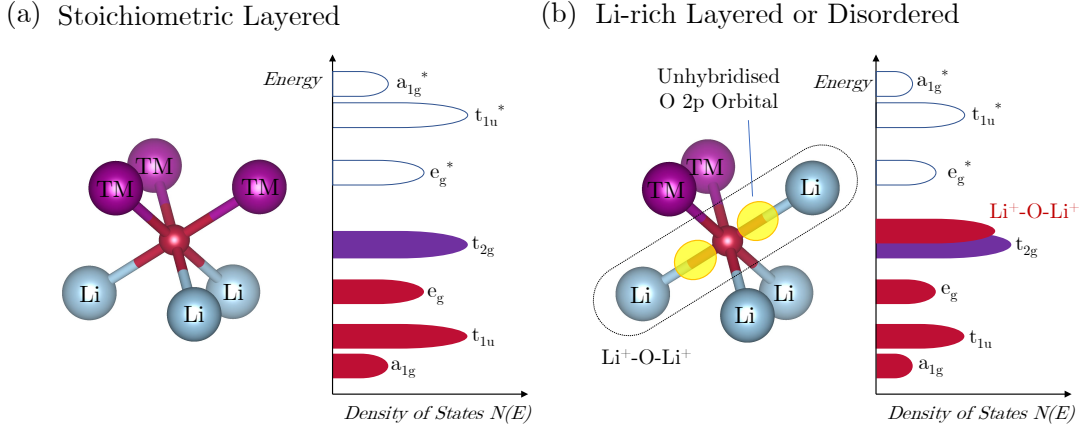


Figure 1.5: Schematic showing the local co-ordination environment around O in (a) a conventional stoichiometric layered material and (b) a Li-rich layered or cation disordered material. Figure adapted from⁴¹

Structure (XANES) spectra continued to evolve over the plateau, suggesting a change in the Mn-O bonding interaction, whereas the Ni and Co did not.

These ideas were underpinned by another important work published concurrently by Ceder and co-workers.⁴¹ Using *ab initio* DFT calculations they plotted the projected Density of States (pDOS) of the oxygen 2p states in cation-mixed LiNiO₂ for different O coordination environments. They showed a substantial increase in DOS near the top of the valence band for the oxygen coordinated by two Ni and four Li. Then, plotting the isosurface to visualise the location of the charge density associated with removal of one electron from LiNiO₂, they revealed an O 2p-like orbital along the Li⁺-O-Li⁺ direction. They proposed that, since the O 2p orbitals along the Li⁺-O-Li⁺ configurations do not have any TM orbitals with which to hybridise, nor do they sufficiently match the energy of the Li 2s orbitals either, these states exist as unhybridised *orphaned* orbitals. They are thus higher in energy than all of the other hybridised O bonding states and roughly comparable to the non-bonding TM states as shown in Figure 1.5. Furthermore, due to them being essentially unhybridised, their energy level is fixed at a more or less absolute value between structures and different TM species. This makes them liable to oxidation before, after or in direct competition with TM oxidation depending on the material composition.

A year later in 2017, another substantial effort to develop the understanding of O-redox in Li-rich NMC materials was published.⁴² In this work, a mechanism to account for the drastically different electrochemical behaviour between the first charge and discharge was proposed. Through structural refinement of *ex situ* synchrotron diffraction data, the authors were able to show that TM ions migrated out of the TM layer during charge (about 6% of all the TM ions present) and predominantly returned back again on discharge (about 4%). Coupling this with Scanning Transmission X-ray Microscopy (STXM) XAS data, which is less surface biased than data collected in TEY or PFY mode, they showed that the spectral changes to the pre-edge of the O K-edge associated with O-redox were representative of the bulk of electrode particles. To explain the loss of voltage on the first cycle, Gent *et al.* proposed a coupling between TM migration and O-redox potential. Specifically, they argued that when TM ions migrate out of the TM layer and into the AM layer they leave certain oxide ions singly coordinated and thus much higher in energy than those doubly coordinated by TMs. This lowers the potential at which they are reduced leading to voltage loss, a point which they supported with DFT calculation. The reversible migration of TM ions back into the TM layer means that this hysteresis mechanism can continue over cycling. RIXS spectra collected on samples cycled 500 times remarkably showed the strong appearance of the characteristic feature attributed to oxidised O, as first reported by Luo *et al.*,^{39,40} demonstrating for the first time that O-redox was truly a reversible phenomenon persisting for many hundreds of cycles. However, while the proposed mechanism might account for the multi-cycle voltage hysteresis outlined in Subsection 1.3.1, it does not explain why the second charge profile deviates so substantially from the first, i.e. why is there no voltage plateau on the second charge? Clearly there is some drastic *irreversible* structural change occurring during the first charge which is not captured by this model. The results and discussion in Chapter 5 of this thesis will present a new theory to explain first cycle voltage hysteresis and unveil the origin of the RIXS signature feature of O-redox.

O-loss and Densification

Given the need from an industrial perspective to suppress gas release from these materials, a lot of research effort has been dedicated to better understanding the mechanism of O-loss and densification. Various works employing, in particular, atomic resolution electron microscopy techniques have directly evidenced the surface reconstruction that takes place alongside loss of oxygen from the lattice.^{43–46} It is now clear that both in-plane and out-of-plane TM migration occur readily at the surface leading to more cation dense defect spinel- and rocksalt-type structures. The degree of densification seen on the first charge has also been quantitatively linked to the amount of O lost as gaseous by-products from OEMS by Strehle *et al.* showing close agreement between the techniques.⁴⁷

While it is widely agreed that the O₂ gas observed when charging Li-rich materials originates from lattice O from the cathode, there has been a great deal of dispute and confusion over the mechanism for CO and CO₂ release. Many have argued that these gases arise predominantly from reaction of oxidised O with the electrolyte,^{39,40,48,49} others instead have claimed they can be accounted for exclusively by Li₂CO₃ residues inevitably present on the surface of pristine electrodes.⁵⁰ Arguably, these conflicting views have stemmed from a similar debate around gas emissions from stoichiometric, predominantly Ni-based cathodes (such as LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂). These materials are not expected to be O-redox active and thus the gas loss was initially proposed to originate from Li₂CO₃ or other contaminants.^{51,52} Since then, a broad consensus has been reached that CO and CO₂ arise to some extent from both Li₂CO₃ and reactive O from densification phenomena, even in non-Li-rich compositions.^{53–57}

More lately, there is evidence to implicate singlet O₂ (i.e. molecular O₂ in an electronically excited state) as the key reactive intermediate released from densification.⁵⁸ This highly reactive form of O₂ attacks electrolyte molecules giving rise to CO₂ as a result of electrolyte breakdown.⁵⁹ Unfortunately, even these findings are still not clear-cut, as singlet oxygen has also been evidenced to arise from electro-oxidation of Li₂CO₃.⁶⁰

A lot of progress has been made characterising the effect of O loss on the surface structure of O-redox cathodes and studies continue to be performed into the breakdown reactions of oxidised oxygen species with the electrolyte. Despite this, relatively little research has focused on what triggers oxygen loss in the first place and a number of questions remain unanswered. How can O loss from covalent *4d* and *5d* TM based systems be explained? Can O loss be avoided in O-redox materials? What strategies might be employed to achieve this? The results and understanding presented in Chapter 4 go some way towards tackling these issues.

***4d* and *5d* TM Systems**

Similar electrochemical behaviour has also been observed in *4d* and *5d* TM-based Li-rich systems including, among others, $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ ⁶¹ and $\text{Li}_2\text{Ir}_{0.75}\text{Sn}_{0.25}\text{O}_3$.^{62,63} In both cases, a high voltage plateau is seen extending well beyond the expected maximum oxidation states of the Ru and Ir present, followed by an S-shaped discharge curve which persists for all subsequent charge and discharge cycles. In these systems, the change in voltage profile has been understood to arise from a structural rearrangement triggered by over-oxidation of the TM. The over-oxidised TMs are reduced by the oxide ions in a ligand-to-metal charge-transfer (LMCT) process coined as *reductive coupling* and the oxidised O subsequently dimerise to form peroxo-like $(\text{O}_2)^{2-}$ species, as summarised in Figure 1.6. The peroxide remains coordinated to the TMs preventing its release as O_2 gas and provides a reversible mechanism for O-redox to occur on subsequent cycles through the breaking and forming of the O-O bond.

Early understanding on these systems was that Ru and Ir conferred greater structural stability to oxygen redox cathodes on account of the greater covalency with which they bond to O versus Mn.^{61,64–66} It was argued that the more covalent TM-O bonding prevented the de-coordination of oxidised O-O species from the lattice altogether as O_2 (termed *reductive elimination*) enabling reversible O-redox. For Mn based materials, the bonding between Mn and O was too ionic allowing O_2 to be released and it was only through the role of Co that O-redox could occur

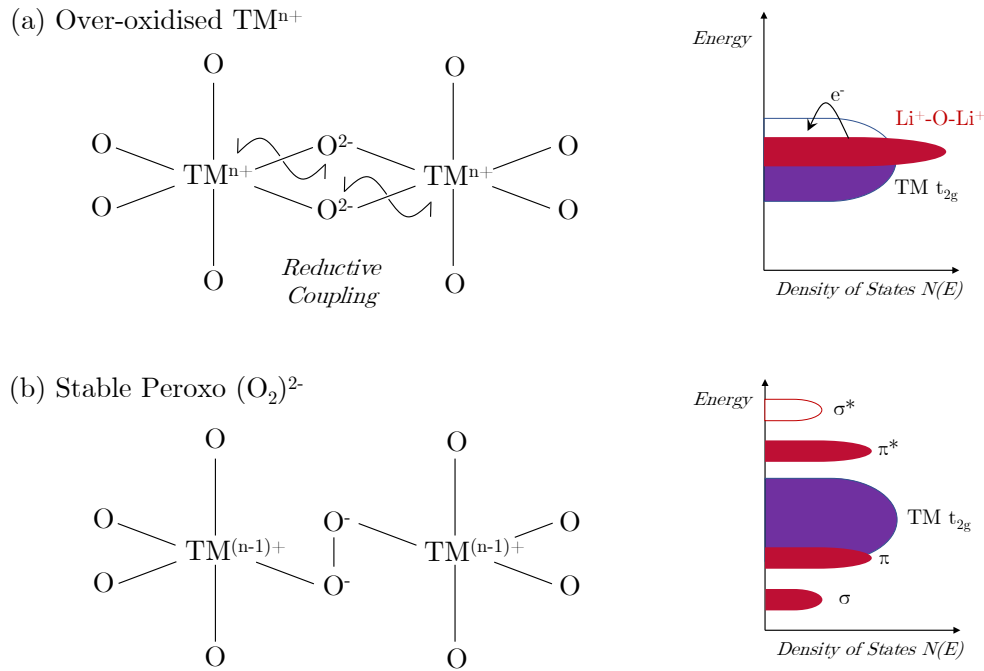


Figure 1.6: Schematic showing the reductive coupling mechanism to explain the occurrence of oxidised oxygen. Over-oxidised TM ions (such as Ru^{6+}) are reduced by co-ordinating oxide ions which, once oxidised, consequently form O-O bonds. Schematic adapted from References [61, 64, 65].

reversibly. However, this theory did not account for the fact that non-negligible amounts of O-loss were also detected for Ir and Ru systems.

Notably, in 2015, this theory was further advanced by atomic resolution electron microscopy images which directly evidenced the lack of substantial structural change in Li_2IrO_3 .⁶² This material exhibits a two-step plateau profile which is reversed on discharge, exceeding the capacity expected from $\text{Ir}^{4+/5+}$ TM redox. Furthermore, a subtle distortion in the oxygen coordination sphere around Ir could be observed, whereby the interatomic O-O distance decreased slightly upon charge, evidence, according to the authors, of peroxo-like $(\text{O}_2)^{n-}$ bond formation facilitating reversible O-redox. However, this model for the behaviour of Li_2IrO_3 has since been refuted.⁶³ Iridium is in fact able to oxidise beyond the +5 oxidation state to +5.5 before the onset of O-redox accounting for the high voltage capacity. The distortions to the oxygen network arise due to Jahn-Teller distortions of the Jahn-Teller active d^4 Ir^{5+} ion. The reversible high voltage plateau is thus not supported by O-redox

but rather TM-redox. O-redox can be promoted in this system by substituting Ir for electrochemically inactive Sn^{4+} which induces the familiar extended charging plateau and subsequent S-shaped discharge. Migration of the TM elements, in addition to peroxo-bond formation, has been implicated to explain this.

Further reports of novel lithium iridate structures which invoke O-redox have also been published. The beta polymorph of Li_2IrO_3 exhibits a third high voltage plateau and almost complete delithiation going beyond even $\text{Ir}^{5.5+}$.⁶⁷ In contrast to the layered honeycomb structure of $\alpha\text{-Li}_2\text{IrO}_3$, $\beta\text{-Li}_2\text{IrO}_3$ is composed of a three-dimensional framework of iridium with lithium ribbons running through the structure rather than two-dimensional lithium layers. The authors claim that this structural configuration confers greater stability and robustness for reversible O-redox. In contrast, another interesting structural motif that arises from the more Li-rich composition Li_3IrO_4 (equivalently written $\text{Li}[\text{Li}_{1/2}\text{Ir}_{1/2}]\text{O}_2$), where Li and Ir form alternating chains within the TM layer,⁶⁸ shows poor structural integrity, decomposing to give O_2 and an amorphous crystal structure. This shows that even covalent Ir-O bonding is not sufficient to prevent structural rearrangement and O_2 release.

1.3.4 Debate on the Nature of Oxidised Oxygen

The nature of oxidised oxygen in charged Li-rich materials continues to be a highly contentious and fiercely debated issue. From an application perspective, it has important implications for the explanation of first cycle voltage hysteresis and towards unlocking the potential to deliver high energy density cathodes. Aside from this, the nature of oxidised oxygen is also an interesting fundamental issue of relevance to the wider solid state chemistry community.

While it is now broadly accepted that $\text{Li}^+\text{-O-Li}^+$ interactions (which are introduced by virtue of having Li in both the Li and TM layers of a Li-rich material) promote the formation of electron holes on O, there are some conflicting views on how the electron holes are stabilised. The key data supporting each of the opposing standpoints are summarised Figure 1.7.

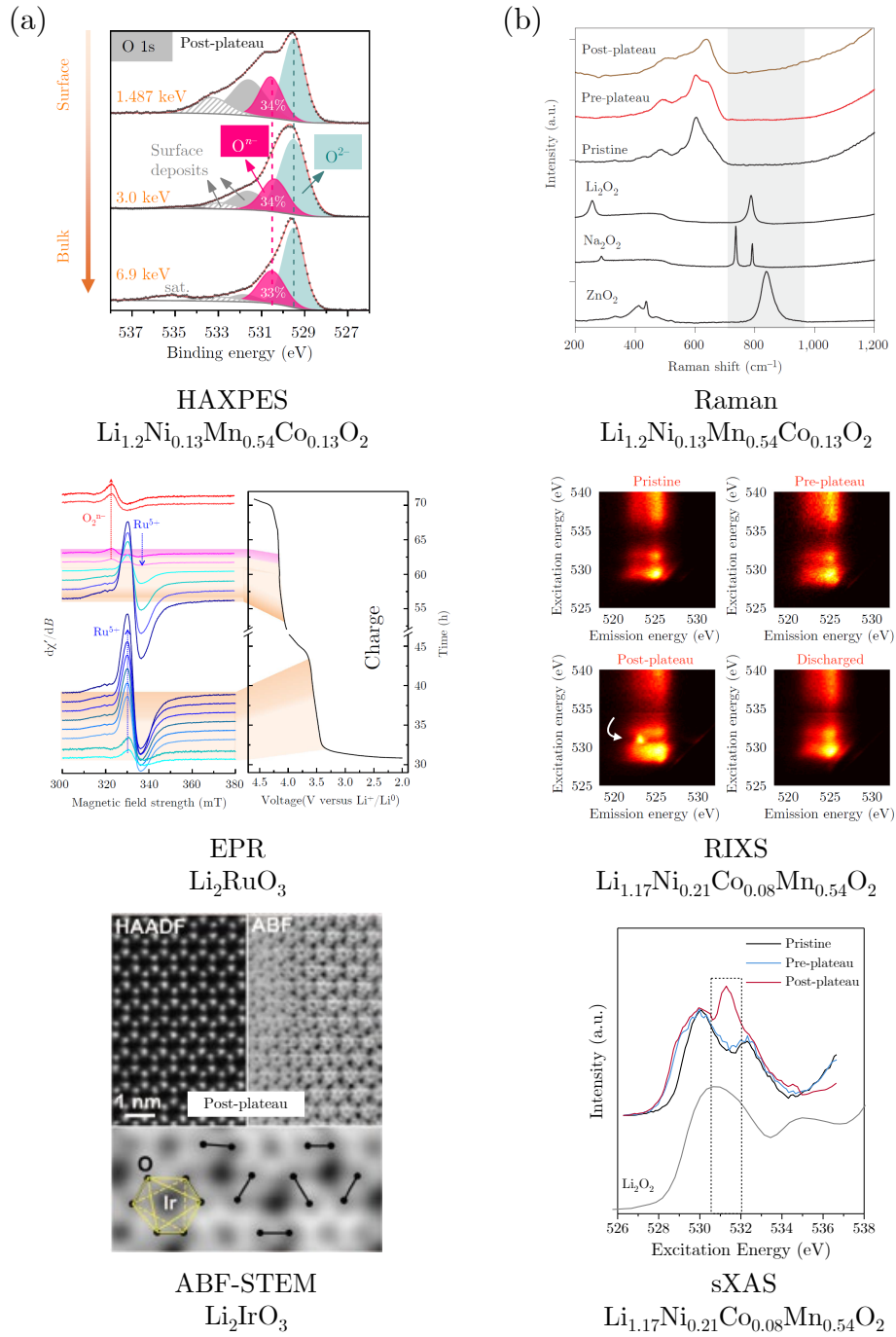


Figure 1.7: (a) Key evidence for the formation of peroxo-like species: depth resolved XPS show the formation of bulk O^{n-} species where $n < 2$, figure adapted from Reference [69]; *operando* EPR show the formation of O_2^{n-} species where $n < 2$, from Reference [70]; ABF-STEM show distortion in the oxygen network around Ir, figure adapted from Reference [62] (b) Raman spectra show no evidence of peroxide species, figure adapted from Reference [39]; RIXS spectra show the formation of localised hole states on O, figure adapted from Reference [42]; sXAS O pre-edge feature for Li_2O_2 (from Reference [71]) is much broader than the feature for oxidised oxygen in O-redox cathodes.⁷²

On one side of the argument, peroxo-like $(\text{O}_2)^{n-}$ dimers where $3 \leq n \leq 1$ are proposed with bond lengths ranging from 1.5 - 2.5 Å. Proponents of this theory point to three main pieces of experimental evidence:

1. An X-ray Photoemission Spectroscopy (XPS) feature that appears on charge at around 530.5 eV, just higher in energy than the O^{2-} peak at 529.5 eV and thus attributable to a less oxidised O species.⁶⁹
2. Electron Paramagnetic Resonance (EPR) data which is consistent with the creation of unpaired electrons on charge.⁷⁰
3. Annular Bright Field - Scanning Transmission Electron Microscopy (ADF-STEM) images for Li_2IrO_3 showing a slight distortion in the O network around Ir on charge and a shortening of interatomic O-O distances.⁶²

Opponents of this theory generally argue that electron holes are localised on O^{2-} ions (i.e. O^{n-}) and that there is insufficient direct evidence for O-O bonding. In particular they cite the following evidence:

1. No features arising from O-O bond stretches are detected from *ex situ* Raman spectroscopy.³⁹
2. Resonant Inelastic X-ray Scattering data show the appearance of electron holes states on O that form a narrow energy band indicating localisation on O^{2-} ions.⁴²
3. The pre-edge profile in O K-edge XAS for peroxide species is significantly broader than the observed peak that appears in charged Li-rich samples and furthermore O-O dimers with a bond length of greater than 1.5 Å exhibit a peak that is too low in energy to match that of oxidised O.^{71,72}
4. Computational results indicate that, due to highly directional TM-O bonding, O $2p$ orbitals that would σ overlap to form an O-O bond are at a 90 degree angle to each other and unable to align without lowering metal co-ordination.⁴¹

The evidence outlined above may be seemingly unequivocal on either side of the debate, but there are nonetheless a number of prominent discrepancies which remain to be addressed. Notably, recent studies scrutinising the RIXS features of Li-rich materials and Li_2O_2 have suggested that the two spectra share similarities which should not be overlooked.⁷³ Furthermore, there have been reports of the appearance of Raman features in the peroxo region during *operando* Surface Enhanced Raman Spectroscopy (SERS) measurements of Li-rich NMC.⁷⁴ Finally, oxygen loss is observed at high states of charge in all Li-rich materials regardless of the TM element in contradiction with the argument that covalency prevents de-coordination of peroxides.^{61,62}

1.4 Na-ion Chemistry

1.4.1 Comparison with Li-ion

Lithium-ions are not the only alkali ions capable of intercalation chemistry. Rechargeable batteries based on sodium-ions have been demonstrated in the lab for many years and are now commercially available. Na-ion batteries are broadly regarded as a cheaper and more sustainable alternative to Li-ion on a number of counts:^{75,76}

Advantages

- The raw material Na_2CO_3 is substantially cheaper than Li_2CO_3 .
- Na is significantly more earth abundant element than Li and more evenly-distributed worldwide.
- The anode current collector, which is usually Cu in a Li-ion cell, can be replaced with Al in a Na-ion cell which is cheaper, safer and lighter. This is because Na does not alloy with Al, unlike Li.
- The larger ionic radius of Na promotes greater structural diversity and versatility towards incorporating different TM elements, notably cheap TMs such as iron and titanium which do not readily form layered Li-ion compounds.

As the production of electric vehicles ramps up, demand for Li, Co and Ni have sky-rocketed and concerns about the availability of these resources have begun to grow as a result. These points provide a compelling motivation which continues to drive research into Na-ion batteries as an alternative.^{75,76} Nevertheless, Na-ion chemistry also suffers drawbacks:

Disadvantages

- The reduction potential of Na^+/Na is marginally higher (0.34 V) than that of Li^+/Li reducing the energy density of Na-ion cells.
- Na-ions are also more than three times heavier than Li-ions (22.99 versus 6.94 g mol⁻¹) which further lowers the energy density of Na-ion cells.
- Some Na-ion cathode materials can only be synthesised in a Na-deficient form presenting difficulties when assembling them into a full cell.
- The greater structural diversity of Na-ion cathodes often means they undergo more phase transformations during electrochemical cycling.

Although there are clear reasons for researching Na-ion cathode compounds with a view to practical application, the materials that are presented in this thesis were chosen as they represent interesting model compounds for studying fundamentals. The versatile structural chemistry of sodium transition metal oxides, afforded by the larger ionic radius, makes certain compositions accessible that would otherwise not be feasible in lithium materials. For instance, layered LiMnO_2 can only be prepared by ion exchange of NaMnO_2 , as LiMnO_2 otherwise forms a corrugated layered structure.^{77,78} Other examples include NaNiO_2 which possesses less cation anti-site disorder than LiNiO_2 ⁷⁹, and NaFeO_2 which is perfectly layered whereas LiFeO_2 is completely cation disordered.⁸⁰ The greater size difference between Na (1.02 Å) and the TMs Ni^{3+} (0.60 Å) and Fe^{3+} (0.65 Å) compared with Li (0.74 Å), which is much more similar, promotes segregation into alternate layers to minimise strain.

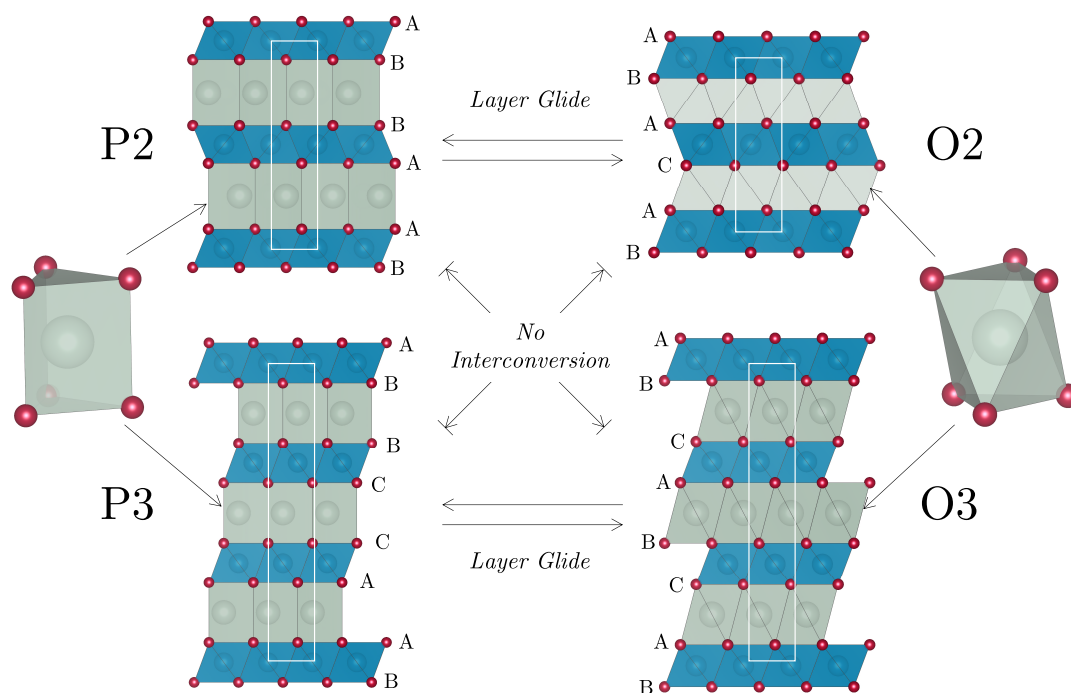


Figure 1.8: Schematic showing the naming convention of typical layered Na-ion structures.

1.4.2 Layered Structure Types

The rich variety of layered Na-ion structures was conveniently classified in 1980 by Delmas *et al.*⁸¹ They proposed that materials could be characterised by: the coordination geometry of Na-ions in the AM layer, either octahedral or trigonal prismatic, given the labels O and P respectively; and the stacking sequence, defined by the number of transition metal oxide layers needed to define the repeating unit, commonly 2 or 3. A summary of frequently observed structure types is given in Figure 1.8.

P2, P3 and O3 are the structure types which are most readily accessed by direct solid state synthesis methods. P2 and P3 compounds tend to form at partial sodium contents (typically around $x = 2/3$) and O3 compounds at near full Na content.^{76,82} During electrochemical desodiation in a cell, $P2 \longleftrightarrow O2$ and $O3 \longleftrightarrow P3$ can inter-convert easily by small lateral displacements of the TMO layers known as *layer glides* and do so in accordance with the lowest energy configuration at a

given sodium content. O2-type structures are only observed upon near-complete desodiation of P2-type compounds and typically are too contracted to contain Na. Due to the multiple possible unique layer glides, O2 structures tend to exhibit broad diffraction peaks on account of the random stacking arrangement.⁸³ $P3 \longleftrightarrow O2$ and $O3 \longleftrightarrow P2$ transitions cannot occur as they require a complete reorganisation of the oxide stacking sequence only possible through breaking the TM-O bonds.⁸⁴

There are additional complexities which require different classification. For instance, some P2 compounds transition to a charged phase consisting of alternately stacked trigonal prismatic and octahedral Na layers. In this compound O-type layers are void of Na and the P-type layers partially filled. This structure is referred to as OP4.⁸⁵ Sometimes the TM layer of Na-ion compounds is slightly distorted from hexagonal, such as in NaMnO_2 which crystallises in the O3-type structure. These distorted phases are labelled with a prime symbol, i.e. O'3 rather than O3.

This naming convention has been usefully extended to describe Li-ion compounds too such as LiCoO_2 which is O3-type in its pristine state. The smaller ionic radius of lithium means that it strongly prefers smaller tetrahedral and octahedral sites over trigonal prismatic ones and so P-type Li-ion structures are not observed. Nevertheless, this difference in size and coordination tendency between Na and Li can be usefully exploited to synthesise mixed Na/Li compositions which segregate Li and Na into the TM (octahedral) and AM (trigonal prismatic) layers respectively. This leads to compositions, such as P2-type $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, which can be considered to be Na-ion analogues of Li-rich materials.

1.4.3 O-redox in Na-ion Cathodes

Some of the earliest synthesis work benefiting from the substantial size difference between Na and Li to access Na-ion compounds with Li substituted TM layers were led by Paulsen and Dahn around the year 2000.^{84,86} Over a decade later, these materials were tested in Na-ions cells by Yabuuchi *et al.* revealing that they too exhibit an anomalous charging plateau and S-shaped discharge curve.⁸⁷ Initially, this behaviour was attributed to irreversible oxygen loss and structural rearrangements,

similar to the mechanism proposed to explain the Li-rich NMC materials at the time, despite lack of evidence to support this. In a paper by the same author group which shortly followed this, both O loss and reversible redox of the oxide ions were suggested to account for similar anomalous capacity in Mg-substituted P2-type $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$.⁸⁸ This work has been followed up more lately with a study investigating Zn-substituted P2-type $\text{Na}_{2/3}\text{Zn}_{0.22}\text{Mn}_{0.78}\text{O}_2$.⁸⁹ Both Zn^{2+} and Mg^{2+} ions are electrochemically inactive and similar sizes (0.75 and 0.72 Å respectively) so both compounds exhibit very similar first cycle behaviour as a result.

Due to the large size of Na-ions, Na-rich compounds (i.e. $\text{Na}:\text{TM} > 1$) based on *3d* TM elements cannot be synthesised, however, a few compositions based on larger *4d* and *5d* TM elements have been successfully demonstrated. Na_2RuO_3 and its Sn-substituted derivative, both exhibit first cycle voltage behaviours similar to their Li-ion counterparts with a two-step charging profile exceeding $\text{Ru}^{4+/5+}$ redox capacity and a sloping discharge.^{90–92} Curiously, the second charging plateau is only observed below 4 V versus Na^+/Na when the TM layer is ordered in a honeycomb arrangement and is absent in the case of complete in-plane disorder.⁹² The authors attributed this to the fact that a disordered TM layer could not accommodate a cooperative distortion of the oxide sub-lattice which is necessary for peroxo formation and O-redox to occur. The Na analogue material to layered honeycomb ordered Li_2IrO_3 has also been prepared and investigated.⁹³ The two materials show almost identical behaviour including a reversible two-step voltage profile and O loss at high voltage.

1.4.4 First Cycle Voltage Hysteresis

All the materials described so far have shown invariably that O-redox is accompanied by a high voltage charging plateau followed by a low voltage sloping discharge profile. This seemingly overwhelming and incontrovertible correlation has led to the widely held belief that O-redox and voltage hysteresis are intrinsically and inescapably linked phenomena. Initially, it was understood that O-oxidation was an irreversible process leading to O loss and densification explaining the unusual

electrochemistry. More recently, this viewpoint has been overturned by evidence that O loss can only account for a small amount of the charging capacity and that O-redox is predominantly a reversible process.^{13–15,39,40} What then is the reason for voltage hysteresis? Is TM migration sufficient to explain the change and is it irreversible or reversible as some have posited?

To make the puzzle yet more challenging to solve, there has been a handful of prominent reports of O-redox in the absence of voltage hysteresis. In 2016, a new Mn-based material was published with a reversible high voltage plateau at an average voltage of 4.2 V vs Na^+/Na .⁹⁴ With a remarkably similar composition to that of $\text{Na}_{5/6}\text{Li}_{1/4}\text{Mn}_{3/4}\text{O}_2$,⁸⁷ $\text{Na}_{0.6}\text{Li}_{0.2}\text{Mn}_{0.8}\text{O}_2$ does not appear to exhibit any significant differences in structure apart from possessing a P3-type rather than P2-type stacking sequence. The authors could not find any significant evolution in structure from diffraction data during the first cycle or over multiple cycles and thus concluded that O-redox formed an amorphous secondary phase with oxidised O trapped as peroxides anions.⁹⁴

Further data was later published on P3-type $\text{Na}_{0.6}\text{Li}_{0.2}\text{Mn}_{0.8}\text{O}_2$ evidencing the reversible interconversion of the pristine structure with a second very poorly crystalline phase over the first cycle.⁹⁵ They argued, citing the appearance of a peak at 2.5 Å in neutron Pair Distribution Function (nPDF) data, that the primary difference between the structures was a slight distortion to the oxide sublattice forming peroxo-like O-O dimers as a result of O oxidation. They likened this mechanism to the example of Li_2IrO_3 despite acknowledging that Mn-O bonding is significantly more ionic than Ir-O.

Another notable example of O-redox without hysteresis, $\text{Na}_2\text{Mn}_3\text{O}_7$, was presented by Mortemard de Boisse *et al.* at around the same time.⁹⁶ This material, alternatively written as $\text{Na}_{4/7}[\square_{1/7}\text{Mn}_{6/7}]\text{O}_2$, was found to possess transition metal vacancies (represented as $\square$) in the TM layer in a unique ordering configuration. The reversibility of the high voltage plateau here was attributed to the presence of vacancies which allowed for π -type orbital hybridisation between the orphaned O 2p orbital and Mn.

In a very recent effort (2019) to unify all known examples of O-redox and first cycle hysteresis under a single theory, some of the main proponents of the argument that covalency is key to stabilising peroxo-type bonds and preventing O loss have abandoned this in favour of the idea that it is rather the number of electron holes on oxygen that is the critical defining parameter.⁹⁷ In short, provided that the number of electron holes per O is less than the threshold value of 1/3, reversible, high voltage O-redox will occur with long O-O bond lengths (2.5 Å). Straying too far above this value will result in irreversible TM migration and the formation of peroxide (O_2)²⁻ species and eventually O_2 loss inducing voltage hysteresis. Despite this, there are a number of materials which defy this explanation exhibiting hysteresis below the threshold number of holes. In particular, Na_2RuO_3 (0.4 Na extracted beyond $\text{Ru}^{4+/5+}$ equating to 0.13 h^+ per O)^{91,92} and high Ni, low Li content Li-rich materials, i.e. where $x < 1/3$ in $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]\text{O}_2$ (0.25 Li extracted beyond $\text{Ni}^{2+/4+}$ equating to 0.13 h^+ per O).^{9,10}

So, in spite of the fervent efforts of researchers to find a satisfying explanation substantiated by convincing scientific evidence for the reported behaviours of all O-redox compounds, the much sought after conclusion to the debate remains elusive.

1.5 Disordered Rocksalt Cathode Materials

1.5.1 Percolation Theory

In the search for suitable intercalation materials for Li^+ , researchers have almost exclusively pursued highly ordered crystal structures which possess well-defined pathways for facile Li diffusion. It was well known that $\alpha\text{-LiFeO}_2$ and LiTiO_2 , which crystallised into cation disordered rocksalt structures, were electrochemically inactive.⁹⁸ Furthermore, in 1998, Obravac *et al.* extended this observation to other LiTMO_2 compositions (where TM = Ni, Co, Mn), which were successfully prepared with the same disordered rocksalt structure as $\alpha\text{-LiFeO}_2$ by high energy ball-milling. All of these materials exhibited very poor electrochemical performance with the exception of LiMnO_2 , which appeared to retain some degree of order and reversible

capacity, reinforcing the view that disorder was not a desirable structural property and instead long-range crystalline order should be sought.⁹⁸

For years the disordered rocksalt class of materials received no attention from the battery research community, until in 2014 Lee *et al.* proposed that disordered Li-rich compositions could exhibit significantly enhanced Li^+ diffusivities than their stoichiometric counterparts.⁹⁹ They presented the curious behaviour of $\text{Li}_{1.211}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$ which, while starting as a layered Li-rich material, quickly disordered over cycling through the ready migration of Mo and Cr. Unexpectedly, this did not severely impact the amount of Li that could be reversibly cycled. The authors attributed this to the influence of excess lithium which increases the number of low energy pathways through which Li can diffuse thereby creating a *percolating network* of diffusion channels. This became known as *percolation theory*.¹⁰⁰

In rocksalt structures, Li must diffuse between octahedral environments via an intermediate tetrahedral site. The site energy of lithium in this tetrahedral environment is determined by the number of face-sharing TMs which, in greater numbers, make lithium occupancy increasingly unfavourable. In perfectly ordered, layered materials, all tetrahedral vacancies in the AM layer are adjoined by 3 face-sharing Li and 1 TM (labelled 1-TM) through which Li can diffuse easily, as shown in Figure 1.9. However, in disordered structures, there is a random distribution of tetrahedral sites each with different numbers of face-sharing TMs leading to 0-TM, 1-TM and 2-TM channels. The authors argued that the small size of tetrahedral sites in cation disordered rocksalts rendered 1-TM and 2-TM sites inaccessible for lithium and hence 0-TM sites were the only sites through which Li could diffuse (i.e. those surrounded exclusively by Li). Due to the statistically small number of 0-TM sites in stoichiometric rocksalts, there is an insufficient amount of them form an uninterrupted chain of 0-TM, otherwise referred to as a percolating network. By increasing Li:TM ratio, more 0-TM sites are introduced into the structure dramatically increasing the probability of uninterrupted chains facilitating Li diffusion.

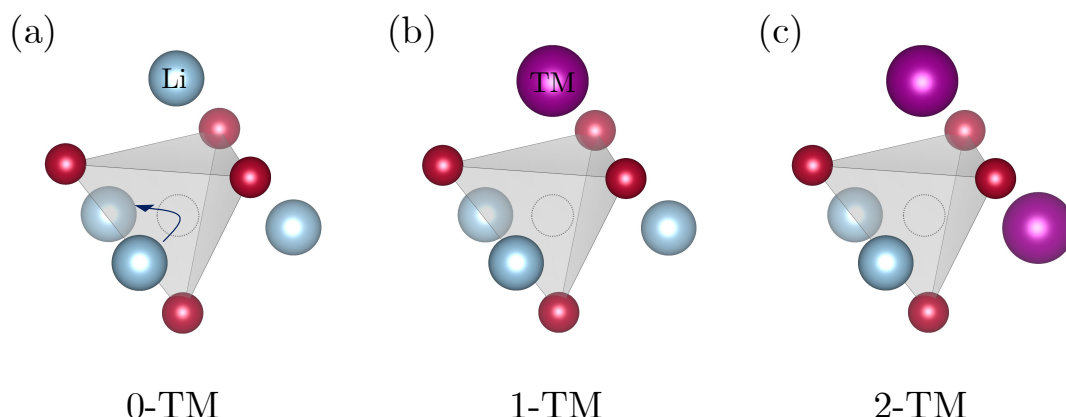


Figure 1.9: Structural schematic showing the three possible diffusion pathways for Li between octahedral sites in the disordered rocksalt crystal structure. Each tetrahedral interstitial site is surrounded by (a) no TM ions (0-TM), (b) 1 TM and 3 Li^+ ions (1-TM), or (c) 2 TM and 2 Li^+ ions (2-TM). Diffusion through 0-TM sites is facile.

This radical change in understanding has sparked a rapid proliferation in the number of known Li-rich disordered rocksalt compounds and led to the discovery of materials exhibiting strong potential as energy dense Li-ion cathodes.

1.5.2 Oxides

Synthesis of disordered rocksalts has focused primarily on derivatives of Li transition metal oxide compounds already known to form crystalline cation disordered phases including Li_2TiO_3 and Li_3NbO_4 . These compounds contain d^0 TMs which promote disorder but also suffer from low conductivity and electrochemical inactivity due to the lack of valence electrons in the d shell.¹⁰¹ However, by introducing a TM with multiple accessible valence states such as Ni, while ensuring a sufficient excess of Li, enhancements in redox activity and Li diffusivity can be realised.¹⁰²

Li_2TiO_3 derivatives

Very early reports of solid solution phases between LiFeO_2 and Li_2TiO_3 had revealed unusual electrochemical behaviour in these compounds before the percolation theory had been proposed. In stark contrast to the inactivity of the end member phases, almost all of the Li could be extracted from compositions such as $\text{Li}_{1.2}\text{Fe}_{0.4}\text{Ti}_{0.4}\text{O}_2$ via a long charging plateau at 4.3 V although this was accompanied by huge voltage

hysteresis on discharge leading the authors to suspect O loss.^{103,104} A much later revisit of these materials showed the appearance of an unusual feature before the pre-edge of the O K-edge at 528 eV which was suggested to indicate the existence of electron holes in the O 2*p* band, i.e. O-redox.¹⁰⁵

The following year, a composition between LiMnO₂ and Li₂TiO₃ was discovered which showed very promising electrochemical behaviour and a first cycle load curve strikingly reminiscent of that of layered Li-rich NMC.¹⁰⁶ When cycled at 50 °C (to enhance the relatively poor ionic conductivity), Li_{1.2}Ti_{0.4}Mn_{0.4}O₂ exhibited a discharge that delivered 300 mAh g⁻¹ capacity at an average voltage of 3.4 V, equivalent to an energy density of over 1,000 Wh kg⁻¹. This material, based on earth abundant Ti and Mn and harnessing both TM and O-redox, demonstrated the immense promise of disordered rocksalt compounds.

Li₃NbO₄ derivatives

Inspired by the opportunity to make new high performance materials within the unexplored disordered rocksalt space, Yabuuchi *et al.* undertook a thorough investigation introducing 3*d* TMs into Li₃NbO₄.^{106,107} This led to the discovery of several compounds Li_{1.3}Nb_{0.3}TM_{0.4}O₂ (where TM = Mn³⁺, V³⁺, Fe³⁺) and Li_{1.3}Nb_{0.43}TM_{0.27}O₂ (where TM = Ni²⁺, Co²⁺) each of which showed significantly enhanced Li intercalation chemistry than either of the end member phases. Interestingly, each one appeared to show a large degree of capacity beyond the available TM redox states thus implying the participation of O, but also significant voltage hysteresis. The only exception to this was the V-containing material which only appeared to oxidise according to the available V^{3+/4+/5+} redox states. Tweaking the composition to increase the amount of V to give Li_{1.25}Nb_{0.25}V_{0.5}O₂ showed that systems with TMs undergoing multiple valence state changes could also deliver high energy densities and with substantially lower hysteresis.¹⁰⁸

Mn-based rocksalts

Preparation of Mn-only disordered rocksalts is challenging via conventional solid state synthetic routes due to the strong tendency to form highly stable, ordered

phases such as LiMnO_2 and Li_2MnO_3 . Nevertheless, disordered lithium manganese oxide phases have been successfully accessed via high energy mechanochemical ball-milling.^{109–111}

Most notably, $\text{Li}_4\text{Mn}_2\text{O}_5$, a defect rocksalt with anion vacancies, was reported in 2015 by Freire *et al.*¹⁰⁹ This compound exhibited an exceptionally high capacity of 355 mAh g^{-1} on discharge albeit over a large voltage window (1.3 V to 4.8 V) and at low current rates (6 mA g^{-1}). The authors invoked oxidation of Mn from +3 to +5 in addition to some O-redox to explain this large capacity. This was later supported by DFT computation from others who qualified the existence of Mn^{5+} with migration from octahedral to tetrahedral sites - the only environment in which it has ever been evidenced.¹¹² However, since then, in light of new spectroscopic evidence, the original authors have retreated from this contentious claim in favour of O participation.^{113,114}

Counter to the percolation theory, disordered rocksalt LiMnO_2 and NaMnO_2 have recently been shown to exhibit high degrees of reversible intercalation, over 80% of the alkali ions present.¹¹¹ Neither of these compounds possess enough Li to surpass the percolation threshold and as such would be anticipated to be electrochemically inactive if the theory held true.

1.5.3 Oxyfluorides

The disordered rocksalt crystal structure has also proved to be a versatile system for accommodating anion disorder as well as that of the cation. In pioneering work, Chen *et al.* demonstrated the possibility of synthesising lithium transition metal oxyfluorides (with mixed oxide and fluoroide anions) by high energy ball-milling.^{115–117} Specifically, the compound $\text{Li}_2\text{VO}_2\text{F}$ showed capacities in excess of 300 mAh g^{-1} based on the vanadium +3/+4/+5 redox couples. Comparing this compound with that of Li_2VO_3 , with V in the +4 oxidation state revealed the clear advantage of targeting oxyfluoride phases. Not only could monovalent fluorine be used as a lever to lower the TM valence in the compound at a given amount of Li excess to access larger TM capacities, but also fluorine raised the voltage through the inductive effect.¹¹⁵

This sparked a number of studies investigating the use of different TMs undergoing multiple valence state changes such as $\text{Cr}^{3+/4+/5+}$,¹¹⁷ $\text{Ni}^{2+/3+/4+}$,¹¹⁸ and $\text{Mo}^{3+/4+/5+}$.¹¹⁹ All of these compounds exhibited high capacities (300 mAh g^{-1}) at high voltages (around 3.0 V vs. Li^+/Li) by virtue of the fluorine-containing Li-rich composition. More recently, another strategy has been introduced to lower the TM valence state further. By substituting some of the active TM for inactive TM of a higher valence (i.e. Ti^{4+} , Nb^{5+}), an even greater range of redox state changes can be accessed. This was demonstrated for $\text{Li}_2\text{Mn}_{1/2}\text{Ti}_{1/2}\text{O}_2\text{F}$ and $\text{Li}_2\text{Mn}_{2/3}\text{Nb}_{1/3}\text{O}_2\text{F}$, where Mn is able to cycle between the $+2/+3/+4$ oxidation states.¹²⁰ This strategy implements understanding from the disordered rocksalt oxides where Ti and Nb were found to promote cation disorder and were mixed with active TMs to make high performance materials.

1.5.4 O-redox in Disordered Rocksalt Cathodes

O-redox extends beyond the realm of layered Li-rich structures. As argued by Seo *et al.* the structural motifs responsible for triggering O-redox are linear $\text{Li}^+-\text{O}-\text{Li}^+$ configurations which led to more labile oxygen electrons in the conjoining O $2p$ orbitals.⁴¹ In layered materials an excess of Li-ions in the TM layer is required to introduce these bonding environments into the structure. However, for disordered rocksalts, where there is no cation order present, $\text{Li}^+-\text{O}-\text{Li}^+$ configurations are much more prevalent, even in compositions without Li-excess as shown in Figure 1.10. In other words, O-redox can be promoted more easily in cation disordered structures than ordered ones and might not require Li-rich compositions.

While linear $\text{Li}^+-\text{O}-\text{Li}^+$ configurations have been shown to raise the energy of oxygen electrons, it remains to be seen whether oxygen electrons can be further raised in energy by the cumulative effect of multiple $\text{Li}^+-\text{O}-\text{Li}^+$ configurations around a single O. Such configurations will be common in disordered systems where O will often be found coordinated by 4, 5 or 6 Li^+ ions. This would further blur the boundaries between TM and O-redox and might lead them to appear as concerted processes, unlike layered Li-rich counterparts.

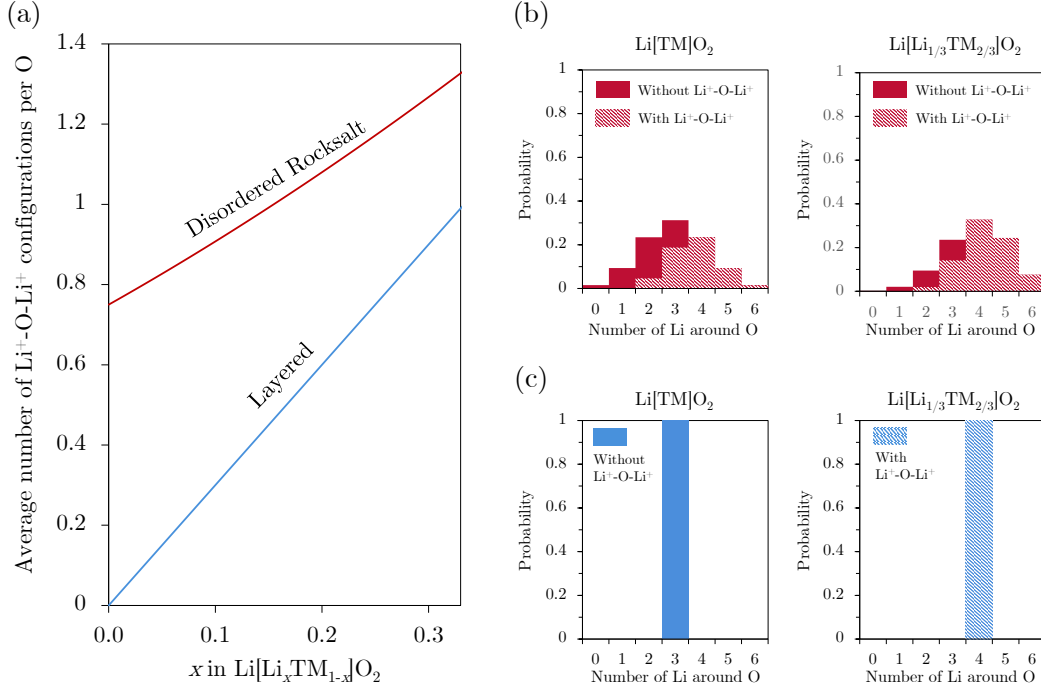


Figure 1.10: (a) Plot of the average number of $\text{Li}^+\text{-O-Li}^+$ configurations in layered and disordered rocksalt structures as a function of Li-excess. (b) Probability distribution of co-ordination environments around O with different numbers of Li in disordered rocksalt materials. Arrangements with 4 or more co-ordinating Li may have more than 1 $\text{Li}^+\text{-O-Li}^+$ configuration. (c) Probability distribution of co-ordination environments around O with different numbers of Li in layered materials. For honeycomb ordering of Li and TM in the TM layer, each O has only one $\text{Li}^+\text{-O-Li}^+$ configuration.

1.6 Thesis Objectives

While battery research is generally driven by a strong performance-driven ethos in the relentless pursuit of marginal gains in cycle life, energy density and cost, the work included in this thesis is rather devoted to understanding the fundamental processes that underpin O-redox. As such, the majority of the materials studied within cannot, in their present forms, be considered as viable replacements for state-of-the-art battery cathodes and were instead chosen as they represent useful model compounds to elucidate certain aspects of the properties of O-redox.

It has now been clearly demonstrated and widely accepted that lattice oxygen can support reversible oxidation and reduction in Li- and Na-rich transition metal oxide compounds explaining why these materials show such large capacities.

However, there remain several important unanswered questions which this thesis will seek to address:

1. Can O-redox be triggered in systems which don't have an excess of alkali ions?
2. What structural or chemical change triggers the loss of oxidised oxygen from the lattice?
3. What causes the first cycle voltage hysteresis observed in layered Li-rich O-redox systems?
4. Can reversible high voltage O-redox be achieved?
5. How can both TM and O-redox be effectively harnessed in disordered rocksalt systems?

The answers to these questions will have important ramifications for future materials research into high energy density cathodes and inform the discovery of new materials which better utilise O-redox.

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2

Experimental Techniques

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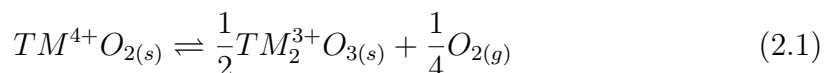
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2.1 Synthetic Techniques

2.1.1 Solid-state Synthesis

By far the most common methodology employed to make ordered mixed-metal oxide compounds is the solid-state route. In its simplest form, solid precursor materials (typically oxides, carbonates, nitrates etc.) are mixed together and then heated at high temperature lending the name *shake-and-bake*.¹ Due to the slow reaction kinetics between solids, the precursor materials must be intimately mixed to reduce the length scales over which the atoms need to diffuse to react together. This can be achieved well by ball-milling the precursor mixture together. The mixture is then pressed into a tightly compacted pellet using a hydraulic press and die set ensuring good particle-particle contact during the synthesis.

The reaction itself commonly requires high temperatures (500 - 1000 C) and prolonged time periods (10 - 100 hours) to form pure, crystalline phases. This is necessary to decompose the precursor compounds and further enhance diffusion. Often, the temperature must be set within a specific range in order to favour the formation of certain ordered phases over others, or to control the oxidation state of the metals in the system. At high temperatures, lower oxidation states are favoured on entropic grounds due to the release of O₂ which accompanies metal reduction, for instance the forward reaction of:



The reaction can be further controlled by the choice of atmosphere. Flowing O₂ over the sample during heating raises the partial pressure of O₂ favouring the left side of the equilibrium and higher oxidation states at a given temperature. Conversely, flowing Ar or H₂ lowers the partial pressure favouring the right side and metal reduction.

Finally, the cooling rate after the annealing step can often be a critical control parameter. Rapid cooling (quenching) is the best way to capture the thermodynamically favoured product at the annealing temperature. Slow cooling, however, can be used to promote ordering phenomena such as Na ordering or ordered arrangements of the TM layer elements which might otherwise be random at high temperature.

2.1.2 ^{18}O Isotopic Labelling

Isotopically labelling the oxygen atoms in a mixed-metal oxide can be achieved by exploiting the relation in Equation 2.1. By exposing the precursor mixture to a vacuum during the high temperature annealing stage, the metals are reduced releasing O_2 . Subsequently applying an atmosphere of ^{18}O -enriched O_2 gas promoted metal oxidation and uptake of labelled oxygen.

2.1.3 Ball-milling Synthesis

Ball-milling is a process that is conventionally used to reduce particle size or for thorough mixing of dry powders. The powder is contained within a jar made from a high density, abrasion resistant material (typically zirconia) along with balls of the same material. The jar is sealed and then rotated at high speeds by a milling machine. Ball-milling solid precursors together at sufficiently high rotation speeds can induce a chemical reaction.^{2,3} During mixing, the balls collide with each other and the walls of the jar with very high kinetic energy, generating a large amount of high localised heat which increases the temperature of the powder. Collisions with the powder also generate large mechanical stresses on the particles, causing abrasion, shearing and intimate mixing of the components. Under these high temperatures, high stress conditions 'mechanochemical' reactions can lead to the formation of metastable phases which would otherwise require very high temperature furnaces and high pressure apparatus to make.

2.2 Long-Range Structural Characterisation

2.2.1 Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

Quantitative determination of the elemental composition of a sample is a key analytical technique for confirming the true identity of a compound. Optical Emission Spectroscopy is an effective way of measuring this and is based on the principle that each element exhibits characteristic emission spectra corresponding to unique electronic orbital transitions.⁴ To achieve optical emission, the electrons must first be excited by atomising the compound at high temperature, often by using a flame or a plasma. In ICP-OES, a plasma is generated from argon gas by ionising some of the argon atoms with a spark. The freed electrons are then accelerated by a magnetic field colliding with other argon atoms and freeing more electrons in the process. This chain reaction (known as Inductive Coupling) continues to ionise the argon gas forming a hot plasma into which the sample is delivered. The atoms in the sample are then also ionised and excited by the hot plasma triggering them to emit photons at specific wavelengths thereby revealing their identity. The intensity of these emissions can also be correlated to the abundance of these elements.

Careful sample preparation is important for getting accurate results. Solid samples must first be digested in concentrated acid (aqua regia or conc. nitric) and diluted by such a degree that the elements to be analysed are present in a suitable concentration for accurate detection. The solution is then delivered by a nebulizer into the plasma in the form of a fine aerosol. The intensity of the light measured by the detector is compared to the light emitted by a series of standards of known concentrations and the precise concentration of the solution is then determined from a calibration curve.

2.2.2 Scanning Electron Microscopy (SEM)

The resolution of optical microscopes is fundamentally limited by the wavelength of light being used due to the diffraction-limit.⁵ This is problematic when trying to resolve features on the sub-micron scale. Electron microscopy overcomes the

diffraction limit through the use of a high energy beam of electrons with significantly shorter wavelengths than that of visible light. The highly focused beam is scanned across the sample to generate a 2D image yielding valuable information about the particle morphology. When the electron beam interacts with the sample a number of scattering and absorption events occur. The detection of low-energy secondary electrons emitted from the sample by inelastic scattering is the most common imaging mode. These electrons originate from the very surface of the sample (first few nanometres) and their intensity is determined by the steepness of the surface from which they are emitted, offering detailed topological information at a resolution of about 1 nm.⁶

2.2.3 Powder X-Ray Diffraction (PXRD)

Powder x-ray diffraction is a powerful technique for identifying the arrangement of atoms in the crystal structure of the sample. It can also be used to quantify phase fractions of crystalline mixtures and determine the occupancy of certain points in the crystal structure by certain elements.⁷ These experiments can be performed routinely using laboratory equipment or using synchrotron radiation to obtain significantly higher resolution data. Besides x-rays, neutrons can also be used to conduct diffraction experiments.

Diffraction arises from the scattering of radiation by a crystal whose periodic array of atoms produces an interference effect in the outgoing radiation. Typically this is performed using a beam of x-rays that is both collimated (all the x-ray waves are parallel) and monochromatic (all the x-ray waves are of a single, well-defined wavelength). When the incident beam enters a crystal it is scattered by the electrons belonging to atoms in the structure. Since the crystal is a highly ordered array of atoms, the scattering can be considered to reflect off of planes of atoms in the structure at an angle identical to the angle of incidence. Each of these planes can be described by 3 values h , k and l , known as the Miller indices, which are the inverse values of where the planes intercept with the a , b and c axes respectively. If the crystal is aligned relative to the incident beam such that

the difference in path length of x-rays scattered by parallel planes is equal to an integer number of wavelengths, then constructive interference occurs and a peak in intensity is observed in the detected radiation. This condition is known as Bragg's Law,⁸ Figure 2.1 and Equation 2.2:

$$n\lambda = 2d_{hkl}\sin(\theta) \quad (2.2)$$

Where n is an integer, λ is the wavelength of radiation, d_{hkl} is the perpendicular distance between atom planes of defined Miller indices hkl , and θ is the incident angle of the beam relative to the hkl plane. The number and position of peaks in the diffraction pattern is thus determined by the space group and unit cell parameters of the crystal which sets the inter-planar spacing, d_{hkl} , of the planes. The absolute intensity, I_{hkl} , of each of these peaks, however, is determined by the scattering ability of the atoms within each of the hkl planes, which is represented in the structure factor, F_{hkl} , as per Equation 2.3.

$$I_{hkl} \propto |F_{hkl}|^2 \quad (2.3)$$

The structure factor is defined as in Equation 2.4:

$$F_{hkl} = \sum_{j=1}^N f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \quad (2.4)$$

Where x_j , y_j , and z_j are the positional coordinates of the j^{th} atom in the unit cell and f_j is the scattering factor of the j^{th} atom. The atomic scattering factor (also known as form factor) is determined by the scattering amplitude of an atom. For x-rays, this increases with the electron density around the atom and hence atomic number, the wavelength of radiation used, λ , and the Bragg angle, θ . For neutron radiation, which interacts with the nuclei and not the electron cloud, the scattering length varies erratically with atomic number and does not exhibit a dependence on the scattering angle. This allows for the detection of lighter elements, especially Li, and stronger diffraction at high angles.

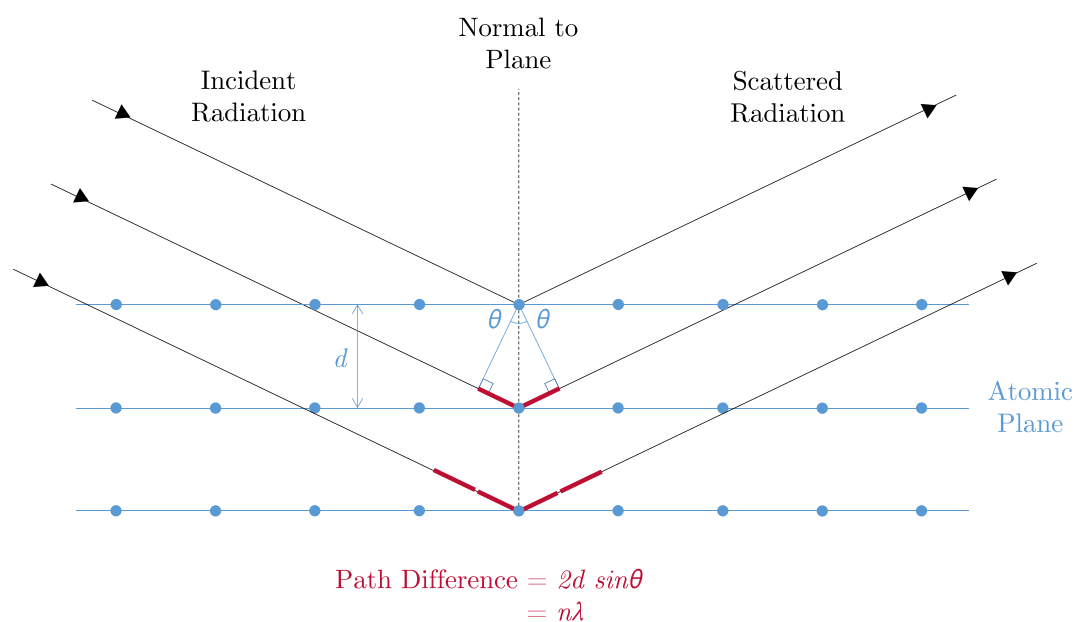


Figure 2.1: Schematic showing how Bragg's Law relates the d spacing between atomic planes to the diffraction angle and the wavelength of the radiation.

X-ray Diffraction

In laboratory instruments, x-rays are generated by accelerating electrons at a metal target (typically Cu, but also Mo, Ag) triggering the emission of x-rays at a number of wavelengths characteristic to the metal. The x-ray light must then be monochromated to select for the most intense wavelength of radiation, Cu $K_{\alpha 1}$ (1.541 Å). Cu K_{β} can be removed using a Ni filter which selectively absorbs this wavelength over the Cu K_{α} and a Germanium monochromator can be put in place to remove the Cu $K_{\alpha 2}$. An additional problem that can be encountered with laboratory source x-ray diffraction is fluorescence where elements in the sample absorb and emit radiation intensely at the wavelength of radiation used. The absorption decreases the diffracted signal and the fluoresced radiation increases the background noise. This can be a particular problem in the study of battery materials since Co and Fe are the two elements that fluoresce the most from Cu source radiation.

Synchrotron radiation is an invaluable tool for diffraction experiments offering a high intensity, highly collimated beam of x-rays of tunable wavelength. This

ultimately gives reduced instrumental peak broadening, significantly enhanced signal to noise and thus better peak resolution. X-ray radiation is generated at a synchrotron by passing a high energy beam of electrons through an undulator consisting of a complex array of magnets. This induces an oscillating motion to the beam which triggers the electrons to emit x-ray radiation as they change direction. The x-rays are then directed to beamlines where they are monochromated with optics to the desired wavelength. Measurements are usually carried out in transmission mode (Debye-Scherrer) where the beam is stationary and the detector is scanned in 2θ . This is in contrast to lab instruments which typically scan both the source and detector each in θ (parallel beam) or the sample and the detector in θ and 2θ respectively (Bragg-Brentano).

Sample Preparation

Sample preparation is an important consideration to avoid unwanted artefacts in diffraction patterns. Powders need to have sufficiently small crystallites to ensure that a statistically large number of them are exposed to the x-ray beam. This is necessary so that enough orientations of the crystal are sampled by the beam to give a diffraction pattern that is truly representative of the crystal structure. Orientation effects can be particularly problematic for samples exhibiting plate-like or needle-like morphologies which prefer to lie in a particular way on the sample plate. This means that certain orientations are sampled by the beam more than others resulting in a systematic variation in peak intensity. These effects are non-negligible for the samples studied in this thesis; layered Na-ion compounds tend to exhibit plate-like particle sizes which sit preferentially on the *ab* plane. This can be reduced through careful preparation methods such as scattering the powder over an adhesive and avoiding pressing with a flat surface.

Peak Broadening

The width of diffraction peaks can be a useful indicator of average crystallite diameter. This can be calculated using the Scherrer equation:

$$diameter = \frac{K\lambda}{\beta \cos\theta} \quad (2.5)$$

Where K is a factor depending on the shape of the particle ~ 1 , λ is the wavelength of radiation used, β is the full width half maximum size of the peak and θ is the Bragg angle. It is important to know that there are several other factors besides crystallite size that can contribute to peak broadening, such as instrumental broadening (from imperfect monochromation and beam divergence) and sample broadening (from lattice strain that can be induced by defects such as stacking faults). Sample size and strain broadening can usually be separated since their dependencies on the Bragg angle, θ , are different.

Operando Experiments

Measurement of the properties of a functional material while it is operating is an immensely insightful, if somewhat challenging, technique. To perform *operando* x-ray diffraction a special cell must be used which remains sealed against the atmosphere whilst allowing the penetration of x-rays through the cell wall into cathode material. One of the only materials suitable for this purpose is beryllium metal which is transparent to x-rays but conductive to electrons allowing it to double as a current collector. Be is also able to provide a sufficient degree of rigidity to enable stack pressure within the cell, which is necessary for electrochemical cycling.

2.2.4 Rietveld Refinement

Rietveld refinement is a structural refinement methodology developed to extract the defining parameters of a crystal structure from experimental data in a rigorous way.⁹ The method employs a least-squares refinement to match a calculated diffraction pattern generated from a model structure to the observed data as closely as possible. To start with, a conceivable initial structural model is chosen with approximate values for key refinement parameters. The peak positions, intensities and shapes are then calculated from this model structure and compared with the experimental data

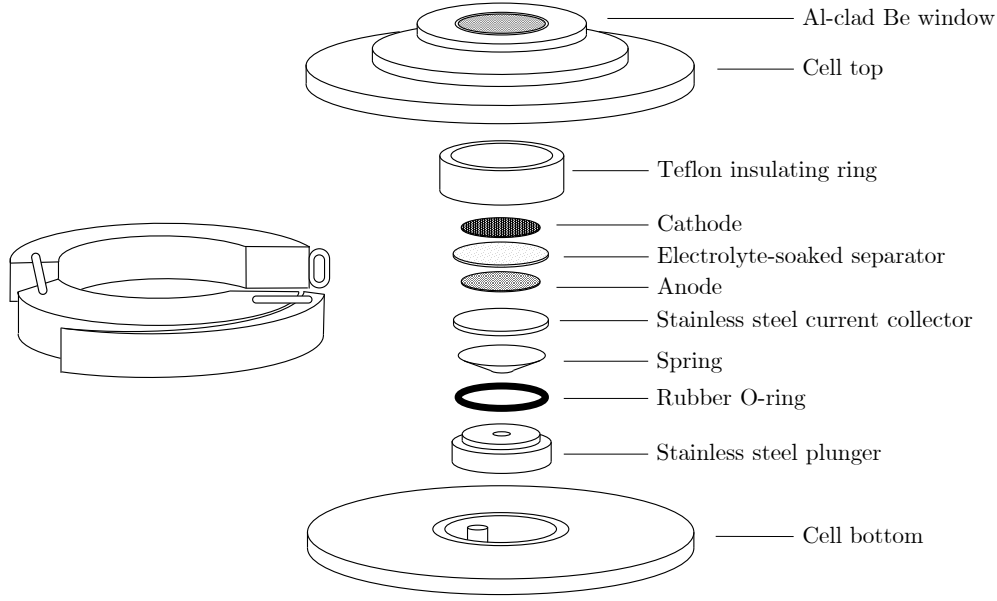


Figure 2.2: Schematic illustrating the construction of the operando XRD cell used in this thesis. This cell was designed and provided by Rigaku.

to determine the goodness of fit. The refinement parameters are then systematically varied to improve the fit until the match is satisfactory.

There are a number of ways of determining the goodness of fit between the model and the data.^{10,11} R_w , the weighted profile factor, is calculated from the square of the difference between the observed and computed peak intensities summed and weighted by peak intensity, Equation 2.8. R_{exp} , the expected R factor, is the best possible value for R_w given the degrees of freedom allowed in the refinement, Equation 2.7. Finally, χ^2 represents how close R_w is to the best possible value, Equation 2.6.

$$R_w = \left(\frac{\sum_i w_i [y_i(obs) - y_i(calc)]^2}{\sum_i w_i [y_i(obs)]^2} \right)^{1/2} \quad (2.6)$$

$$R_{exp} = \left(\frac{N - P}{\sum_i w_i [y_i(obs)]^2} \right)^{1/2} \quad (2.7)$$

$$\chi^2 = \frac{R_w^2}{R_{exp}^2} \quad (2.8)$$

Where y_i is the peak intensity, w_i is the weighting, N is the number of data points and P is the number of varied parameters.

2.2.5 Thermogravimetric Analysis coupled with Mass Spectrometry (TGA-MS)

Thermogravimetric analysis is a technique which allows the precise measurement of the mass of a sample while it is subjected to a heating regime under a selected atmosphere. In this way, samples can be assessed for phase purity and reactivity. Furthermore, by coupling this with a mass spectrometer which measures the evolved gases in real time, the identity of the emissions can be easily determined.

2.3 Short-Range Structural Characterisation

2.3.1 Annular Dark Field - Scanning Transmission Electron Microscopy (ADF-STEM)

A Scanning Transmission Electron Microscope (STEM) is an instrument that can perform angstrom-resolution imaging by using a highly focused electron beam that passes through the sample to be detected on the other side.¹² In Annular Dark Field (ADF) imaging, an annular (ring-shaped) detector is used to measure only the electrons that are scattered by the atoms in the sample as the beam is rastered over them and not simply the intensity variation of the transmitted beam. In this way, atoms will appear as bright contrast (rather than dark contrast from them obscuring the transmitted beam). Scattering is generally only well resolved when atoms align in columns along the path of the beam and if the atoms themselves are strong scatterers (i.e. have high atomic number, Z). Electron microscopes are typically not limited in resolution by the wavelength of the electron beam but rather aberrations from the optics which cause blurring or distortion of the image. The addition of aberration-correctors to the microscope overcomes this issue to provide sub-angstrom resolution imaging.¹³

Samples are dispersed in a liquid and drop cast onto a mesh of conductive carbon (typically lacey or holey carbon). As a result, individual particles are suspended by the mesh and their protruding edge can then be imaged by the electron beam. Since the sample material attenuates the electron beam, only edges of the particle can be effectively studied where the sample thickness is sufficiently small to allow enough

transmission. The grid is examined for a particle that happens to be lying in the correct orientation such that the zone-axis is aligned with the direction of the beam.

2.3.2 Electron Energy Loss Spectroscopy (EELS)

Electron Energy Loss Spectroscopy (EELS) is the energy resolved measurement of inelastically scattered electrons from a sample in a STEM experiment.¹⁴ As the incident electrons pass through a sample they lose energy to the electrons in the structure triggering electronic transitions. These transitions are unique to each element present in the material and will give rise to characteristic absorption edges that are detected in the intensity profile of scattered electrons. These absorption edges are the same as those measured in Absorption Spectroscopy and thus give insight into the identity, quantity and oxidation state of the elements present in the sample. Furthermore, since STEM is a highly spatially resolved technique, absorption spectra can be measured at very specific locations in the structure allowing for spatial mapping and line-scan experiments. This can be very valuable for profiling elemental composition as a function of depth into a particle from the surface.

2.3.3 Neutron Pair Distribution Function (PDF)

Pair distribution function analysis is a valuable tool for probing the local atomic structure of a material and can be performed using x-ray or neutron radiation.^{15–17} In this thesis, the latter was chosen for its sensitivity to Li. To perform PDF, firstly, total scattering data (Bragg and diffuse) is collected and scattering from background sources is carefully subtracted. The Fourier transform of this data is taken to convert from reciprocal into real space, revealing a plot of the distribution of atom-atom pairs as a function of increasing separation. The intensity of the peaks in the PDF is determined by the scattering lengths of the atom pairs and the peak broadness contains information on atomic displacements and thermal vibrations. Since PDF is performed using total scattering data, meaningful structural information can be gathered on amorphous or poorly crystalline materials.

2.3.4 Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance spectroscopy is a highly sensitive, element-specific probe of local environment.^{18,19} It is based on the principle that the nuclear spin of an atom is influenced by the local magnetic fields of surrounding nuclei and electrons, resulting in detectable changes to the behaviour of the nuclear spins under a sequence of applied radio frequency pulses. The perturbation of the nuclear spins from alignment with an external magnetic field is measured by moving the sample within a coil of wire inducing a voltage decay. The Fourier transform of this voltage decay response with time gives the NMR plot of intensity versus frequency, whose peak position, intensity and broadness hold valuable information on the identity, number and valence state of nearby atoms.

In solid state NMR the sample is spun at an offset of 54.7 degrees to the external magnetic field (Magic Angle Spinning or MAS). This averages out anisotropic interactions resulting in sharper signals with sets of spinning sidebands separated by the frequency of rotation.

In this thesis, ^6Li solid state MAS NMR was employed to gain insight into the local environment specifically around Li. Although the most abundant isotope of Li is ^7Li (92.4 % versus 7.6 %), ^6Li offers improved resolution due to its lower quadrupolar interaction (less peak broadening) and gyromagnetic moment (more disperse sideband manifolds).²⁰ Therefore, ^6Li -enriched cathode samples were prepared for the NMR analysis. The dominant influence on the Li spectra observed for the materials studied herein is localised spin coupling with unpaired electrons on paramagnetic Mn. This through-bond interaction results in a Fermi contact shift which increases the chemical shift of the Li in proportion to the number and proximity of Mn atoms around Li.¹⁸

2.4 Electrochemical Techniques

2.4.1 Electrode Preparation

Once synthesised, cathode powders need to be mixed with additional components to improve their performance in electrochemical cells. Typically, transition metal oxides do not conduct electrons well, so to improve their conductivity finely divided carbon powder is added (usually 10 wt. %). Carbon sits between the electrode particles and creates a conductive network to carry electrons from the particles to the current collector. To ensure that this mixture remains well-bound together, a polymer binder is also added (usually 10 wt. %). The long polymer chains wrap around the particles immobilising them in a composite film. Mixing can be performed dry in a pestle and mortar or, as standard industry practice, by dispersion in a solvent to create a slurry. This slurry is cast out onto the current collector and dried to remove the solvent. Following this, the film is pressed or rolled to increase inter-particle contact and the packing density of the electrode. While high densities are desirable, it is important to maintain a degree of porosity to allow electrolyte penetration and wetting of the electrode particles. Finally, the electrodes are cut to the desired size and weighed for the experiment.

2.4.2 Coin Cell Assembly

To test cathode materials they must be paired with an anode material, separated with an ionically conductive electrolyte, and cased in a hermetically sealed container. On a lab scale this is achieved through constructing coin cells which each contain about 10 - 30 mg of cathode material.²¹ Coin cells, see Figure 2.3, are button-like in shape and size and are often used to power watches and remote controls. They are made from a stainless steel base and lid which double as current collectors and are electrically isolated from each other by a plastic ring gasket. Inside, the cathode is kept separate from the anode by a disk of porous glass fibre soaked with electrolyte which is typically a Li or Na salt (LiPF_6) dissolved in a cyclic carbonate-based solvent (such as propylene carbonate). The anode itself is usually a thin disk of Na

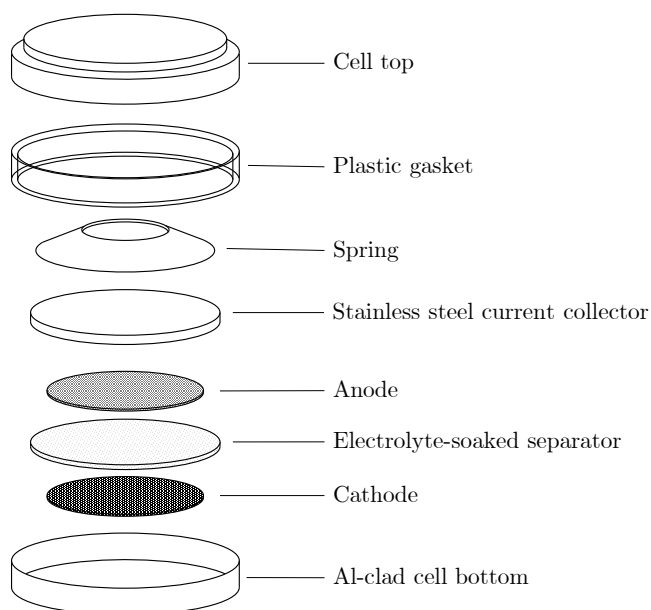


Figure 2.3: Schematic illustrating the key components of a coin cell.

or Li metal foil that has been pressed and cut into this form. Finally, there is a stainless steel spacer and spring to ensure that the cell is under sufficient pressure to give good internal electrical connection and penetration of the electrolyte.

2.4.3 Cell Cycling

The most common test procedure employed in battery research is galvanostatic cycling, so-called since the current is kept constant and the voltage response is observed. A constant current, determined by the mass of active material and desired charging rate, is applied to the cell until the voltage reaches a defined upper limit. At this point, the current is reversed and the cell discharges to a defined lower cut off limit. The current rate is determined in one of two ways: either as simply the current per unit mass of cathode (mA g^{-1}); or as a C-rate, which is commonly used in industrial applications. The C-rate determines the current according to the length of time it takes to fully charge or discharge a cell of a known capacity; 1C means the current is set such that full charge or discharge takes 1 hour. Since in most academic work the capacity of new materials is not necessarily well defined, current rates tend to be expressed in mA g^{-1} .²²

Alternatively, cells can be charged/discharged potentiostatically by setting a constant voltage and observing the current response. Under these conditions the current tends to exhibit an exponential decay as the electrode reaches the equilibrium state at that potential. This is distinct from the galvanostatic experiment which, at very low current rates, tracks the reaction at close to equilibrium conditions throughout. In commercial devices, batteries tend to be charged by CCCV (constant current constant voltage) which is a sequence of these two regimes. Firstly, a constant current is applied to drive the cell to the upper cut off potential, then the potential is set and the device 'trickle charges' until the current drops below a certain fraction (1/10 or 1/20) of that used in the CC step. This achieves near complete charge while avoiding an overpotential that drives the cell beyond the upper voltage limit.

Given the small amount of active cathode material in each coin cell, only very small currents (typically 0.1 - 1 mA) are required to charge and discharge the cell at appreciable rates (C/10 - 1C). To deliver these currents accurately and precisely, specialist battery cycling equipment is used such as Biologic or MACCOR which also continuously log the voltage of the cell.

2.4.4 *Operando* Electrochemical Mass Spectrometry (OEMS)

This technique enables the detection and quantification of gases that are evolved from the electrochemical cell whilst it is operating. A special cell designed with inlet and outlet gas ports allows for a constant stream of inert carrier gas to be flowed through the cell collecting any evolved gases, Figure 2.4. The outlet flow is sampled by a mass spectrometer which ionises the gases with an electron beam and separates them based on their mass to charge ratio (m/z). Coupling the variation in intensity of the detected species resolved over time with the electrochemical response of the cell, the gases can be attributed to certain parts of the charge/discharge process.

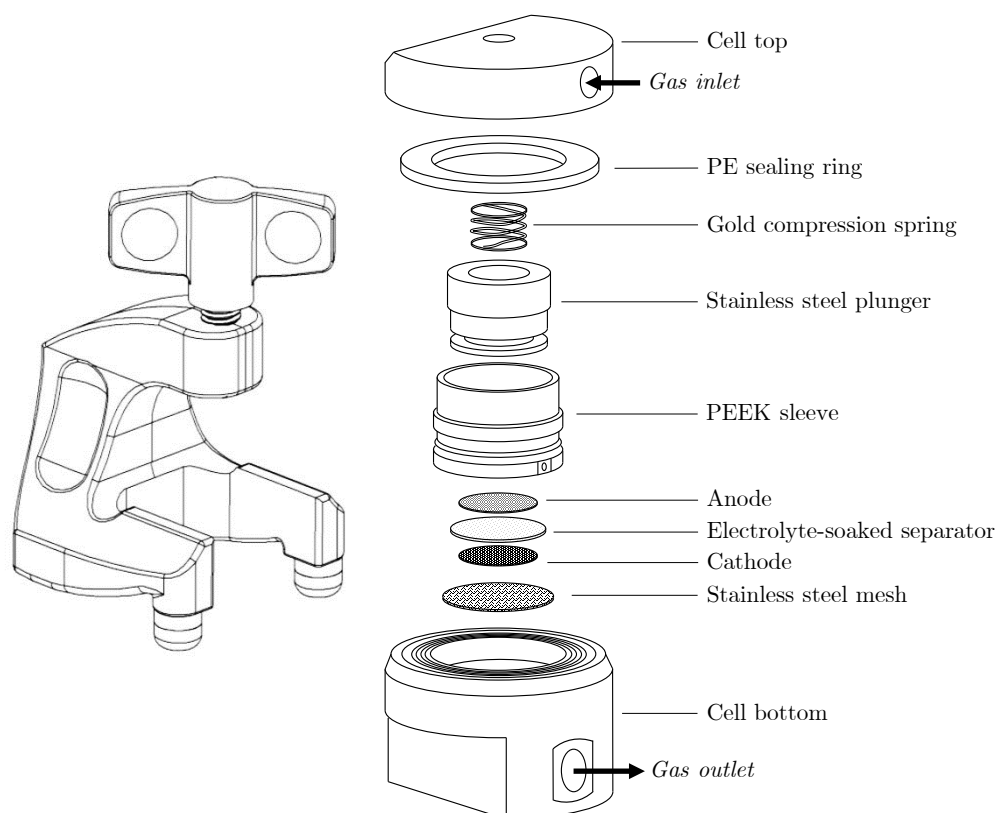


Figure 2.4: Schematic illustrating the construction of the OEMS cell used in this thesis. This cell was designed and provided by EL-CELL.

2.5 Spectroscopic Characterisation

2.5.1 X-ray Absorption Spectroscopy (XAS)

X-ray Absorption Spectroscopy (XAS) is an indispensable, element-selective tool for determining oxidation state and coordination geometry in the bulk of a crystal structure²³. XAS relies on the absorption of high energy photons by atoms in a crystal structure promoting electronic transitions from filled to empty orbitals. As such, XAS is subject to selection rules which only allow electronic transitions between adjacent shells, $s \rightarrow p$, $p \rightarrow d$, $d \rightarrow f$... such that the change in orbital angular momentum $\Delta l = \pm 1$. The edges are labelled K , L and M ... according to the principle quantum number of the lower level as illustrated in Figure 2.5.

The metal L-edges and the oxygen K-edge require low energy x-rays (500 - 1000 eV referred to as 'soft') whereas the metal K-edges require higher energies (5 - 10 keV or 'hard').²⁴ The energy of the x-rays also determines how penetrating the radiation

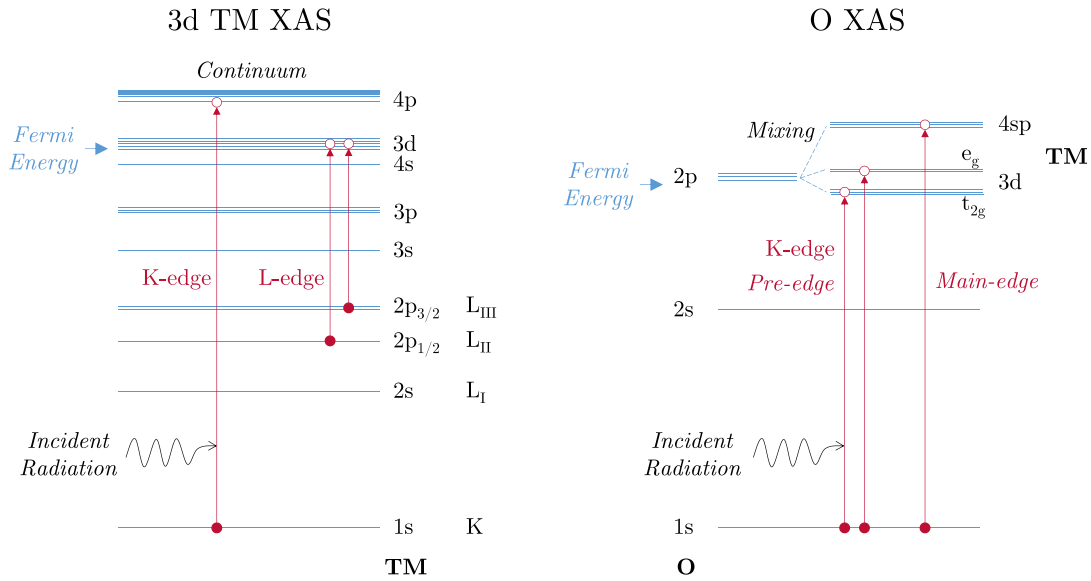


Figure 2.5: Schematic illustrating the key XAS transitions relevant to this thesis: the 3d TM L- and K-edges and the O K-edge.

is for a given sample. This means that experiments with hard x-ray radiation can often be performed in transmission mode, reflecting the nature of the bulk of the particles, whereas, soft x-rays can usually only be used in a reflection geometry using fluorescence. The attenuation of the x-ray beam by the sample is described by the Beer-Lambert Law and exhibits an exponential decay with increasing depth, Figure 2.6 (a). This means that fluorescence experiments using soft x-rays are inherently surface-biased since a greater proportion of the measured photons come from the surface than the bulk. It is also worth noting that the attenuation coefficient, μ , exhibits a dependence on the incident energy which means that the probe depth will also change as a function of energy, Figure 2.6 (b). This latter dependence between μ and energy is what is being exploited in an XAS measurement.

In a typical transmission XAS experiment, the incident x-ray energy is continuously adjusted by the monochromator and the intensity of the incident, I_0 , and transmitted, I_t (or reflected) light are measured with detectors. The absorption coefficient (proportional to $\ln(I_0/I_t)$) is then plotted as a function of energy. As the energy becomes sufficiently high to excite the electrons between orbitals, the absorption coefficient increases sharply giving an *absorption edge*. The position

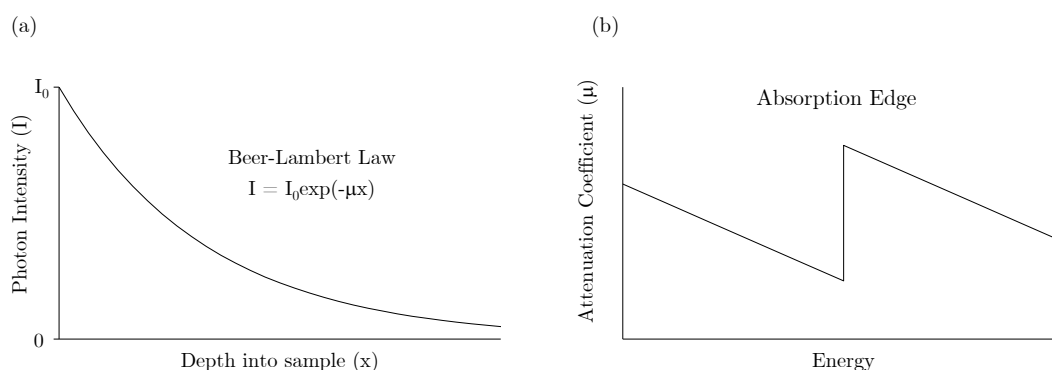


Figure 2.6: Schematic illustrating (a) the exponential dependence of beam intensity with sample depth and (b) the change in attenuation coefficient with energy across an edge.

and shape of this edge give a fingerprint of the oxidation state of the element with higher edge energies generally indicating more oxidised systems.

X-ray Absorption Near Edge Structure (XANES)

For the metal K-edges, the energy required to trigger the electronic transition from $1s \rightarrow 4p$ is very close to the $1s$ ionisation energy to continuum.²³ This means that after the absorption edge the absorption coefficient remains high giving a step-like profile. The main edge portion of this spectrum is known as the XANES and is shaped by the oxidation state and coordination environment of the metal. The trailing end at higher energy is referred to as the EXAFS region which will be described in more detail in Subsection 2.5.2. In some materials a pre-edge feature can be observed immediately before the main edge. This arises predominantly from the dipole-forbidden $1s \rightarrow 3d$ transition which is seen due to mixing between the $3d$ and $4p$ orbitals as a result of distortion of the centro-symmetric coordination environment.

Soft X-ray Absorption Spectroscopy

To study the metal L-edges and oxygen K-edge, soft x-rays are required.²⁴ Since x-rays of this energy are easily attenuated by the sample and the air, these measurements must be performed under ultra-high vacuum (UHV) conditions and in

fluorescence mode. Fluorescence involves the emission of a range of different photon energies. Either these can be measured cumulatively to give Total Fluorescence Yield (TFY) data, or only over certain energy ranges to give Partial Fluorescence Yield (PFY) data. Since the fluoresced photons can themselves be absorbed by other elements in the sample, self-absorption can be a problem resulting in distortions to the measured edge shape. To avoid this, inverse PFY (iPFY) mode measurements, where the edge of interest is detected from its attenuation of another edge of slightly lower energy, can be employed.²⁵

Due to spin-orbit coupling (between the electron spin $s = \pm 1/2$ and the orbital angular momentum $l = 1$ to give $j = 1/2, 3/2$), the $2p$ orbitals are not degenerate in energy giving $2p_{1/2}$ and $2p_{3/2}$. Correspondingly, XAS at the metal L-edge tends to exhibit two edge features known as L_{II} and L_{III} respectively.²⁶ The O K-edge is strongly influenced by mixing with the TM orbitals. The main edge feature represents $1s \rightarrow \text{O } 2p/\text{TM } 4sp$. Often, the main edge is preceded by a pre-edge feature which arises from $1s \rightarrow \text{O } 2p/\text{TM } 3d$ transitions. The shape of the pre-edge is determined by the electron hole distribution among the t_{2g} and e_g orbitals that arise from crystal-field splitting of the $3d$ orbitals under octahedral coordination geometry, Figure 2.5.²⁷

2.5.2 Extended X-ray Absorption Fine Structure (EXAFS)

In a XANES experiment the trailing end of the absorption profile after the edge often exhibits oscillations. These oscillations contain information about the atoms in the local vicinity of the absorbing atom. Since the incident energy above the edge is high enough to excite electrons into the continuum, they escape from the atom as photoelectrons. These photoelectrons are scattered by neighbouring atoms causing interference with the out-going photoelectrons from the absorbing atom, hence modulating the intensity of the observed absorption coefficient.^{28–30}

Data reduction is necessary to extract meaningful structural data from EXAFS.^{31,32} Firstly, the edge is normalised with a baseline defined by the pre-edge line (set to 0) and the upper limit defined by the post-edge line (set to 1) fitted through the

EXAFS region. Secondly, a background function is subtracted from the data to isolate the fine structure. The resulting plot is known as *k-space*. To enhance the oscillations at higher energies the plot is *k-weighted* by multiplying by a k^2 or k^3 function. Next, a window function is applied to remove the oscillations arising from the main edge (low k) and those which are too weak or noisy (high k). Finally, the Fourier Transform of this data is performed to deconvolve the different oscillatory contributions. The result is a plot of *r-space* which shows a series of peaks plotted as a function of r (this can be considered as the radial distance from the absorbing atom - although the numbers do not correspond directly to real distances unless a phase shift is applied). Each peak in this plot corresponds to the neighbouring atoms around the absorbing atom, i.e. the first peak is from the first nearest neighbour atoms and so on. The intensity of the peak is related directly to the number of atoms at that radial distance and their scattering ability.

2.5.3 Resonant Inelastic X-ray Scattering (RIXS)

Resonant Inelastic X-ray Scattering (RIXS) is the study of photons that have been inelastically scattered by a sample during an x-ray absorption experiment.³³ In a RIXS experiment, the incident photon energy is scanned across the absorption edge and a detector is used to resolve the scattered photons by emission energy, rather than detecting just photons of the same energy as the incident beam (transmission XAS) or all photons irrespective of energy (Total Fluorescence Yield XAS). The scattered photons arise from the relaxation of electrons in filled valence states near the Fermi level down into the core-hole in the O1s orbital created during the absorption experiment, 2.7 (a). In this way, RIXS probes the valence states specifically on the element of interest. Since the emitted energies from the valence band relaxation are lower than the incident energy required to excite into the conduction band, the measured photon energies are commonly plotted out as energy loss from the incident energy. Emission spectra collected at different excitation energies can be plotted together as a RIXS map, Figure 2.7 (b), or as individual spectra for a given excitation energy, Figure 2.7 (c). In this thesis, RIXS has been

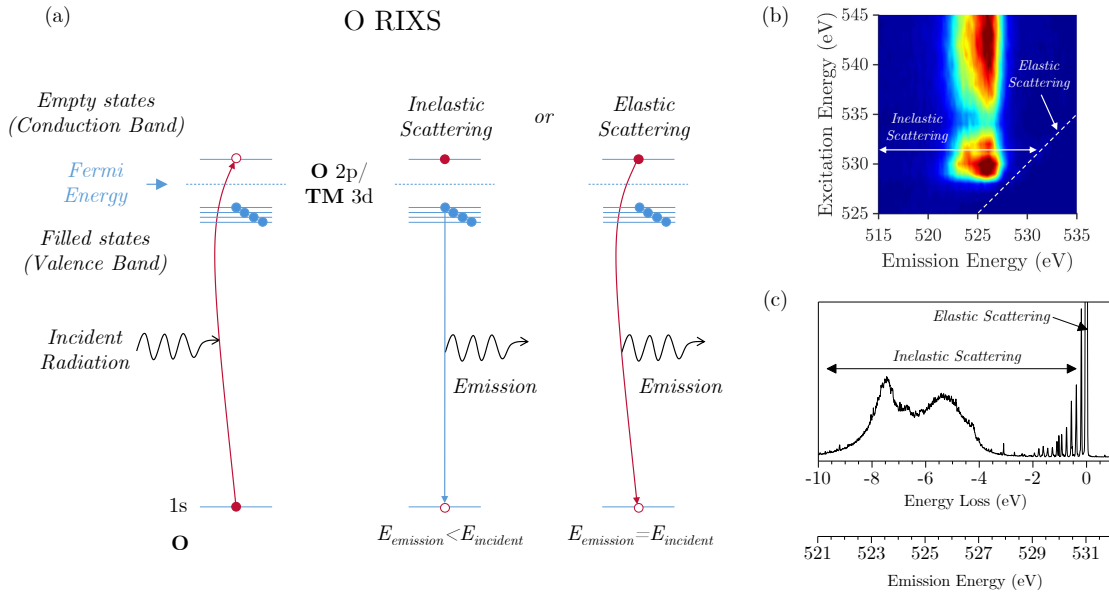


Figure 2.7: (a) Schematic illustrating the electronic transitions giving rise to RIXS emission via inelastic and elastic scattering at the O K-edge pre-edge. In RIXS, photons emitted from the relaxation of electrons in the valence band into the core-hole in the O1s orbital are measured and resolved by emission energy. (b) Map of RIXS emission energy as a function of different incident photon energies (or excitation energies). (c) RIXS emission spectrum at a specific excitation energy of 531 eV. This data can equivalently be plotted as energy loss from the incident photon energy of 531 eV.

carried out at the O K-edge (more specifically the O pre-edge), although in principle RIXS spectra can be obtained from any of the edges.

Thanks to the ever improving brightness of synchrotron sources along with advances in manufacturing technology for gratings, RIXS spectrometers are making significant advances in resolving power. As a direct result of the higher resolution offered by beamlines such as ADRESS at SLS and i21 at Diamond, the true nature of oxidised oxygen has been revealed for the first time through the results presented in this thesis. RIXS allows a much more detailed interrogation of the O species giving rise to hole states measured at the pre-edge of the O K-edge by also probing its valence band structure. Given the very narrow range of excitation energies required to give rise to the new features observed at 531 eV, the electron holes reside in a very narrow band of electronic states. From this observation the electron holes must therefore be localised on an O species with very well defined energy levels, and not one with a broad spread of heavily hybridised states.

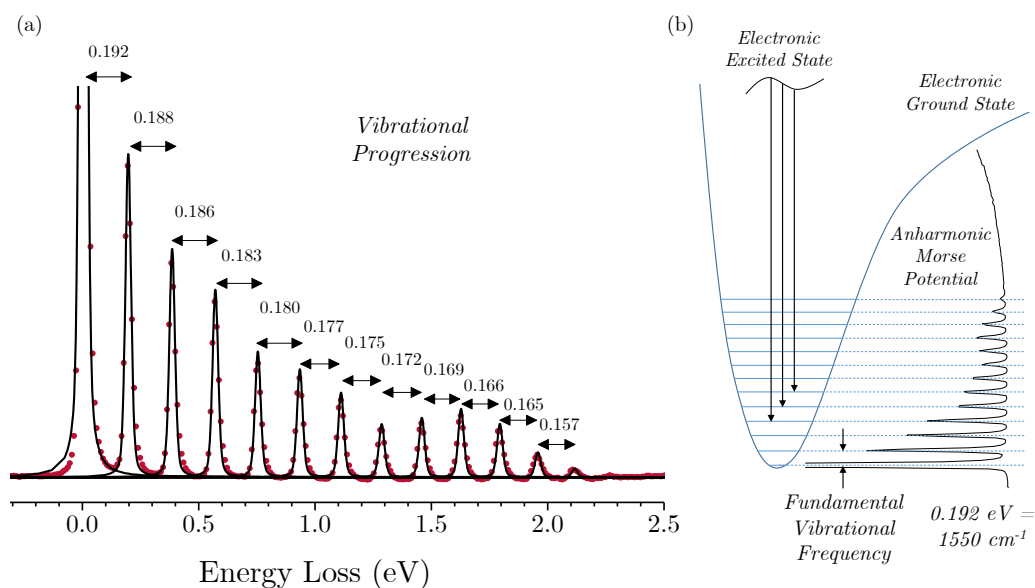


Figure 2.8: (a) RIXS data collected at 531 eV fitted to extract peak spacing which decreases in size with increasing energy loss. (b) Schematic illustrating the origin of the RIXS peak progression derived from the vibrational energy levels of an anharmonic oscillating O₂ diatomic.

The series of sharp, intense peaks observed at low energy loss gives further evidence of the true nature of this new O species. The energy spacing of these peaks is consistent in magnitude with the energies of vibrational transitions (0.01 eV - 1 eV) as opposed to electronic transitions (typically 100 - 10,000 eV). Closer analysis of the peak spacing reveals that, with increasing energy loss, the peaks get gradually closer together, Figure 2.8 (a). This is consistent with the anharmonic behaviour of vibrating diatomic molecules which, according to quantum mechanics, exhibit quantised vibrational energy levels which become increasingly closely spaced at higher energies due to the bond dissociation, Figure 2.8 (b). Furthermore, the energy spacing of the lowest two peaks corresponds closely to the fundamental vibrational frequency of molecular O₂ (0.192 eV or 1550 cm⁻¹).

After absorption of a photon at 531 eV, O (in the form of O₂) is in an electronically excited state. When this excited state relaxes back to the electronic ground state (through an electronic transition from the valence band to fill the core-hole), it is possible for the O₂ molecule to transition to a higher vibrational energy level than

the ground vibrational state. When it does so, the energy of the emitted photon is less than the elastic energy by the same amount as the energy difference between the two vibrational energy levels, hence giving rise to a vibrational progression of peaks. This phenomenon is similar in principle to rotational-vibrational spectroscopy used by molecular spectroscopists to characterise gas molecules using Infrared or Raman, but here with RIXS the peak progression reveals the spacing of the vibrational energy levels through electronic transitions rather than the rotational energy levels through vibrational transitions.

2.5.4 Raman Spectroscopy

Raman Spectroscopy allows the study of the vibrational frequency of Raman-active chemical bonds (those which undergo a change in polarisability when vibrating).³⁴ When a sample is irradiated with a monochromatic laser light (usually in the visible range) a tiny fraction of the light is scattered inelastically having triggered an excitation between vibrational energy levels. For a simple diatomic this energy loss (typically measured in wavenumber (cm^{-1})) is characteristic of the elements at either end of the bond and its bond strength. By approximating the diatomic to a harmonic oscillator, the oscillation frequency, f , can be related directly to the force constant, k , and the reduced mass, m , using Hooke's Law,

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (2.9)$$

Where the reduced mass is given by,

$$m = \frac{m_1 m_2}{m_1 + m_2} \quad (2.10)$$

In solid state materials which consist of a network of multiply-bonded atoms, the vibrations are much more complex and depend on the symmetry of the crystal structure.³⁵ Generally, symmetric breathing mode stretches, where all of the coordinating atoms around a central atom move towards and away from the centre in synchronisation, tend to be the most intense. The identity of Raman peaks arising from vibrational modes within a crystal can be modelled computationally or

correlated to measured reference standards containing the same structural motif. Isotopic or elemental substitutions can give further information on the nature of the vibrating structural unit by shifting the frequency of the peak according to the change in mass and/or bond strength.

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3

Oxygen Redox Chemistry without Excess Alkali-ions

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3.1 Introduction

Oxygen redox has been demonstrated in a number of Li-rich and Na-rich materials (i.e. those whereby the alkali metal/transition metal ratio > 1).¹⁻⁵ These are typically layered materials with alkali metal (AM) ions, such as Li^+ or Na^+ substituted into the transition metal (TM) layer. It has been previously reported that Li^+ -O- Li^+ interactions are responsible for promoting O-redox giving rise to *orphaned*,

or unhybridised, O 2*p* orbitals.⁶ In this Chapter, P2-type $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ is investigated as a model system with Mg^{2+} , instead of Li^+ or Na^+ , occupying the TM layer in a honeycomb arrangement. Through a combination of XAS, RIXS and OEMS, this study shows that oxygen redox can be promoted by Mg and furthermore that this inhibits O-loss - a phenomenon otherwise ubiquitous among O-redox materials.^{3,7-10} This reveals the importance of iono-covalency in regulating the energy of the bonding electrons around O, and that sufficient ionicity, afforded by Li, Na or Mg, can allow access to these electronic states below the oxidative stability limit of the electrolyte.

3.2 Experimental

$\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ was prepared by solid-state reaction between stoichiometric amounts of Na_2CO_3 (Sigma 99%), MgO (Sigma 99.99%) and Mn_2O_3 (Sigma 99.9%). A 5 wt. % excess of Na was used to account for evaporation. The precursors were mixed for 2 hours at 400 rpm in a Retsch PM100 planetary ball-mill and then pressed into 13 mm diameter pellets. The reaction was carried out at 800 C for 10 hours under flowing O_2 gas with heating and cooling rates of 5 C min⁻¹. As described in more detail later, the resulting product contained a small amount of sodium carbonate. To remove this carbonate residue the as-prepared powder was subjected to a subsequent heat treatment whereby the powder was heated to 750 C at a rate of 10 C min⁻¹ and then immediately cooled to room temperature under flowing argon gas. The heat-treated material was then transferred into an Ar-filled glovebox without exposure to air.

¹⁸O-labelled $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ was prepared using the same methodology as above, except that the reaction was carried out in a sealed atmosphere of ¹⁸O₂ gas (BOC 99.9%). To ensure a clean O₂ atmosphere, the initial temperature ramping was carried out under flowing unlabelled O₂ gas to remove any CO₂ evolved from the precursors. When the temperature reached 600 C the gas was exchanged for ¹⁸O-labelled O₂ by evacuation and sealed for the remainder of the reaction.

Unless explicitly mentioned otherwise, all of the experiments in this chapter were conducted on $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ that had undergone heat-treatment under argon.

Electrodes were prepared by mixing 80 wt. % active material, 10 wt. % conductive Super P carbon and 10 wt. % polytetrafluoroethylene (PTFE) polymer binder in a mortar and pestle and then rolling out thin $\sim 100\text{ }\mu\text{m}$ free-standing films. Electrochemical testing was carried out in 1 M NaPF_6 (99.0% Kishida) in propylene carbonate (PC) (>99.0% BASF Selectilyte) electrolyte. Galvanostatic charge-discharge was carried out in CR2032 coin cells using a Maccor Series 4000 at a rate of 10 mA g^{-1} .

All diffraction measurements were conducted on an in-house 9kW Rigaku Smart Lab x-ray diffractometer using unmonochromated Cu K_α radiation and parallel beam geometry. The GSAS-II software package was used for Reitveld refinement.^{11,12} The *operando* XRD experiment was carried out using a custom-built electrochemical cell with an aluminium-coated beryllium window which acted as the positive current collector. XANES measurements were conducted at beamline B18, Diamond Light Source, Harwell. Data were reduced using Athena.¹³ Electrodes collected *ex situ* were washed with dimethyl carbonate (DMC) and dried under vacuum, then dispersed in boron nitride, pressed into pellets and sealed from the atmosphere in clear plastic for measurement without air exposure. Soft XAS and high resolution RIXS data were collected from Swiss Light Source (SLS), Paul Scherrer Institut, Switzerland. RIXS maps were collected from Advanced Light Source (ALS), Berkeley, California.

TGA-MS measurements were conducted on an in-house Netzsch Jupiter STA 449 F3 thermogravimetric analysis instrument coupled with a Netzsch Aeolos QMS 403 D mass spectrometer. Elemental composition analysis was carried out using a Perkin Elmer Optima 8000 ICP-OES. Electrodes were digested in 1 mL aqua regia and diluted with 0.2 M nitric acid for analysis in solution phase. Operando Electrochemical Mass Spectrometry (OEMS) measurements were carried out using a modified electrochemical cell from EL-CELL with gas inlet and outlet ports linked to a Bronkhorst mass flow controller and benchtop Thermo Fischer quadrupole mass

spectrometer respectively. Raman spectra were obtained using a Renishaw InVia spectrometer equipped with a diode laser ($\lambda = 785$ nm) and a low laser power of 1.5 mW. Electrode samples were sealed between two glass slides under argon atmosphere.

3.3 Results and Discussion

3.3.1 Structural Characterisation

$\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ was prepared as outlined in Section 3.2. It did not prove possible to prepare phase pure samples of $\text{Na}_{2/3}[\text{Mg}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ with complete honeycomb substitution of Mg. Instead, the composition $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ was chosen in line with the composition reported by Yabuuchi *et al.*¹⁴ which possesses some Mn^{3+} .

Powder x-ray diffraction (PXRD) data were used to refine the structure of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, which can be well described by the $\text{P6}_3/\text{mcm}$ space group, Figure 3.1 and Table 3.1. As pictured in Figure 3.2, $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ possesses the P2 structure type with Na occupying trigonal prismatic sites in the AM layer and an ABBA stacking arrangement of oxide layers. Due to charge repulsion, Mg^{2+} and Mn^{4+} order in a honeycomb arrangement within the TM layer. TM layers stack such that Mg aligns in columns along the c axis. These ordering phenomena give rise to unique Bragg peaks at 20.5 and 26.0 degrees 2θ which are additional to those arising from the P2 structure. This ordering is captured in the refinement by the $\text{P6}_3/\text{mcm}$ space group.

Atom	Wyckoff Positions	x	y	z	Occupancy	U_{iso}
Mg	2b	0	0	0	0.84	0.0102(3)
Mn	2b	0	0	0	0.16	0.0102(3)
Mn	4d	1/3	2/3	0	1	0.0102(3)
Na	4c	1/3	2/3	1/4	0.407	0.0734(18)
Na	6g	0.314(2)	0	1/4	0.399	0.0734(18)
O	12k	0.344(1)	0.344(1)	0.085(2)	1	0.0074(12)
$a = 5.0059(1)$ Å, $c = 11.2263(2)$ Å. Space Group: $\text{P6}_3/\text{mcm}$.						
$R_w = 6.91$ %, $R_{\text{exp}} = 2.36$ %.						

Table 3.1: Table of XRD Rietveld refinement parameters for $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$.

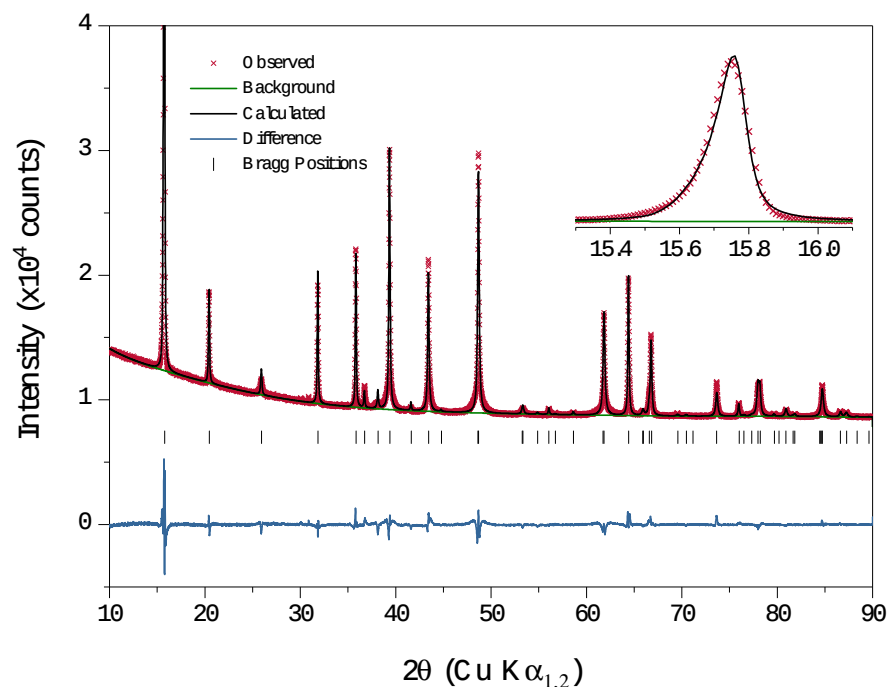


Figure 3.1: Rietveld refinement of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. Diffraction data were collected using an unmonochromated laboratory $\text{Cu K}\alpha$ X-ray source. Inset shows the fitting for the most intense P2 peak.

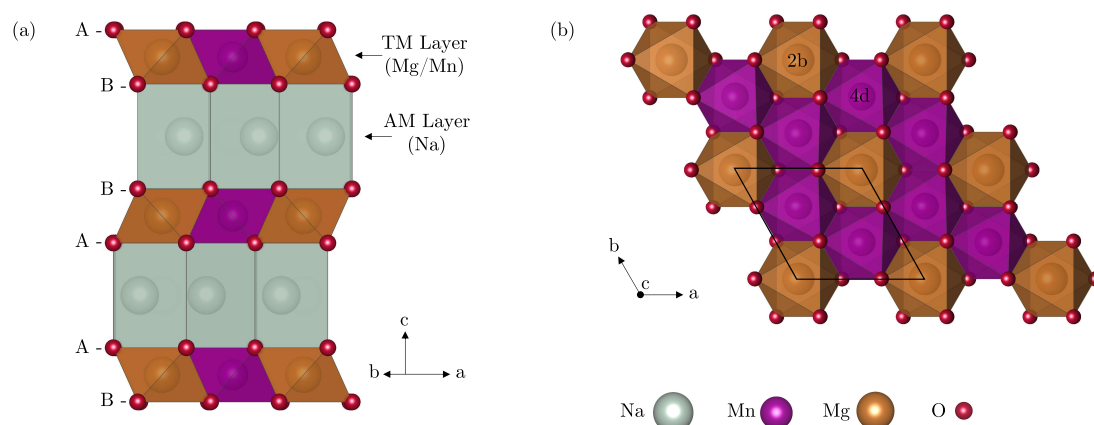


Figure 3.2: The structure of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. (a) P2-type structure with alternating octahedral TM and trigonal prismatic AM layers. Oxide layers are stacked in an ABBA arrangement. (b) Honeycomb ordering of Mg and Mn within the TM layer.

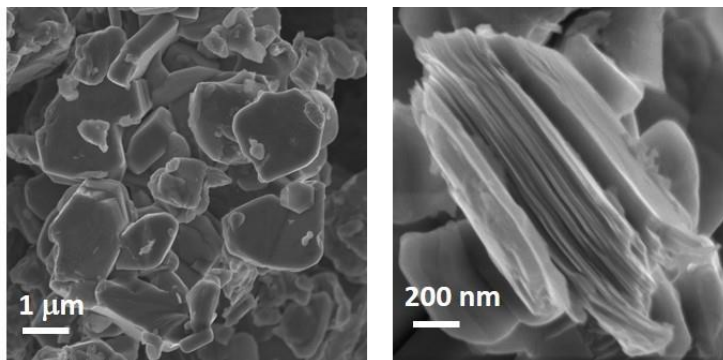


Figure 3.3: SEM images of pristine $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ powder. Particles exhibit a plate-like morphology which are typically 2-3 μm in diameter and 500 nm in thickness.

A Scanning Electron Microscopy (SEM) imaging study was conducted to understand the particle morphology of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. The images obtained, Figure 3.3, reveal a plate-like morphology with particles typically 2-3 μm in diameter and 500 nm in thickness. From the side view, the particles appear to be composed of multiple stacked slabs consistent with the layering of the crystal structure along the c-axis. This anisotropic morphology may result in c-axis dependent peak broadening in the diffraction data and would furthermore promote preferred orientation. To avoid this issue, samples were prepared for diffraction by scattering the powder over an adhesive without flattening.

3.3.2 Electrochemical Characterisation

The electrochemical behaviour of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ was examined versus a Na metal negative electrode. Since $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ is only partially sodiated in the AM layers, the material can either be charged or discharged from the pristine state. The first cycle charge-discharge load curves are shown in Figure 3.4. Upon discharging the material from the pristine state (in blue), $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ can be almost fully sodiated through a low voltage process nominally associated with reduction of Mn^{4+} to Mn^{3+} . This process is reversible, exhibiting very little difference in potential between charge and discharge.

Upon charging the material from the pristine state (in red), the load curve exhibits a short sloping region commensurate in capacity with the oxidation of the

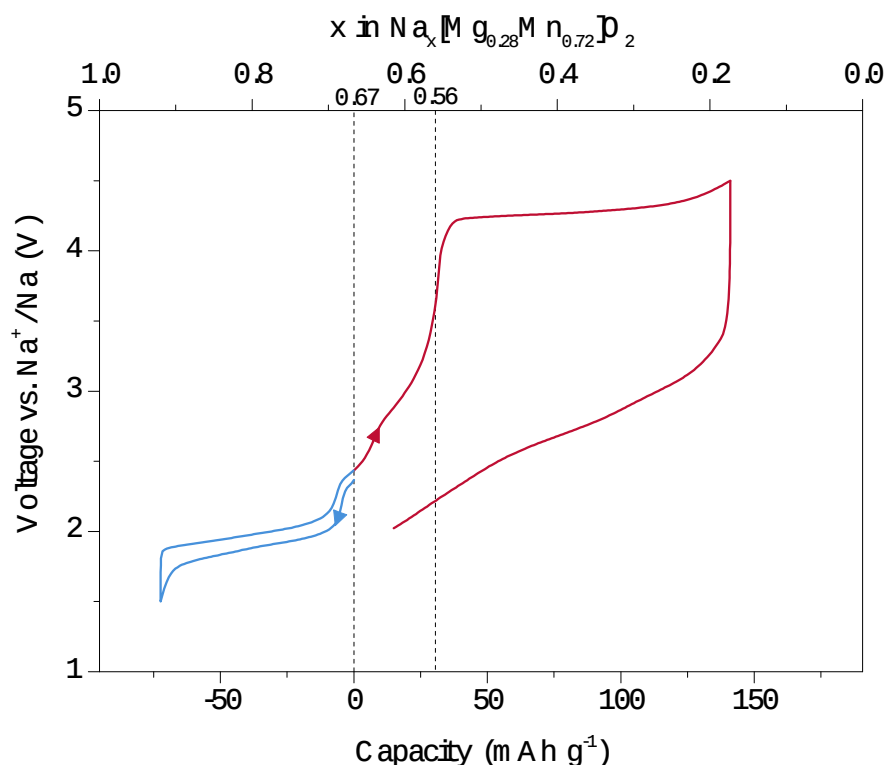


Figure 3.4: The first cycle load curve of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ cycled at 10 mA g^{-1} . Blue: discharged to 1.5 V then charged to 2.4 V. Red: charged to 4.5 V then discharged to 2.0 V.

0.11 moles of Mn^{3+} per mole of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ to Mn^{4+} . Following this, the voltage profile flattens into a long plateau at around 4.2 V with a capacity that extends far beyond the limit of Mn oxidation. Overall an additional 0.4 moles of Na and electrons can be extracted per mole of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. On subsequent discharge, almost all of the Na removed on charge can be reinserted into $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, but at a significantly reduced average potential of 2.8 V. The dramatic change in voltage profile accompanying this high potential charge compensation process clearly indicates an irreversible structural change is occurring across the plateau.

3.3.3 Structural Change

To investigate the structural evolution of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ accompanying this electrochemical behaviour, *operando* x-ray diffraction was carried out. As shown in Figure 3.5, smooth variations in the peak positions can be seen on initial charging

indicative of single phase behaviour and consistent with the sloping voltage profile. During the plateau, the peaks remain stationary but decrease in intensity as the electrode undergoes a two-phase transition. The second phase exhibits only one pronounced Bragg peak at $2\theta = 18.2$ degrees characteristic of the most prominent diffraction peak belonging to an O2-type layered structure with decreased interlayer spacing (approximately 4.9 Å vs. 5.6 Å for pristine $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$). This peak can be indexed as 002 arising from the periodic stacking of TMO_2 layers along the axis normal to the layers (c-axis).

The P2 to O2 transition is well known in layered Na-ion positive electrode materials.^{15–18} Upon removal of sufficient Na^+ from the AM layers, the TMO_2 slabs, whose oxide layers align directly with one another on opposite sides of the AM layers, shear, changing their stacking from ABBA to ABAC thereby replacing the trigonal prismatic AM sites with octahedral sites. In P2-type $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, the two phase transition to O2 is fully reversible on discharge, reforming P2 as Na is reinserted via a two phase discharge process.¹⁵ However, in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, there is no reverse plateau and instead a continuous sloping voltage profile is observed from the electrochemistry indicative of a single phase reaction process. This is directly corroborated by the diffraction data where a continuous shift of the 002 peak is observed back to a similar 2θ angle to that of the pristine P2. In contrast to the pronounced inversion between clearly separated P2 and O2 phases that occurs on charge, this implies that on discharge the interlayer spacing increases uniformly throughout the electrode. The resulting Bragg peaks at the end of discharge do not possess the same sharpness or intensity as those of the pristine, implying a mix of stacking types remains and that the P2 has not completely reformed.

The distinct difference in structural reversibility of the P2-O2 transition between $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, which is a close analogue system with honeycomb ordering but with sufficient Ni redox capacity to account for all Na extracted, would appear to be related to oxidation beyond the TM limits. To understand this in more depth, it is important to address the question, 'what

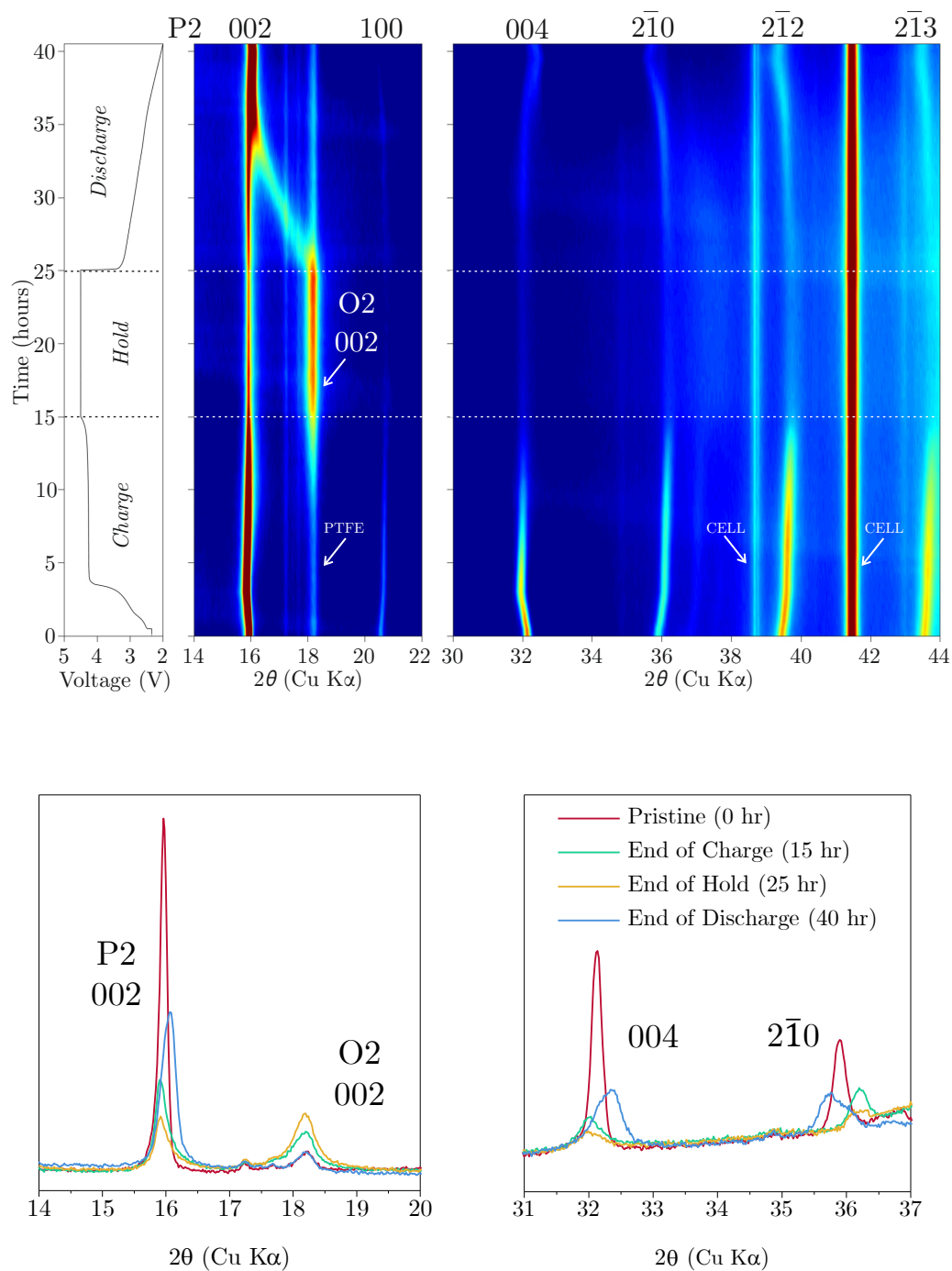


Figure 3.5: The first cycle load curve of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ monitored by *operando* XRD. The cell was charged galvanostatically to 4.5 V, held at a potential of 4.5 V for 10 hours, then discharged galvanostatically to 2.0 V. The current was set at 10 mA g^{-1} on charge and discharge.

is the redox mechanism in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ that compensates the removal of Na beyond oxidation of the TM?’

3.3.4 Oxygen Loss

One possible explanation for the anomalous charging capacity is irreversible oxidation and loss of oxide ions from the lattice either directly as evolved O_2 and/or as CO_2 gas from reaction with the electrolyte molecules.^{7,19,20} This necessarily means that any capacity observed on subsequent discharge must be from TM reduction alone, on account of loss of the oxidised species from the electrode. Such phenomena have been observed before in many materials exhibiting capacity beyond TM oxidation and is generally accepted to contribute, at least in part, to the excess capacity observed.^{8,9,21–23}

The simplest reaction that can be considered:



shows that a direct, quantitative relationship between the amount of evolved O_2 gas and the amount of Na (and electrons) extracted from the electrode on charge can be made. However, for CO_2 , the case is less clear since the reaction pathway involves the breakdown of electrolyte solvent molecules.^{19,20,24,25}

To investigate oxygen loss in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, *operando* electrochemical mass spectroscopy (OEMS) was carried out. The results presented in Figure 3.6 show that, in contrast to all measured examples of materials exhibiting O-redox, no O_2 is evolved throughout the first charge-discharge cycle of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and thus oxidised O is not lost directly as O_2 . A small amount of CO_2 is observed across the plateau, 0.009 moles per mole of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, which, when compared with the amount of excess capacity, 0.4 moles of electrons per mole of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, represents a negligible fraction.

Another possible source of CO_2 gas is electrochemical oxidation of sodium carbonate, a well-known contaminant of Na-ion materials, at potentials above 3.5 V vs. Na^+/Na (3.8 V vs Li^+/Li).^{26–29} This occurs according to the following equation:

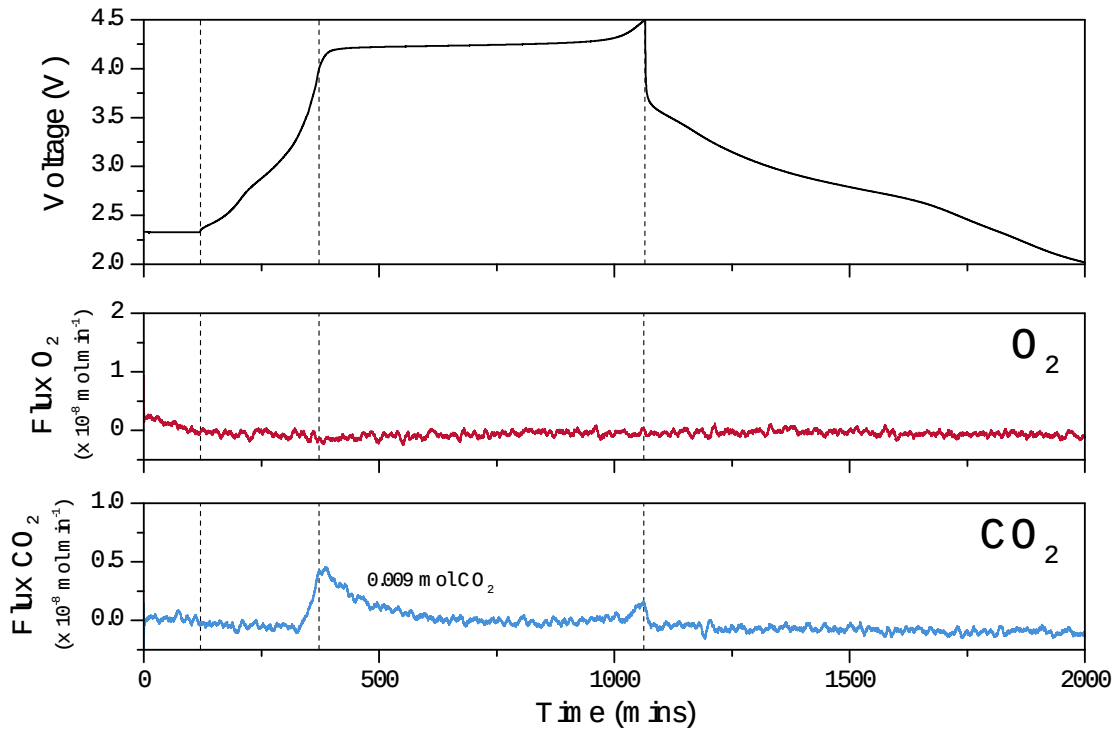
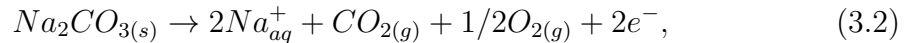


Figure 3.6: The first cycle load curve of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ monitored by *operando* mass spectrometry. Oxygen ($m/z = 32$) and carbon dioxide ($m/z = 44$) were monitored for the duration of the experiment.



To examine whether there was any sodium carbonate present in as-prepared $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, TGA-MS measurements were performed. This technique allows monitoring of the change in mass of a sample as a result of loss (or gain) of gas induced by heating. As shown in Figure 3.7, the sample of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ tested straight after preparation in O_2 at 800 C show a 1 % loss of mass upon heating under argon to 750 C accompanied by some CO_2 and O_2 gas suggesting contamination of the sample by about 2 mol % Na_2CO_3 . To counter this, an additional synthesis step was developed to remove Na_2CO_3 by subjecting the sample to the same heating regime as the TGA-MS measurement under argon to 750 C before cooling the sample to room temperature and transferring into a glovebox without air exposure. Samples prepared with this additional step showed negligible

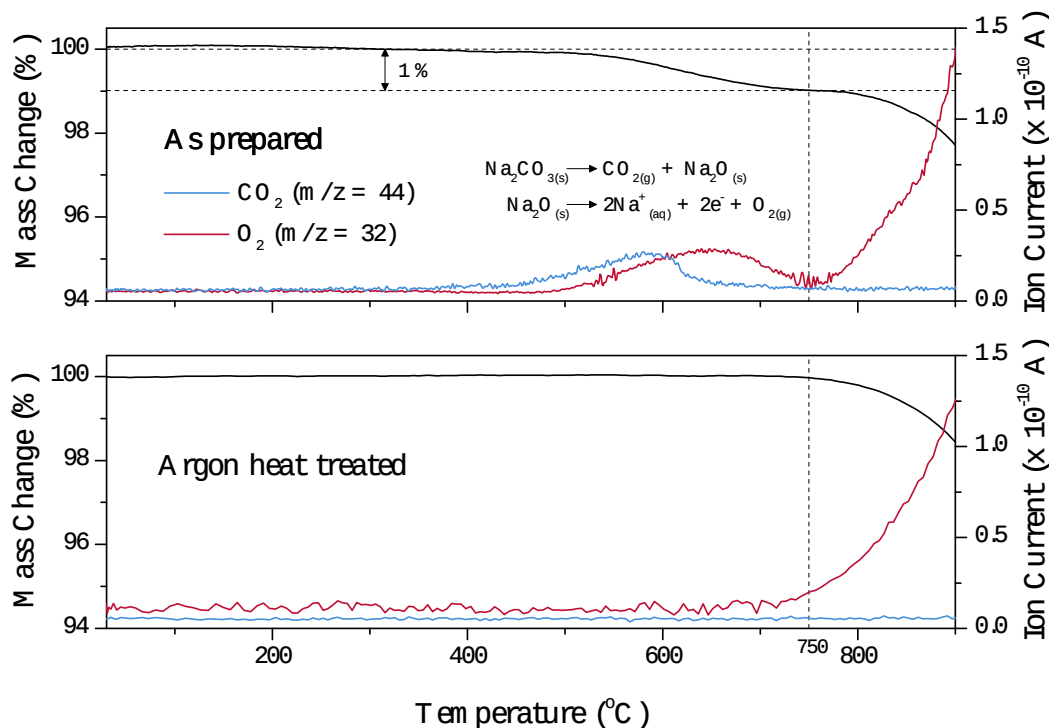


Figure 3.7: Thermogravimetric analysis coupled with mass spectrometry was used to analyse as prepared $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ for Na_2CO_3 impurity. CO_2 and O_2 are evolved below 750 C. After heat treating to 750 C under argon atmosphere, negligible impurity remains.

contamination when tested, Figure 3.7, thus this methodology was employed for making all of the samples characterised in this chapter.

To investigate the effect of sodium carbonate impurities on gas release in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, *operando* electrochemical mass spectroscopy (OEMS) was carried out on samples with different amounts of the contaminant. The data, presented in Figure 3.8 (a) and (c), show samples tested before and after the argon heat treatment synthesis step respectively. During the charging plateau, both samples exhibit a small amount of CO_2 release but no O_2 . Comparing between the responses of these samples it is clear that carbonate residue contributes to the gases evolved on charge.

To confirm the role of Na_2CO_3 as an active participant during the oxidation of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and quantify its contribution, OEMS was conducted on an electrode prepared with 10 wt. % added Na_2CO_3 . The results in Figure 3.8 (b)

show an increased quantity of CO_2 and a larger charging capacity compared with the electrode without carbonate. By finding the difference between the number of moles of Na_2CO_3 present per mole of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ in each sample with the moles of CO_2 gas evolved and electrons passed on charge between each sample it is possible to deduce that the electrochemical oxidation reaction of Na_2CO_3 matches that in Equation 3.2. Using this relation it is clear that the amount of residual carbonate present in the sample tested in Figure 3.6 and Figure 3.8 (c), giving rise to 0.009 moles of CO_2 , is not sufficient to account for any more than 5% of the charging plateau capacity.

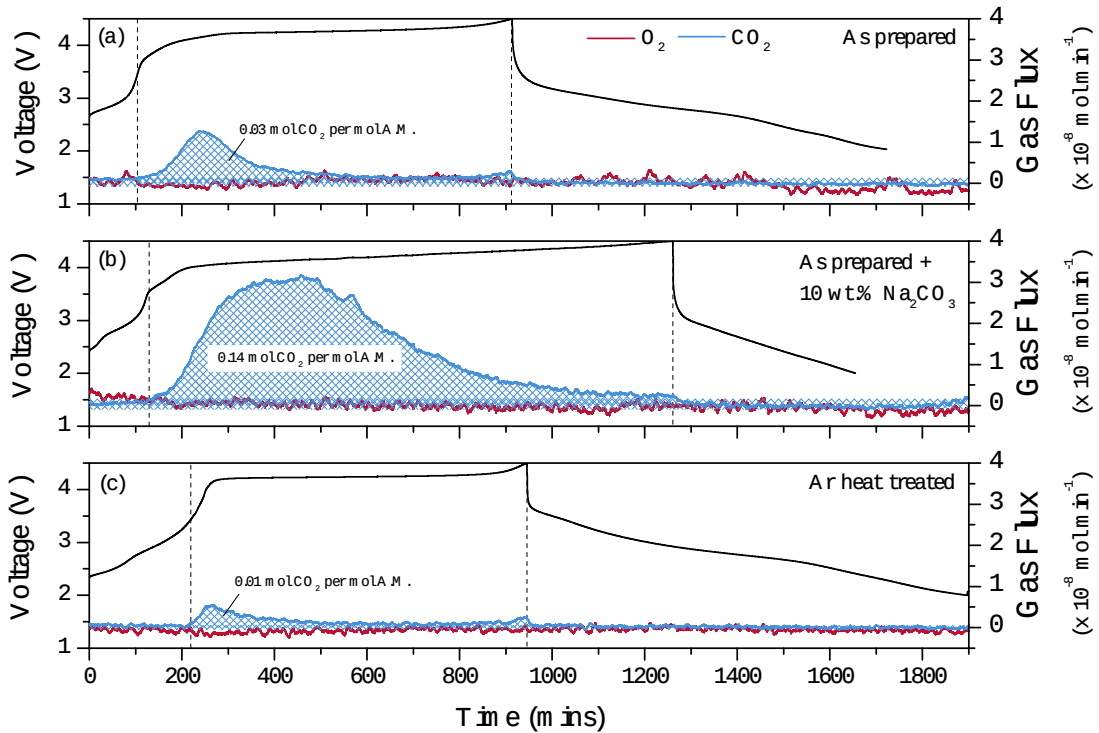


Figure 3.8: The first cycle load curve of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ (black) monitored by *operando* mass spectrometry. Oxygen ($m/z = 32$) and carbon dioxide ($m/z = 44$) were monitored for the duration of the experiment. (a) As prepared $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ without further heat treatment. (b) As prepared $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ mixed with 10 wt. % added Na_2CO_3 . (c) As prepared $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ subjected to post-synthesis heat treatment under argon atmosphere. As prepared $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ was heated to 750 C at 10 C min^{-1} , then removed from the furnace and cooled under ambient conditions, all without exposure to moisture or oxygen.

The absence of evolved O_2 gas is notable, however, it has recently been found that electrochemical oxidation of carbonates results in a reactive, excited state of oxygen

	moles of Na ₂ CO ₃ per mol A.M.	moles of e ⁻ stored per mol A.M.	moles of CO ₂ gas per mol A.M.
As prepared	0.02(1)	0.54(1)	0.03(1)
As prepared + 10wt.% Na ₂ CO ₃	0.11(1)	0.74(1)	0.14(1)
Difference	0.09(1)	0.20(1)	0.11(1)

Table 3.2: Table of charge capacity (e⁻ stored per mol A.M.) and gas quantities for as prepared Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ with and without added Na₂CO₃ from OEMS.

(singlet O₂) that immediately reacts with the electrolyte to form decomposition products thus masking its presence.³⁰

3.3.5 Spectroscopic Characterisation

Having established that the plateau charging capacity is not explained by loss of oxidised oxygen species from the electrode or by carbonate impurities, the origin must therefore be rooted in oxidation processes intrinsic to the cathode. Since Mg²⁺ is redox inactive, the only remaining possibilities are oxidation of Mn beyond +4, or oxidation of oxide ions. To probe changes to the oxidation states of Mn and O, Mn K-edge XANES and O K-edge XAS were employed on *ex situ* samples at different states of charge.

Mn K-edge XANES

As shown in Figure 3.9 (b), the main edge of the Mn K-edge for pristine Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ is at a slightly lower energy than that of Li₂MnO₃, wherein Mn exhibits the +4 oxidation state. This is consistent with the expected average oxidation state of +3.85 for Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂. During charge through the initial sloping region, which is commensurate in capacity with oxidation of the remaining 0.11 moles of Mn³⁺ to Mn⁴⁺, the position of the main edge shifts such that it ends up closely matching that of the +4 reference material. Across the plateau, no further shift in energy of the main edge is evident despite 0.4 moles of electrons being removed from Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂. This indicates that Mn remains at +4 and is not further oxidised as otherwise further continuous shift of the edge would be expected. Upon discharge, the edge gradually shifts back to energies slightly lower than that of

Li_2MnO_3 , but even at the end of discharge still remains significantly higher than Mn_2O_3 , the Mn^{3+} standard, confirming that Mn is not over-reduced on discharge, consistent with the absence of oxygen loss.

O K-edge XAS

Given the absence of oxidation of Mn beyond +4 from XANES, the excess capacity on charge and discharge must be accompanied by redox of the oxide ions in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. O K-edge data, presented in Figure 3.9 (c), show that on charging across the plateau a new feature at 531 eV appears between the two pronounced peaks of the pre-edge. Since the O K-edge represents electronic transitions from the filled 1s core-level to empty O 2p orbitals, which are hybridised with Mn 3d orbitals, an increase in the intensity of the pre-edge indicates a higher density of electron holes in the O 2p/Mn 3d band.^{21,31} From XANES, the Mn oxidation state is shown to remain invariant at +4, thus the new intensity under the pre-edge at 531 eV can be attributed exclusively to electron holes located predominantly on oxide ions.

It is important to note here that, while intensity changes at the O K-edge due to the increased prevalence of a certain O species should be correlated to the number of electron hole states belonging to that specific O species, there are a number of reasons why it is not possible to quantitatively determine the amount of electron holes on one O species compared to another, nor is it possible to measure one O species in absolute terms. Firstly, electronic transitions between orbitals on different O species do not necessarily occur with the same transition strength even for the same excitation energy. Also, different O species will not necessarily have the same density of electronic states at a given energy. Both of these reasons may lead to weaker representation from certain O species than others. Secondly, although fluorescence spectroscopy is sensitive to the bulk of a particle there is inevitably surface bias since the photon beam will be attenuated by the sample to a greater extent the deeper the photons go below the surface. Therefore, if one species is predominantly present in the bulk it will be under-represented in

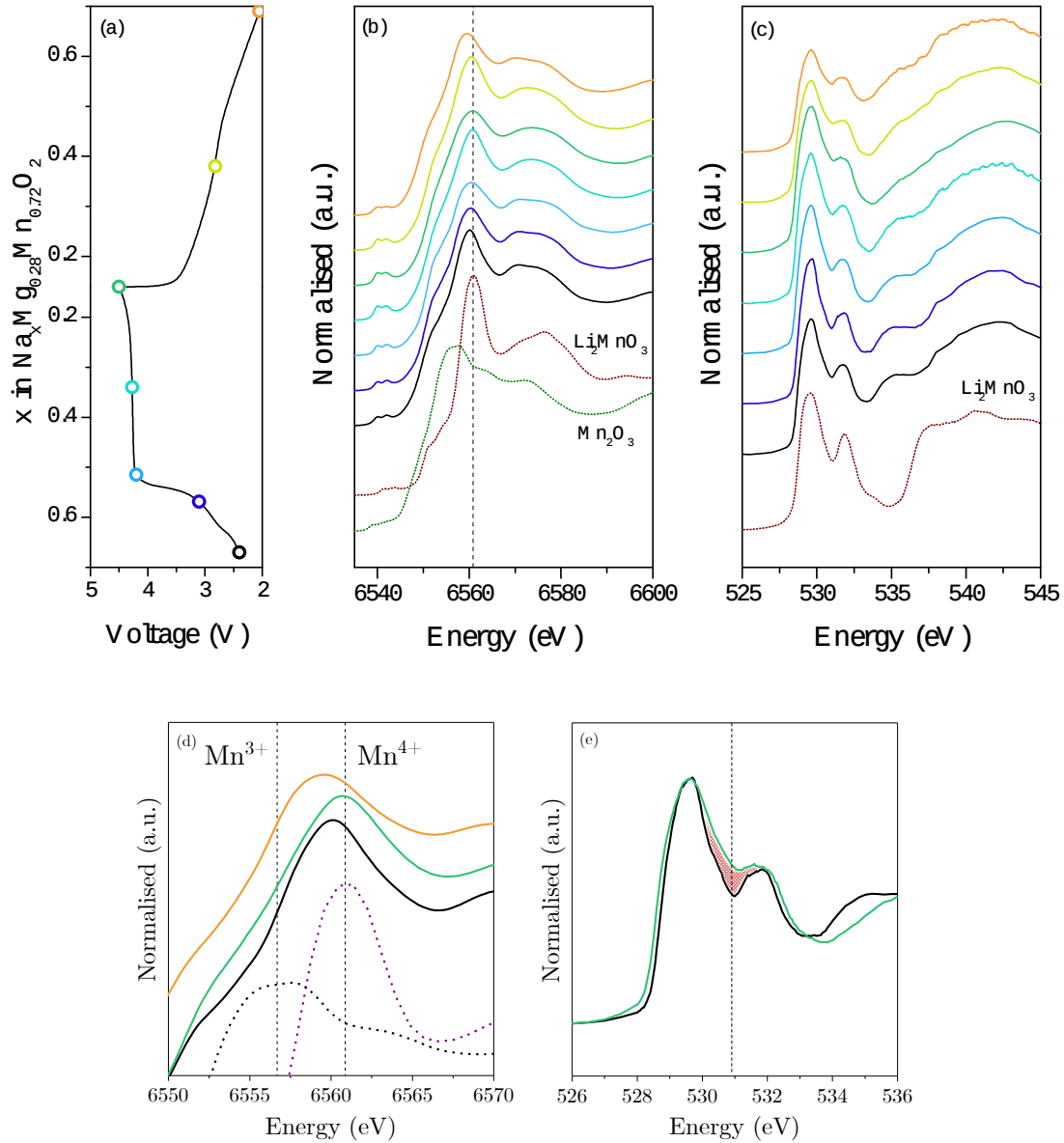


Figure 3.9: (a) The first cycle load curve of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ with states of charge chosen for *ex situ* analysis. (b) *Ex situ* Mn K-edge XAS data as a function of state of charge. Reference spectra for Mn_2O_3 (Mn^{3+}) and Li_2MnO_3 (Mn^{4+}) are shown below. (c) O K-edge XAS data as a function of state of charge. The reference spectrum for Li_2MnO_3 is shown below. (d) Close-up of Mn K-edge XAS data. (e) O K-edge XAS data highlighting increase in pre-edge intensity at 531 eV between pristine and charged states of charge.

the K-edge intensity. Finally, without an internal reference of the specified O species present in a known amount, it is not possible to convert between area and electron hole states to determine the number belonging to that species present in an unknown amount in the sample.

However, from the electrochemical curve, Figure 3.4, it is possible to calculate how many electron holes that should be stored on O at the end of the plateau. Overall, 0.4 moles of electrons and Na^+ ions are extracted per formula unit and, since there is negligible O loss observed, these electron holes must reside on O remaining in the sample. This would correspond to an average oxidation state change from O^{2-} to $\text{O}^{1.8-}$, or, if oxidised O were in the form of $(\text{O}_2)^{2-}$ or O_2 , the percentage of the O that is in the form of each of these species would be 20 % and 10 % respectively.

O K-edge RIXS

To further investigate the nature of these electron hole states on oxygen, RIXS measurements were carried out at different states of charge. RIXS is an inelastic x-ray emission technique which detects radiation emitted from electronic transitions between filled states in the valence band and empty states in the 1s core-levels.³² By varying the excitation energy of the incident x-ray beam across the O K-edge and observing the energy resolved emission spectra, the valence band can effectively be mapped out. These data are presented for $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ at different states of charge in Figure 3.10 (a). Notably, two significant new spectral features can be seen in the RIXS map at the end of charge, highlighted with the letters A and B. The first of which, A, is a narrow inelastic peak at 523 eV emission energy, and the second, B, a faint intensity increase of the elastic peak at 531 eV emission energy. Both of these features are localised in energy appearing only at an excitation energy of 531 eV (± 0.5 eV), corresponding to exactly the same energy of the new feature seen in the O XAS pre-edge.

These unique XAS and RIXS features appearing after the plateau are strong evidence of a reconfiguration of the electronic structure around O as a result of O oxidation. Specifically, they are direct evidence of the creation of new electron

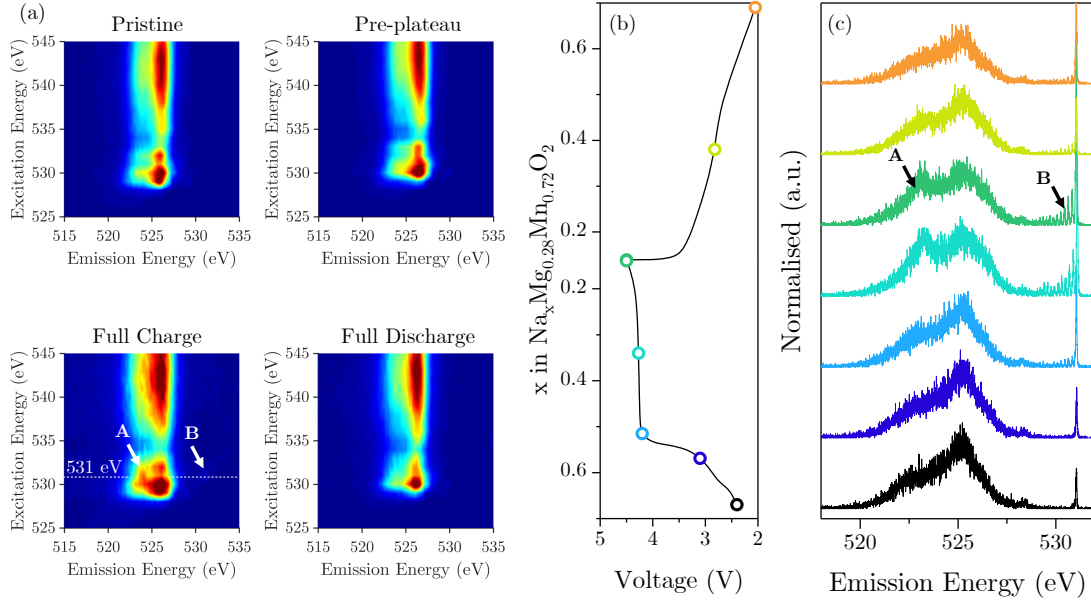


Figure 3.10: (a) RIXS maps of Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ at different states of charge measured at ALS, Berkeley by Dr James Somerville and Dr Urmimala Maitra (b) The first cycle load curve of Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ with states of charge chosen for *ex situ* analysis. (c) High resolution RIXS spectra at 531 eV excitation energy measured at SLS, Switzerland by Dr Urmimala Maitra. The materials were prepared by Dr Urmimala Maitra.

hole states in the conduction band and filled states in the valence band which are localised exclusively on O in Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂. The fact that they are not detected in the discharged samples suggests that whatever restructuring has taken place with O oxidation has been reversed upon reduction. Further insight into these features is provided by higher resolution data obtained at the Swiss Light Source, Switzerland.³³ The data presented in Figure 3.10 (c) show emission spectra collected only at 531 eV excitation energy - the region of interest of the O K-edge. Feature B can now be resolved into a progression of low-energy loss peaks. The origin of these peaks will be discussed in more detail in Chapter 5 but it is important to note their presence here for Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂.

Raman

One theory that has been proposed to explain the nature of oxidised oxygen in O-redox electrode materials is that they exist as peroxo-like species.^{3,9,34,35} In this

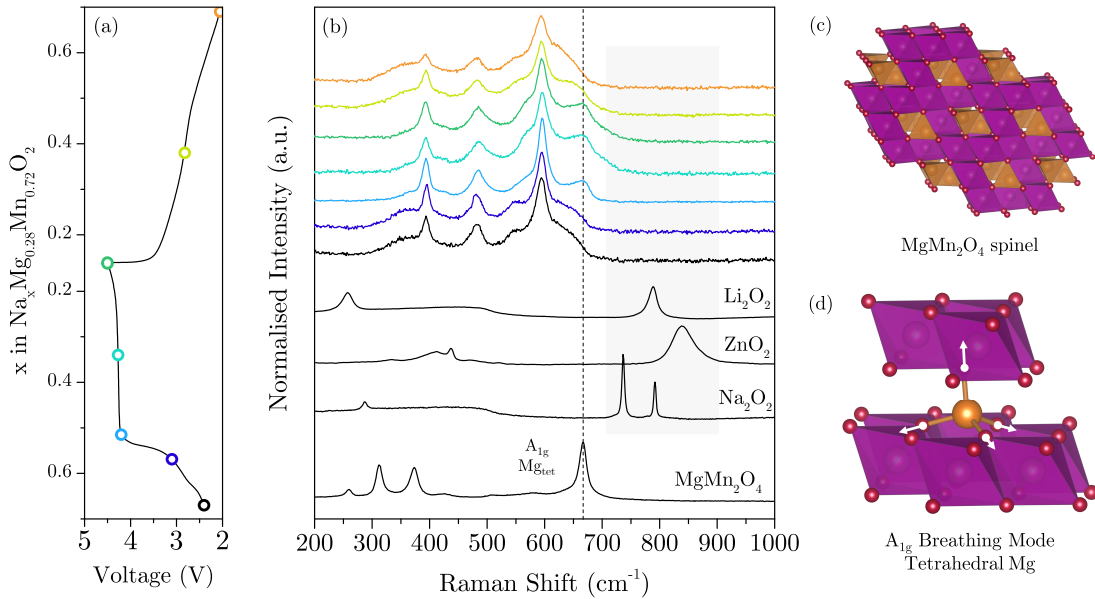


Figure 3.11: (a) The first cycle load curve of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ with states of charge chosen for *ex situ* analysis. (b) *Ex situ* Raman spectra as a function of state of charge. Reference spectra for $(\text{O}_2)^{2-}$ peroxide-containing Li_2O_2 , ZnO_2 and Na_2O_2 and MgMn_2O_4 spinel with tetrahedral Mg^{2+} are shown below.

theory, the removal of electrons from oxide ions is accompanied by a distortion of the oxide sublattice resulting in shorter O-O distances (from around 2.5 Å to 1.4 - 1.9 Å) resembling that of peroxides $(\text{O}_2)^{2-}$. To probe the possibility of peroxo-like O-O dimers being present here in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, Raman spectroscopy was employed. Unlike Infrared spectroscopy, Raman is sensitive to vibrations of homonuclear diatomic species making it a well suited tool to detect O-O bonding.³⁶ Raman spectra were collected for $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ at different states of charge and are shown in Figure 3.11 along with spectra collected for three peroxide reference samples. The data show a striking absence of features for $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ within the range of shifts characteristic of peroxide O-O vibrations from 700-900 cm^{-1} , ruling out the presence of peroxo-like species.³⁷

Instead, a new feature at 665 cm^{-1} appears across the charging plateau and disappears on charge. This feature is an exact match to one belonging to MgMn_2O_4 spinel, Figure 3.11, (c). In this material (and related spinel phases) the peak arises from the A_{1g} breathing mode of the Mg-O bonds around a Mg atom in tetrahedral coordination Figure 3.11, (d).^{38,39} The tetrahedral sites in spinel structures are face

sharing with octahedral vacancies which themselves are surrounded by a plane of 6 octahedral Mn atoms. This structural motif bears remarkably close resemblance to the structure of fully desodiated O2-type $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ where Mg has displaced out of its site in the honeycomb ordered TM layer into a face-sharing tetrahedral vacancy in the AM layer. The close match of the Raman shifts between MgMn_2O_4 and charged $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ could suggest that Mg migration out of the TM layer is occurring during the charging plateau in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ leaving a honeycomb ordered arrangement of vacancies in the TM layer. As demonstrated later in Chapter 5, this ordered vacancy configuration is in fact highly unstable and liable to Mn migration.

3.3.6 Role of Magnesium

Previous work on layered Li-rich electrode materials, such as $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$, has demonstrated the important role of the Li in the AM layer in promoting O-redox.^{6,22,23} With Li in both the AM and TM layers, certain O^{2-} ions are coordinated on either side by Li^+ in a linear $\text{Li}^+-\text{O}-\text{Li}^+$ configuration. The ionic nature of the Li-O bonding places these O $2p$ states at the top of the valence band allowing access to bonding electrons at a voltage sufficiently low (4.5 - 4.6 V vs. Li^+/Li or 4.2 - 4.3 V vs. Na^+/Na) to lie below the oxidative limit of the electrolyte (~ 4.8 V vs. Li^+/Li or ~ 4.5 V vs. Na^+/Na).⁶ The remaining O $2p$ states are situated much lower in the valence band due to more covalent bonding with Ni, Co and Mn, whose $3d$ orbitals overlap well with O $2p$. In this way alkali ions in the TM layer effectively promote O-redox.

In $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, despite having no excess alkali ions in the TM layer, there is still substantial O-redox capacity showing that excess alkali ions are not essential to promote O-redox. Instead, electrochemically inactive Mg^{2+} sits in a honeycomb arrangement surrounded by Mn^{4+} such that each O^{2-} is coordinated by one Mg^{2+} and two Mn^{4+} . As a Group 2 element, Mg^{2+} has $3s$ valence states that overlap poorly in energy with the O $2p$ states leading to ionic Mg-O bonding similar to that of Li-O. This ionic bonding environment around the O again places

the O 2p states at the top of the valence band rendering them readily accessible for oxidation within the electrolyte stability window, Figure 3.12. This shows that the trigger to O-redox is not simply the presence of excess AM ions in the TM layer, but rather, more broadly, ionic bonding interactions around O that can be promoted by elements other than Li and Na.

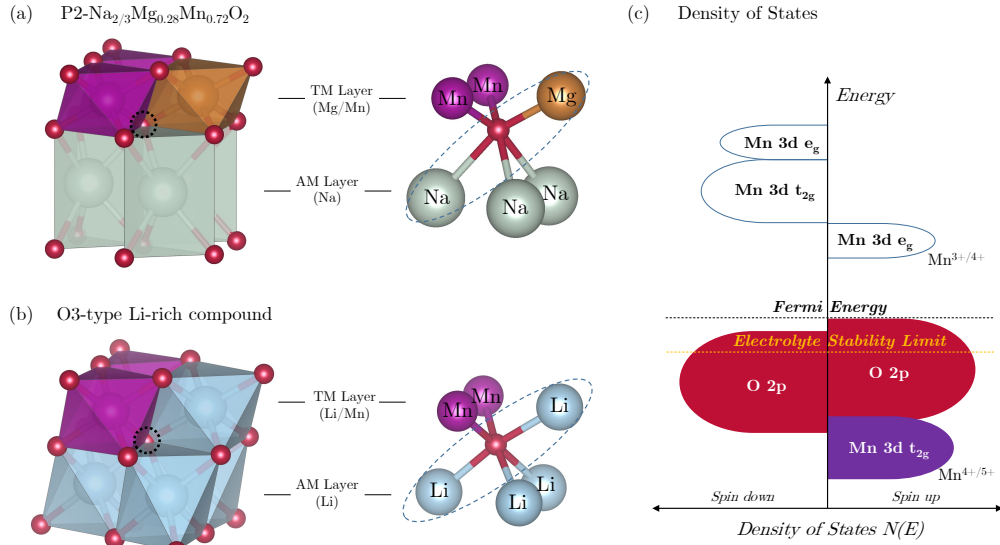


Figure 3.12: (a) The local coordination environment around O in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. (b) The local coordination environment around O in a lithium rich compound such as $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$. (c) Spin resolved Density of States schematic for ideal $\text{Na}_{2/3}[\text{Mn}_{1/3}\text{Mn}_{2/3}]\text{O}_2$. As a result of the ionic bonding environment around O, O 2p states are dominant near the top of the valence band and accessible within the voltage stability window of the electrolyte. The $\text{Mn}^{4+/5+}$ redox couple is too high in voltage to be accessed since the filled Mn 3d states are too deep in energy.

In stark contrast to all measured examples of Li-rich (and Na-rich) electrode materials, $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ does not lose O. In most Li-rich materials, upon charge, Li-ions are removed from both the TM and AM layers leaving a host structure with a significant density of vacant cation sites.^{40,41} Specifically, at high degrees of deintercalation oxidised oxygen starts to become severely under-bonded by cations (i.e. fewer than three remaining) exposing some O 2p orbitals that are completely uncoordinated. It is at these highly delithiated states that O-loss is observed from experiment suggesting that under-bonded, oxidised O is the reactive precursor to

O₂ formation and evolution. However, in Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ there are no AM ions in the TM to be removed on charge, instead, Mg²⁺ ions occupy the centre of the honeycomb in the TM layer. To examine whether Mg²⁺ ions are completely extracted from the material on charge, ICP-OES chemical analysis was employed on electrode samples collected *ex situ*. The results presented in Table 3.3 show that, despite the mobility of Mg²⁺ ions within Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ suggested by Raman, Mg is completely retained by Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ throughout the first charge-discharge cycle. This means that, even at the highest state of deintercalation at the end of charge, oxidised O remains coordinated by at least 3 cations. This will be explored in more detail in Chapter 4.

	Na	Mg	Mn
Pristine	0.66(2)	0.26(2)	0.72
4.5 V	0.17(2)	0.26(2)	0.72
2.0 V	0.77(2)	0.26(2)	0.72

Table 3.3: Elemental composition data of Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ from ICP-OES at different states of charge.

3.4 Conclusion

The presence of excess AM ions in the TM layer of O-redox compounds is not essential to promote O-redox. Here, studies on the model material Na_{0.67}[Mg_{0.28}Mn_{0.72}]O₂ show that O-redox can be achieved with Mg²⁺ in the TM layer. The important chemical trigger for O-redox is ionic bonding between O and coordinating cations on opposite sides (Na⁺-O-Mg²⁺ in this case) that gives rise to O 2*p* orbitals whose electronic states consequently appear near the top of the valence band. These ionic O 2*p* bonding states are higher in energy than those covalently bonded to TMs and are sufficiently high in energy (low in voltage) to be accessible below the oxidative voltage limit of the electrolyte.

Furthermore, the presence of Mg²⁺ in the TM layer in place of AM ions suppresses oxygen loss. Although Mg²⁺ appears to displace from octahedral sites in the TM layer to tetrahedral sites in the AM layer during charge, it is not removed from

$\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. This prevents oxidised oxygen from becoming severely under-bonded and reacting to form O_2 gas. The structural triggers for O-loss will be explored in more depth in Chapter 4.

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4

Understanding what Triggers Oxygen Loss

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4.1 Introduction

Oxygen loss is very commonly observed in oxygen redox materials. It has been detected in both Li-rich and Na-rich compositions and across systems based on *3d*, *4d* and *5d* TMs including Li_2MnO_3 , $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$, $\text{Li}_4\text{FeSbO}_6$, $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$, Li_2IrO_3 and Na_2IrO_3 .¹⁻⁶ Despite historic contention in the field around whether O-loss from the lattice can explain all of the anomalous capacity observed from

Li-rich materials, it is now widely accepted that irreversible O-loss only contributes in part to the charge compensation mechanism and the rest can be attributed to O-redox.⁷⁻⁹ Nevertheless, O-loss still represents a critical shortcoming of O-redox materials and the underlying structural and chemical triggers remain largely unknown, lessening their commercial potential.

In Chapter 3, $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ was shown to be a unique exception to the established trend exhibiting O-redox without O-loss. This was attributed to the presence of Mg rather than excess Li or Na in the TM layer. In this chapter P2-type $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ is investigated as a model system to better understand the relationship between alkali-ion excess and O-loss. This compound presents an interesting case for study possessing a TM layer of honeycomb ordered Li and Mn, analogous to other Li-rich O-redox materials but with Na in the AM layer rather than Li. Because of the segregation of Li and Na in this way, the roles of the alkali-ions in the TM and AM layers can be distinguished. Like-for-like comparison of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and its structural analogue $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, reveals that O-loss is triggered by the removal of a sufficient number of alkali-ions from the AM and TM layers such that the number of coordinating cations around O falls below three. This is ultimately governed by the ease of extraction of the TM layer substituent from the lattice.

4.2 Experimental

$\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ was prepared by solid-state reaction between stoichiometric amounts of Na_2CO_3 (Sigma 99%), Li_2CO_3 (Aldrich 99.0%) and Mn_2O_3 (Sigma 99.9%) with a 5 wt. % excess of Na and Li to account for evaporation. The precursors were mixed for 2 hours at 400 rpm in a Retsch PM100 planetary ball-mill and then pressed into 13 mm diameter pellets. The reaction was carried out at 800 C for 10 hours under flowing O_2 gas with heating and cooling rates of 5 C min^{-1} . The resulting product contained a small amount of sodium carbonate. To remove this carbonate residue the as-prepared powder was subjected to a subsequent heat treatment whereby the powder was heated to 700 C at a rate of 10 C min^{-1} and then

immediately cooled to room temperature under flowing argon gas. The heat-treated material was then transferred into an Ar-filled glovebox without exposure to air.

^{18}O -labelled $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ was prepared using the same methodology as above, except that the reaction was carried out in a sealed atmosphere of $^{18}\text{O}_2$ gas (BOC 99.9%). To ensure a clean O_2 atmosphere, the initial temperature ramping was carried out under flowing unlabelled O_2 gas to remove any CO_2 evolved from the precursors. When the temperature reached 600 C the gas was exchanged for ^{18}O -labelled O_2 by evacuation and sealed for the remainder of the reaction.

Unless explicitly mentioned otherwise, all of the experiments in this chapter were conducted on $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ that had undergone heat-treatment under argon.

Electrodes were prepared by mixing 80 wt. % active material, 10 wt. % conductive Super P carbon and 10 wt. % polytetrafluoroethylene (PTFE) polymer binder in a mortar and pestle and then rolling out thin $\sim 100\text{ }\mu\text{m}$ free-standing films. Electrochemical testing was carried out in 1 M NaPF_6 (99.0% Kishida) in propylene carbonate (PC) (>99.0% BASF Selectilyte) electrolyte versus a Na metal anode. Galvanostatic charge-discharge was carried out in CR2032 coin cells using a Maccor Series 4000 at a rate of 10 mA g^{-1} .

X-ray diffraction data were collected at the Advanced Photon Source, Chicago using monochromated X-ray radiation $\lambda = 0.4128\text{ }\text{\AA}$. The GSAS-II software package was used for Reitveld refinement.^{10,11} XANES measurements were conducted at beamline B18, Diamond Light Source, Harwell. Data reduction was performed using Athena.¹² Electrodes were dispersed in boron nitride, pressed into pellets and sealed from the atmosphere in clear plastic for measurement without air exposure. Soft XAS and high resolution RIXS data were collected from Swiss Light Source (SLS), Paul Scherrer Institut, Switzerland.

Elemental composition analysis was carried out using a Perkin Elmer Optima 8000 ICP-OES. Electrodes were digested in 1 mL aqua regia and diluted with 0.2 M nitric acid for analysis in solution phase. Operando Electrochemical Mass Spectrometry (OEMS) measurements were carried out using a modified electrochemical cell

from EL-CELL with gas inlet and outlet ports linked to a Bronkhorst mass flow controller and benchtop Thermo Fischerquadrupole mass spectrometer respectively.

ADF-STEM and EELS data were collected by Dr Juan Lozano on an aberration corrected JEOL ARM 200F operated at 200 kV and equipped with a Gatan GIF Quantum 965 ER. Sets of fast-acquisition multi-frame images were recorded and subsequently corrected for drift and scan distortions using SmartAlign.¹³ EELS line-scans were collected with a step size of 0.3 nm and energy dispersion of 0.25 eV/channel. Plural scattering was removed to account for thickness effects.

4.3 Results and Discussion

4.3.1 Structural Characterisation

$\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ was prepared as outlined in Section 4.2. The 'ideal' honeycomb composition $\text{Na}_1[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ was not targeted due to the tendency for highly sodiated layered phases (Na content > 0.8) to crystallise in the O3 structure type rather than P2.¹⁴ Further increase in the Li content beyond 0.25 in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ lead to substantial Li_2MnO_3 impurity.

Powder x-ray diffraction (PXRD) data were used to refine the structure of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ which can be well-fitted to the $\text{P6}_3/\text{mmc}$ space group, the simplest space group to describe P2 structures, Figure 4.1 and Table 4.1. This space group does not account for in-plane ordering of Li and Mn in the TM layer which manifests as unique superstructure peaks within the region $2\theta = 4.8 - 7.9$ degrees which was excluded from the refinement. To account for the peaks observed within the excluded region of the diffraction pattern, unit cells containing honeycomb ordered layers of Li and Mn were constructed each with a different stacking sequence of ordered layers. As can be seen in Figure 4.2, the primary peak observed at $2\theta = 5.9$ degrees can be described by the P6_3 space group. This model has alternately stacked honeycomb ordered layers giving a zig-zag arrangement of Li columns when viewed along the $[010]$ direction. Refinement of the whole diffraction pattern using this model did not give very good quality fits due to the likely presence of stacking faults which randomly disrupt this ordering and suppress the intensity of this

diffraction peak relative to the others. The remaining peak at $2\theta = 5.0$ degrees corresponds to a small amount ($< 1\%$ from refinement) of Li_2MnO_3 .

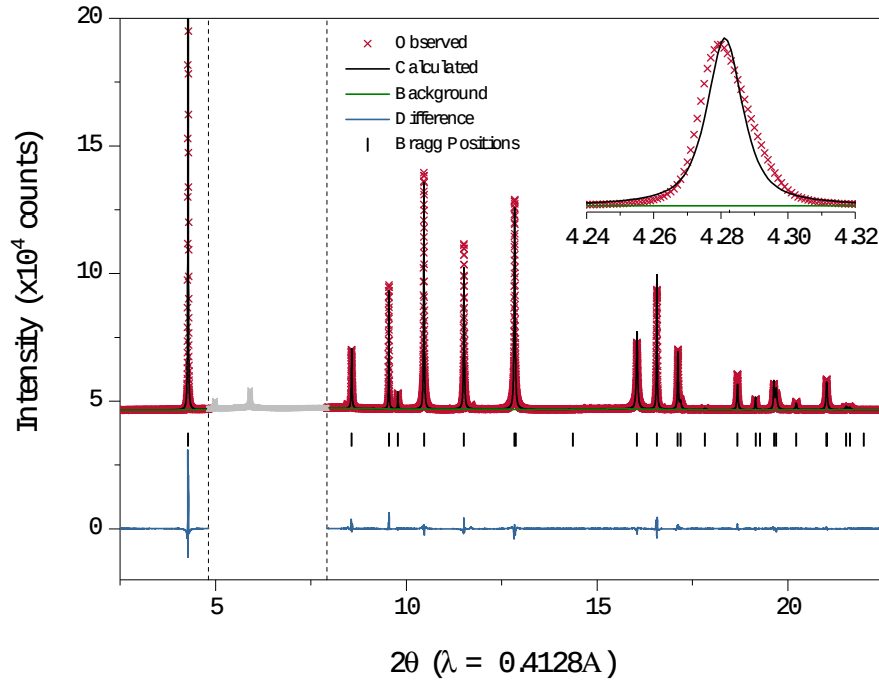


Figure 4.1: Rietveld refinement of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$. The superstructure region (greyed, $2\theta = 4.8 - 7.9$ degrees), was excluded from the refinement. Diffraction data were collected at the Advanced Photon Source, Chicago through their mail-in service using monochromated X-ray radiation $\lambda = 0.4128 \text{ \AA}$.

Atom	Wyckoff Positions	x	y	z	Occupancy	U_{iso}
Li	2a	0	0	0	0.25	0.0058(2)
Mn	2a	0	0	0	0.75	0.0058(2)
Na	2b	0	0	1/4	0.283	0.0559(9)
Na	2d	2/3	1/3	1/4	0.467	0.0559(9)
O	4f	2/3	1/3	-0.0908(1)	1	0.0194(4)
$a = 2.8647(1) \text{ \AA}$, $c = 11.0481(1) \text{ \AA}$, Space Group: $\text{P6}_3/\text{mmc}$.						
$R_w = 15.8\%$, $R_{\text{exp}} = 2.96\%$						

Table 4.1: Table of XRD Rietveld refinement parameters for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$.

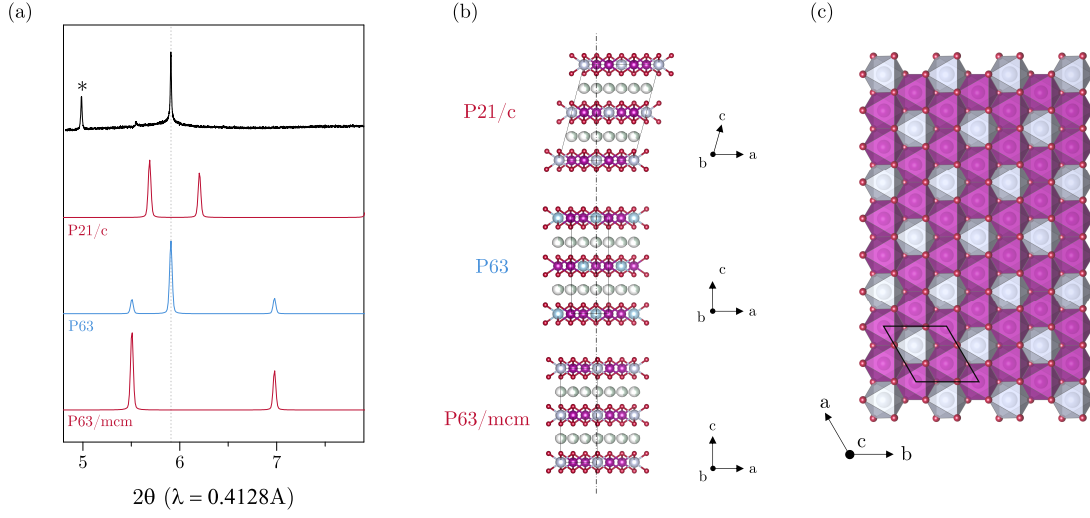


Figure 4.2: (a) Superstructure region of XRD data for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ excluded from refinement. Below, modelled diffraction patterns for different stacking sequences. The diffraction peak labelled with an asterisk belongs to Li_2MnO_3 impurity. (b) Unit cells of each possible stacking arrangement. The pattern for alternating layers (space group P63) best describes the observed diffraction peaks. (c) in-plane 'honeycomb' ordering of Li and Mn within the TM layer in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$.

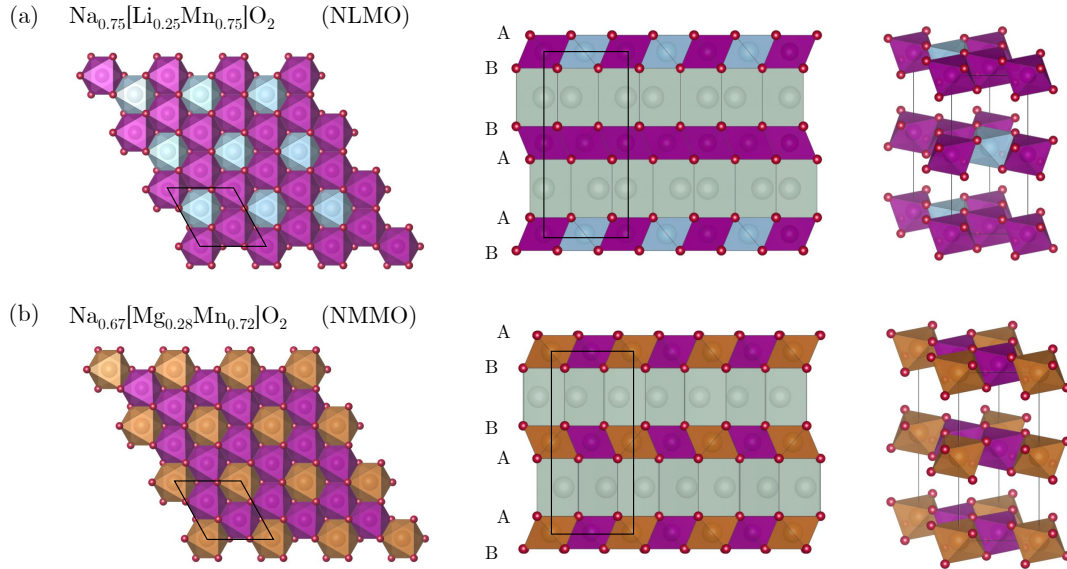


Figure 4.3: (a) $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ with P2-type stacking sequence (ABBA oxide stacking) and in-plane honeycomb ordering of Li and Mn. (b) $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ also possesses the P2-type stacking sequence and in-plane honeycomb ordering of Mg and Mn, however the stacking of honeycomb ordered layers is different. Both compounds possess Mn in the +4 oxidation state and hence exhibit predominantly O-redox charge compensation.

Despite slight differences in composition and stacking arrangements between $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, both structures are analogous to each other in their defining characteristics as shown in Figure 4.3. Namely, they are both P2-type structures with a honeycomb arrangement of Li and Mg in the TM layer and both exhibit charge compensation predominantly by O-redox.

4.3.2 Electrochemical Characterisation

The electrochemical behaviour of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ was examined versus a Na metal negative electrode. Similarly to $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, the AM layers of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ are not fully sodiated and as such the material can be charged or discharged from the pristine state. The first cycle charge-discharge load curves are shown in Figure 4.4. Upon discharge (in blue), $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ can be almost fully sodiated through a low voltage process involving reduction of Mn^{4+} to Mn^{3+} . This TM-redox mediated process occurs with very little voltage hysteresis.

Upon charging (in red), a short sloping region at low voltage consistent with a small amount of Mn^{3+} oxidation (approximately 0.05 moles from the excess Na used in synthesis) is followed by an extended shallow sloping region at an average voltage of 4.2 V. This region extends well beyond the limit of Mn redox storing an additional 0.5 moles of electrons per formula unit. On subsequent discharge down to 2.0 V the material can be almost fully resodiated to the pristine state, however the average voltage is significantly lower than on charge. This behaviour is a close reflection of that of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ which also exhibits voltage hysteresis between oxidation and reduction of O.

4.3.3 Spectroscopic Characterisation

To follow the electronic changes that accompany the charge and discharge processes occurring in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and how charge compensation is achieved, Mn K-edge XANES, O K-edge XAS and RIXS were employed on *ex situ* samples at different states of charge.

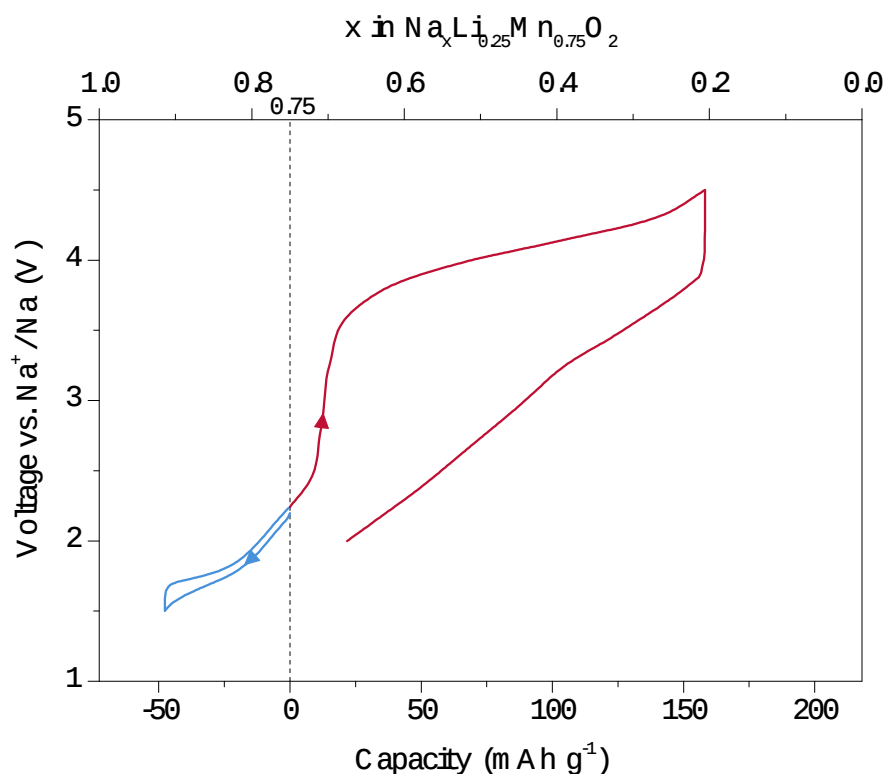


Figure 4.4: First cycle load curve of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ cycled at 10 mA g^{-1} . Blue: discharged to 1.5 V then charged to 2.2 V. Red: charged to 4.5 V then discharged to 2.0 V.

Mn K-edge XANES

The Mn XANES data presented in Figure 4.5 show data collected from electrode samples of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ alongside spectra obtained from Mn reference standards of different oxidation state. Comparing the main edge energies there is very little difference between each of the samples and the Mn^{4+} standard indicating negligible change in Mn oxidation state throughout the charge-discharge cycle. Any deviation in oxidation state would induce a shift of the main edge energy as the orbitals around Mn contract or expand from electron shielding effects.¹⁵ This data is a clear indication that Mn is primarily a spectator species in the charge-discharge behaviour of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$.

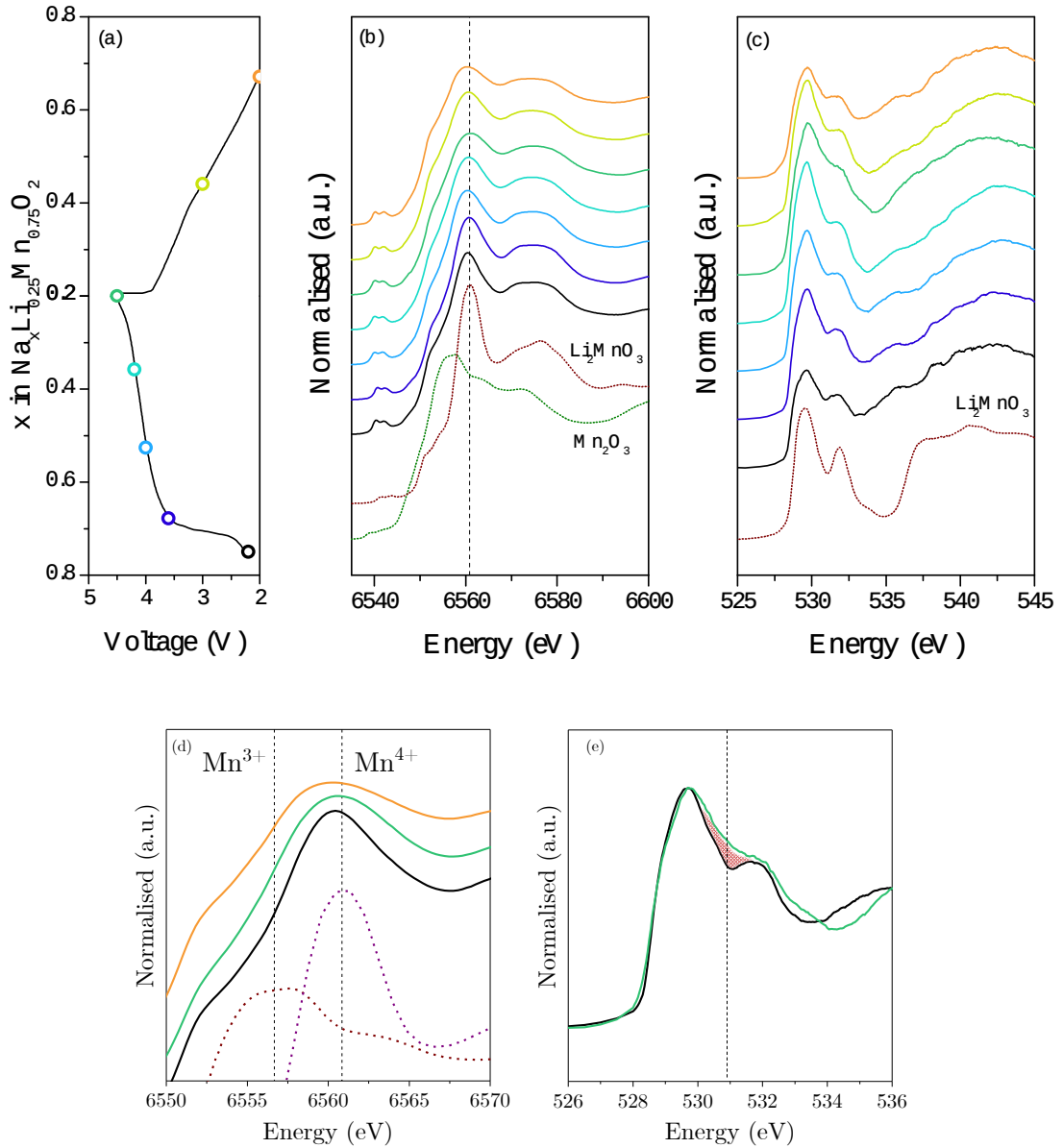


Figure 4.5: (a) The first cycle load curve of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ with states of charge chosen for *ex situ* analysis. (b) *Ex situ* Mn K-edge XAS data as a function of state of charge. Reference spectra for Mn_2O_3 (Mn³⁺) and Li_2MnO_3 (Mn⁴⁺) are shown below. (c) O K-edge XAS data as a function of state of charge. The reference spectrum for Li_2MnO_3 is shown below. (d) Close-up of Mn K-edge XAS data. (e) O K-edge XAS data highlighting increase in pre-edge intensity at 531 eV between pristine and charged states of charge.

O K-edge XAS

Turning now to the O K-edge data in Figure 4.5 (c), similar changes can be observed here as for $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. Upon oxidation of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ the area underneath the pre-edge appears to increase consistent with the creation of electron holes in O $2p$ /Mn $3d$ hybridised orbitals.^{16,17} Since the Mn oxidation state does not change beyond +4 from XANES, these new hole states can be attributed primarily to oxidation of oxide ions and are thus located in O $2p$ orbitals. The increase in the pre-edge is localised at 531 eV lying mostly underneath the first peak of the pre-edge but which appears to broaden both pre-edge peaks.

O K-edge RIXS

To directly probe these O hole states, RIXS measurements were performed on $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ at different states of charge. The data shown in Figure 4.6 (b) were recorded at the same excitation energy of 531 eV corresponding to the new localised hole states that appear at the pre-edge in the XAS. This shows that, as the intensity of the pre-edge feature grows with increasing O oxidation, so does the intensity of two unique energy loss features labelled A and B. These are identical to those observed in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and whose origin will be discussed in more detail in Chapter 5. The RIXS data shown in Figure 4.6 (c) are taken at different excitation energies across the O pre-edge each one for the sample of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ that had been charged to 4.5 V. They reveal that the features A and B are uniquely observed at an excitation energy of 531 eV (± 0.5 eV) in the same way as observed in the RIXS maps for $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$.

These XAS and RIXS features are mirrored between both $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ indicating that the same mechanism of O-redox charge compensation is occurring in both materials. In each material Mn remains electrochemically inactive beyond +4 and the electron holes that are created during charge become localised on oxygen manifesting as new states that appear in the middle of the O pre-edge.

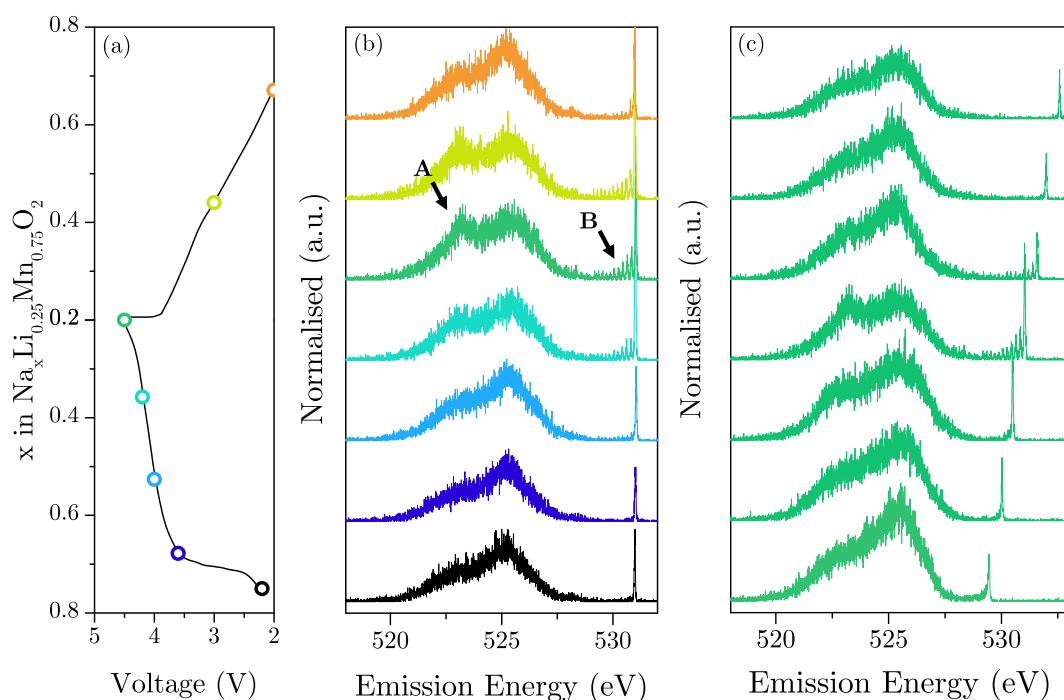


Figure 4.6: (a) The first cycle load curve of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ with states of charge chosen for *ex situ* analysis. (b) High resolution RIXS spectra at 531 eV excitation energy of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ at different states of charge measured at SLS, Switzerland by Dr Urmimala Maitra (c) High resolution RIXS spectra of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ charged to 4.5 V at excitation energies chosen at 0.5 eV intervals between 529.5 eV and 532.5 eV measured at SLS, Switzerland by Dr Urmimala Maitra. The materials were prepared by Dr Urmimala Maitra.

4.3.4 Oxygen Loss

As described in Subsection 3.3.4, it is important to examine the possibility that oxidised oxygen is lost from the electrode material as oxygen-containing gases (i.e. O_2 or CO_2). This mechanism could account for some of the capacity observed during charge, as has indeed been observed numerous times in Li-rich materials.^{1–6,8,9} However, no O-loss was observed from $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ despite 0.4 moles of electrons stored on O. This was attributed to the role of the TM layer substituent Mg remaining in the material during charge. Given the structural similarities of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ to both $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and Li-rich materials, it presents an interesting case to examine the role of Li in the TM layer on O-loss.

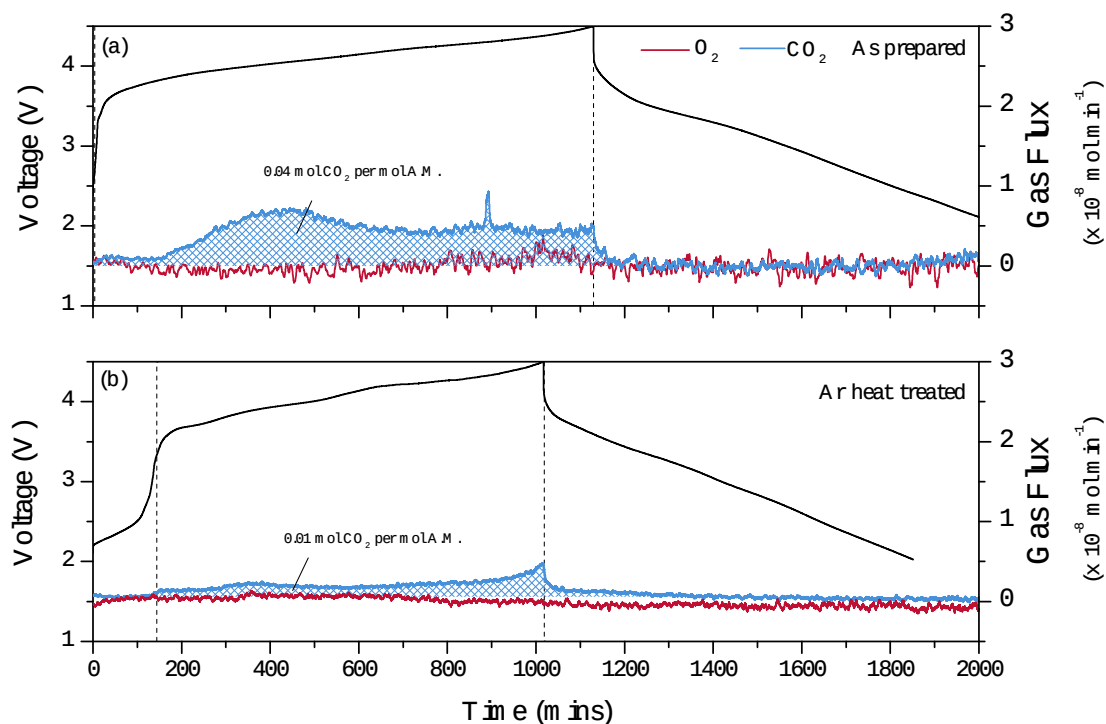


Figure 4.7: The first cycle load curve of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ monitored by *operando* mass spectrometry. Oxygen ($m/z = 32$) and carbon dioxide ($m/z = 44$) were monitored for the duration of the experiment. (a) As prepared $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ without further heat treatment. (b) As prepared $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ subjected to post-synthesis heat treatment under argon atmosphere. As prepared $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ was heated to 700 C at 10 C min^{-1} , then removed from the furnace and cooled under ambient conditions, all without exposure to moisture or oxygen. After Ar treatment negligible O_2 gas was evolved. 0.01 moles of CO_2 per mole of active cathode material was evolved.

OEMS

To investigate oxygen loss in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, OEMS was carried out under identical conditions to $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. The data presented in Figure 4.7 show the traces for O_2 and CO_2 from the mass spectrometer collected on samples tested before and after the Ar heat treatment step that was employed to remove Na_2CO_3 impurity. The quantity of CO_2 released during the charge is four times smaller after the treatment indicating the success of the strategy in removing carbonate. In neither sample is there evidence of O_2 release and for the Ar treated sample the amount of CO_2 detected is less than 2 % of the amount of charge passed (0.01 moles of CO_2 versus 0.5 moles of electrons per formula unit), indicating any loss of oxidised O from the lattice is negligible.

This result is somewhat counterintuitive. Li-rich layered transition metal oxides, such as $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$, exhibit some O-loss when charged to 4.8 V vs. Li^+/Li both as CO_2 and O_2 .^{8,9} Considering the similarity in structure and electrochemical behaviour between $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and Li-rich materials, both of which possess excess Li in the TM layers and undergo a comparable amount of O-redox (0.25 moles of electron holes per O for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and 0.3 moles per O for $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$), $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ might also be expected to exhibit O-loss when charged to the same high potentials (4.5 V vs. Na^+/Na is equivalent to 4.8 V vs. Li^+/Li). However, this is not the case; no O-loss is seen for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ whereas Li-rich materials do exhibit O release from the lattice. This suggests that O-loss is unlikely to be potential dependent.

One other possible explanation is that O-loss is related not to the degree of O oxidation or the potential, but rather the local coordination environment around O. O-loss is predominantly observed towards the end of charge in Li-rich materials when the structure is significantly depleted of Li ions.^{8,9} Specifically, in most instances, the onset of O_2 evolution occurs when more than the amount of Li in the AM layers is removed from the material i.e. Li content, $x < 0.2$ in $\text{Li}_x\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$. At this point, the average coordination number around O drops below 3 coordinating cations. Turning to $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, it is clear from the electrochemistry that insufficient Na is extracted from the AM layer to meet the same condition (only 0.55 out of 0.75 Na is removed). This could explain why no O-loss is observed in this instance.

To investigate whether O-loss could be triggered in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ or $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ by driving them to higher degrees of alkali ion depletion, further OEMS measurements were conducted this time subjecting each electrode to a 5 V potentiostatic charge for 1 hour. Application of a 5 V hold immediately forces the alkali metal content at the surface of each electrode to deplete to a level such that the chemical potential of each material at the surface is commensurate with the applied potential. In this way the electrodes are charged without spending prolonged time at high potential thereby reducing the amount of electrolyte degradation that

is incurred. Despite this, some oxidation of the electrolyte is still inevitable at such high potentials. In order to clearly distinguish between the contributions to the evolved gases from direct electrolyte oxidation and O-loss, $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ were isotopically labelled with ^{18}O .

The results of these experiments are shown in Figure 4.8. On charging $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ at 5 V, no ^{18}O labelled gases are evolved. Only a small quantity of CO_2 is observed which must arise from electrolyte oxidation. In contrast, for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, in addition to a similar quantity of unlabelled CO_2 from electrolyte oxidation represented by the dotted line, $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ exhibits both ^{18}O -labelled CO_2 and more unlabelled CO_2 . These gases are released coincidentally and reach peak flux about 30 minutes into the experiment. These must arise from reaction of oxidised O from the lattice of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and the electrolyte. This process has been studied in depth by Gasteiger and co-workers^{18,19} and is likely to involve reactive singlet O_2 species released by the cathode.

Further to the release of CO_2 induced by O-loss from the cathode, some O_2 is also observed from the onset of the charge. This O_2 is predominantly twice-labelled indicating that it originates exclusively from the electrode, which must itself be well enriched by ^{18}O . The release of O_2 before CO_2 is unusual and suggests that, when released fast enough, singlet O_2 can be detected before the decomposition reaction with the electrolyte to liberate CO_2 has had sufficient time to occur. In total, 0.028 moles of O per mole of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ is lost from the lattice at 5 V and 0 moles from $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$.

EELS

Loss of such an amount of oxygen from the lattice of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ must cause a detectable deviation in composition. To better understand the spatial origin of O-loss, elemental mapping was carried out on electrode particles using electron energy loss spectroscopy (EELS) of the Mn L-edge and O K-edge. The data presented in Figure 4.9 show representative line scans taken on $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ electrodes that had been subjected to charging under (a) galvanostatic and (b)

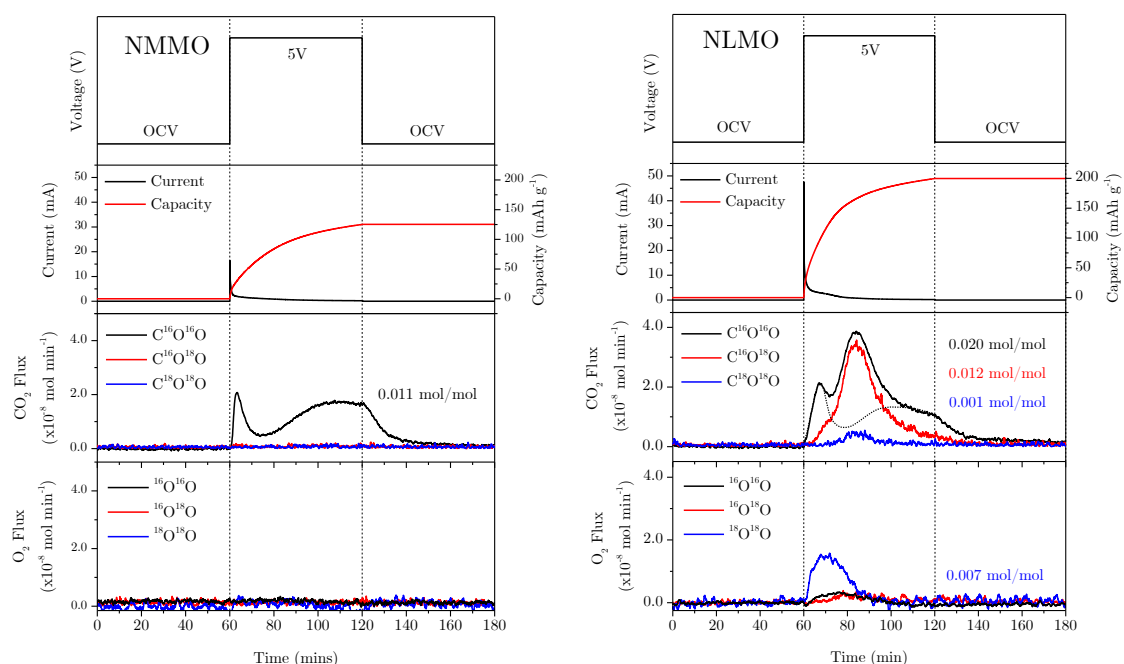


Figure 4.8: $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ (NMMO) and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ (NLMO) subjected to a 5 V potentiostatic charge for 1 hour monitored by *operando* mass spectrometry. For $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ no O_2 gas was evolved. 0.011 moles of CO_2 per mole of active material was evolved all of which was unlabelled and thus originating from residual carbonate and direct electrolyte oxidation. For $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ the same background CO_2 was observed (dotted line) but this time additional unlabelled, labelled and doubly labelled CO_2 were coincidentally evolved 20-30 mins into the potentiostatic step totalling about 0.03 moles per mole of active material. Some doubly labelled O_2 was also observed almost from the onset of the potentiostatic step indicating direct oxygen loss from the lattice.

potentiostatic conditions. The ratio of the areas underneath the Mn L- and O K-edges (after correcting for sample thickness effects) gives the elemental ratio between Mn and O and can be resolved by depth into the particle from the surface. These data show no change in composition for the sample which did not show O-loss in the OEMS experiment but a clear increase in the Mn:O ratio at the surface in the sample that did exhibit O-loss.

This change in Mn:O ratio indicates a loss of O from the material and appears to be predominantly localised to the first 10 nm of the electrode particles. To verify whether O-loss occurs exclusively at the surface, the amount of O-loss implied by the compositional change detected from EELS was calculated and compared with the amount of O-loss observed from the OEMS experiment. For this calculation,

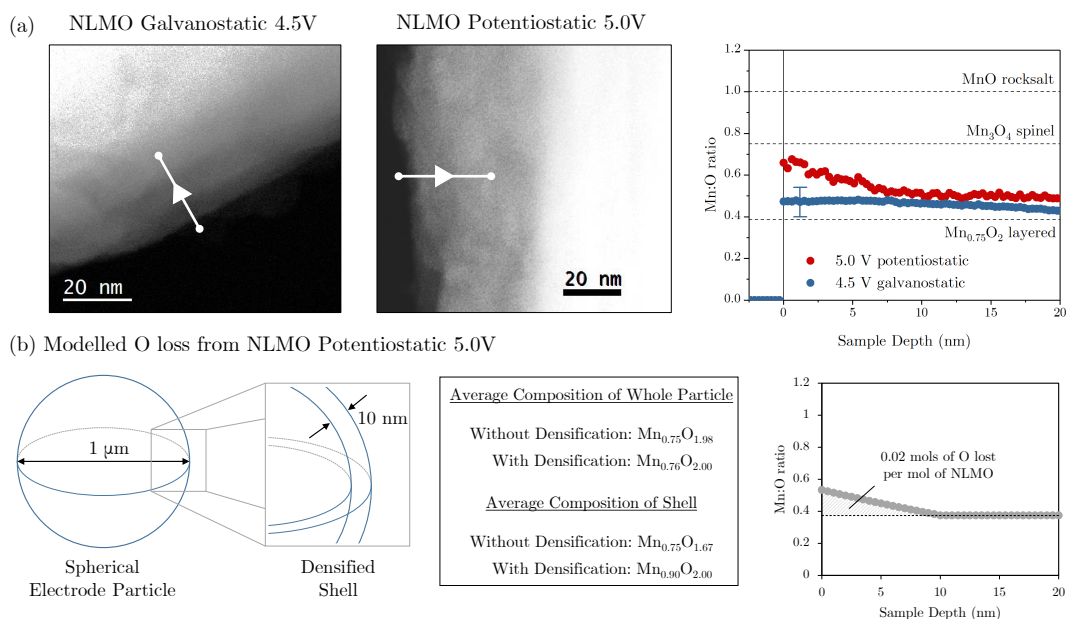


Figure 4.9: (a) STEM-EELS line scans data for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ charged to 4.5 V galvanostatically at 5 V potentiostatically. (b) Modelling the amount of O-loss anticipated from the deviation in particle composition at the surface of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ charged at 5 V potentiostatically. The STEM-EELS data was collected by Dr Juan Lozano. The materials were prepared by me.

the Mn:O ratio was assumed to vary linearly across the first 10 nm shell of spherical $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ particles that were 1 μm in diameter. The results of the modelling in Figure 4.9 (c) reveal an expected loss of 0.02 moles of O compared with 0.028 moles indicating good agreement between the two techniques and that O is primarily lost from the surface.

4.3.5 Li and Mg mobility

Under galvanostatic charging conditions to 4.5 V neither $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ nor $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ exhibit O-loss. However, when charged potentiostatically at 5 V $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ does exhibit O-loss whereas $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ does not. The main difference between these compounds is the presence of Mg^{2+} or Li^+ in the TM layers. Given the higher charge density of Mg^{2+} ions than Li^+ ions, they interact much more strongly with the host structure and generally exhibit much lower ionic diffusivities.^{20,21} To probe whether either ion is sufficiently mobile to participate in the de-intercalation process under each charging condition, electrodes

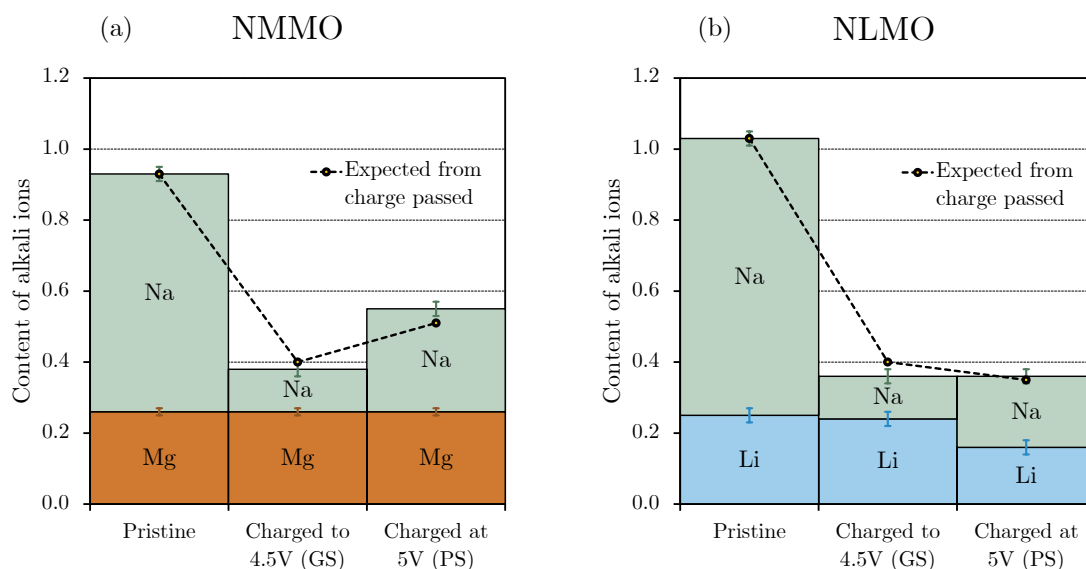


Figure 4.10: (a) $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ (NMMO) and (b) $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ (NLMO) electrodes subjected to different charging regimes and analysed by ICP-OES.

were collected *ex situ* and subjected to ICP-OES elemental analysis. The results of this analysis are presented in Figure 4.10. The data show a good agreement between the total measured alkali content of each electrode from ICP-OES and that expected from the amount of charge passed during the charging process. Furthermore, they show that Mg is completely retained in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ under even the most harsh charging condition, whereas Li is only extracted when electrodes of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ are charged to 5 V.

To further examine the mobility of Li in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ under each charging regime, ^6Li NMR was employed. This element-specific technique is a highly sensitive probe of the local environment and can detect subtle changes in coordination geometry and proximity to other nearby elements.²² The data for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, presented in Figure 4.11 (a), show a distinct change in spectral shape occurs upon desodiation. The pristine material shows one predominant Li environment (red) centred at 1850 ppm which corresponds to Li in octahedral sites exclusively in the TM layer surrounded by 6 Mn^{4+} (Li_{TM}).²³ After charging, this environment diminishes in intensity and is instead replaced by a new environment centred around 600 ppm (blue). On the basis of previous work, this new environment can be assigned to Li in octahedral sites in the AM layer (Li_{AM}).²⁴

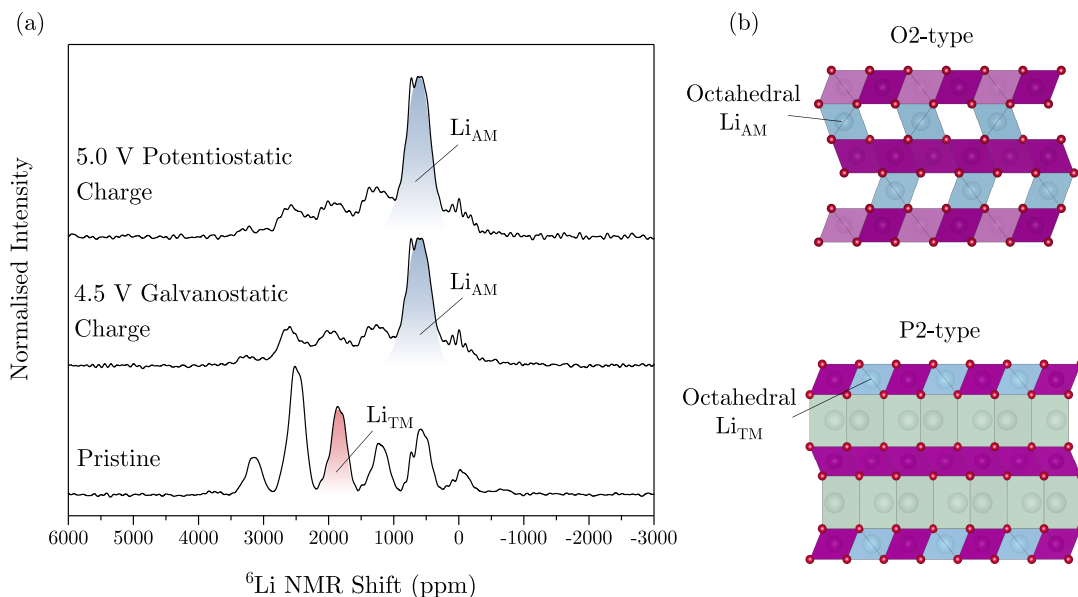


Figure 4.11: (a) ^6Li NMR data of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ before and after potentiostatic and galvanostatic charging regimes (b) Structural models of the charged state O2-type $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ with Li in octahedral sites in the AM layer (Li_{AM}) and pristine state P2-type $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ with Li in octahedral sites in the TM layer (Li_{TM}). Shaded peaks represent the isotropic shifts which were determined by repeating the measurement at different rotor spinning speed. These sample dependent peaks remain invariant with spinning speed whereas the remaining peaks change shift and are therefore spinning side bands. Spectra were collected, processed and fitted by Dr Liyu Jin. The materials were prepared by me.

These data imply that a substantial structural change is occurring during charge. In a similar way to the transition seen on charging $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, Subsection 3.3.3, as $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ is desodiated the TMO_2 layers glide past each other and the structure transitions from P-type to O-type stacking. As a result, the trigonal prismatic sites in the AM layer become octahedral and thus more favourable for lithium to occupy. The near complete change in shift in the ^6Li NMR shows that almost all of the lithium must displace into the AM layer, creating a large number of vacant octahedral sites in the TM layer as shown in Figure 4.11 (b). Given the similarity in the NMR spectra between the samples charged galvanostatically and potentiostatically, it is evident that the same structural transformations occur in both cases. The primary structural difference, therefore, between $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ that has been charged potentiostatically (O-loss) and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ that has been charged galvanostatically (no O-loss) is that Li is

lost from the structure during the former and not from the latter. The fact that Li is mobile between the TM and AM layers in each is not important for triggering O-loss.

4.3.6 What Triggers O-loss?

It might be supposed that O-loss is triggered above a critical onset potential for all O-redox materials (i.e. > 4.6 V vs. Li^+/Li) as typically O-loss is seen towards the upper voltage limit at the end of charge.^{3-6,8,9} However, comparing the OEMS responses of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ (no O-loss) and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ (O-loss) when charging at 5 V vs. Na^+/Na) shows that this is not the case.

It might also be considered that the degree of O oxidation determines whether O-loss is triggered or not (i.e. above a certain critical number of electron holes (h^+) per O, O becomes destabilised and forms O_2).²⁵ However, this seems unlikely when comparing $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ which can store 0.25 h^+ per O with no O-loss with an analogous Li-rich compound $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ which stores 0.28 h^+ per O but shows pretty severe O-loss. This is further confirmed when considering other prominent examples from literature.^{3-6,8,9} As seen in Figure ??, there is in fact no strong correlation between the degree of O oxidation and the onset of severe O-loss, instead, a better correlation is seen with the coordination number around O. Specifically, when the coordination number begins to drop below the critical value 3, O-loss is triggered.

The link between composition and O-loss that emerges from literature aligns well with the results presented in this chapter on the O-loss characteristics of $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$. For $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, with Mg^{2+} in place of Li^+ in the TM layer, no O-loss is observed even when charging under very severe conditions. As shown by ICP-OES, Mg^{2+} remains in the host structure preventing the coordination sphere around O from falling below three. The same is true for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ when charged galvanostatically to 4.5 V. Although Li displaces from the TM to the AM layers as shown by the ^6Li NMR, it is not removed from the structure altogether. Only upon application of a 5 V constant potential charge is there sufficient driving force to remove Li. Under these conditions, there

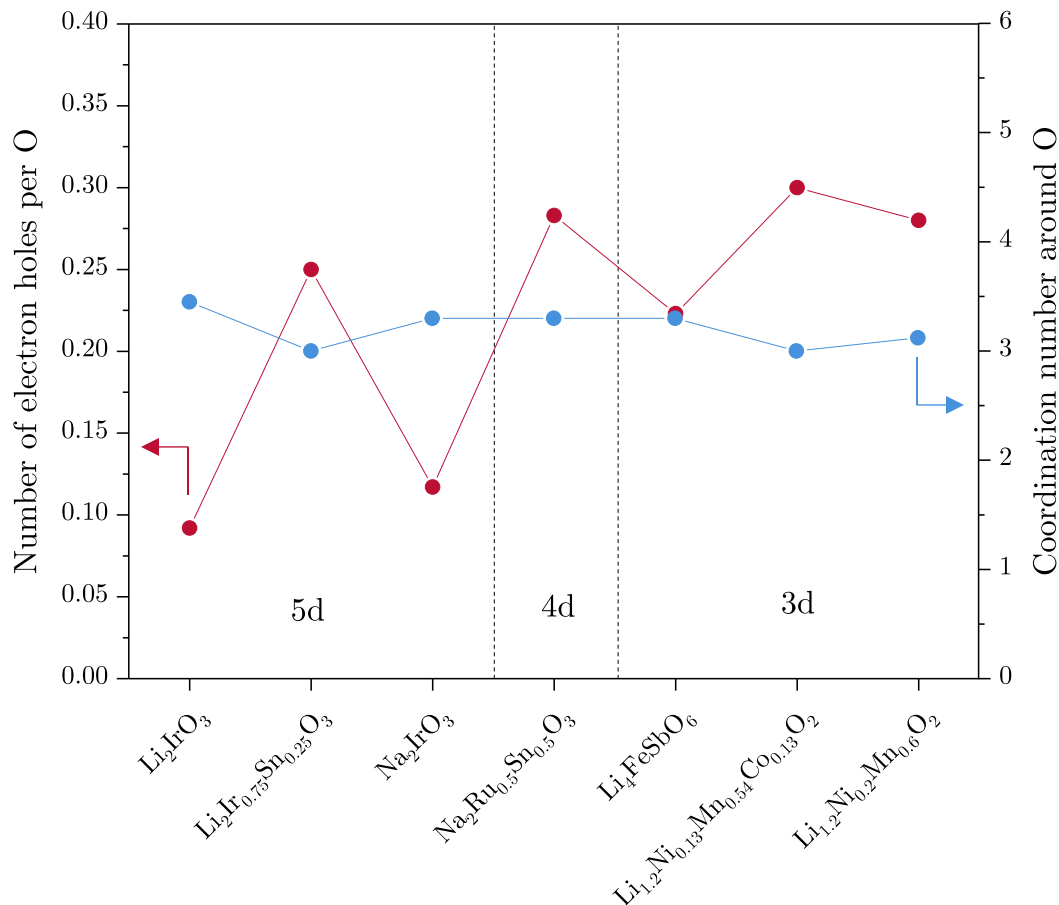


Figure 4.12: Plot showing the number of electron holes per O and average coordination number around O at the onset of O-loss for several prominent layered O-redox compounds based on 3d, 4d and 5d transition metals.^{3–6,8,9} The red points correspond to the number of electron holes per O and the blue points to the coordination number around O.

is a significant deviation in composition of the surface away from that of the bulk as ionic diffusion of Na and Li from the bulk to the surface becomes rate limiting, see Figure 4.13. As both Na and Li are removed from the surface, the coordination number around O drops below the *underbonding* threshold value of three, whereupon O becomes sufficiently underbonded by cations to destabilise it and trigger O-loss.

From the STEM-EELS line scan data, this process is observed to occur predominantly at the surface of the electrode. The oxygen that is lost gives rise to a detectable change in the TM:O ratio that is most severe at the edge of the particle but extends into the first 10 nm gradually diminishing with depth. The result is a densified surface layer that approaches the composition of a spinel phase in

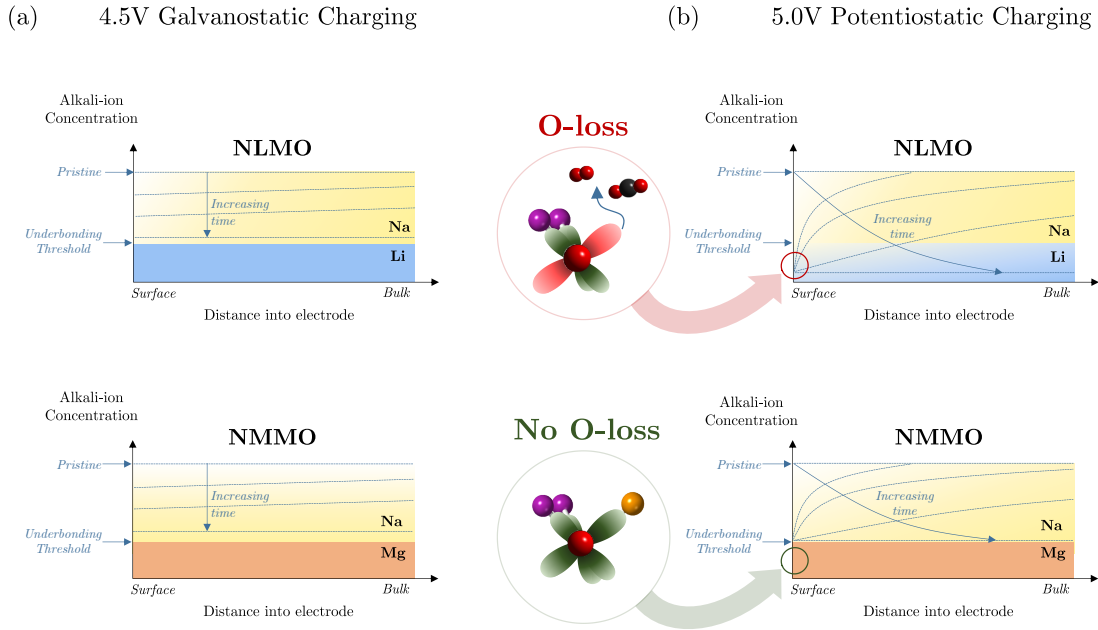


Figure 4.13: Schematic of evolution in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ electrode composition with charging time under (a) 4.5 V galvanostatic and (b) 5.0 V potentiostatic charging conditions.

a similar way to what is observed for Li-rich materials.^{2,7,26–28} Given the harsh charging conditions, it might not be unexpected that O-loss and densification only occur at the surface, since this is where the alkali-ion composition is the most depleted for most of the charging process. However, it is clear from the OEMS response that the O-loss mechanism is self-limiting since the rate of gas release peaks and tails off around 30 mins into the experiment. This implies that O-loss is primarily a surface localised phenomenon.

4.4 Conclusion

Oxygen loss is not an inevitable consequence of oxygen redox. It is neither triggered beyond a certain potential nor a critical degree of O oxidation, instead, oxygen loss is determined by cathode composition and is only observed when the coordination environment around O depletes sufficiently such that fewer than 3 cations remain. No O-loss is observed from $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ even when charged at 5 V vs. Na^+/Na . This is because Mg is retained in the crystal structure and the

coordination number around O remains > 3 . Similarly, no O-loss is observed from $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ when charged to 4.5 V vs. Na^+/Na despite charging to the same potential as Li-rich layered materials where O-loss is observed (4.8 V vs. Li^+/Li). Under these conditions Li displaces to the AM layer but is retained in the crystal structure showing that creating TM layer vacancies is not sufficient to trigger O-loss.

O-loss is triggered in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ by charging at 5 V vs. Na^+/Na . Under this harsh charging regime it is possible to remove Li from the cathode material giving rise to underbonded O with fewer than 3 coordinating cations. O-loss originates exclusively from the near surface (10 nm) of the electrode particles forming a TM densified surface layer. The results suggest that in order to access the full capacity benefits of Li-rich cathodes while avoiding O-loss, the surface composition must be carefully controlled to prevent the formation of underbonded O.

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5

Untangling Voltage Hysteresis and Oxygen Redox

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5.1 Introduction

In Chapter 3 and Chapter 4 it was established that the oxidised oxygen species formed on charge in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ are predominantly retained within the bulk of the cathode materials. In both cases it was also seen that, in contrast to the low voltage reversible $\text{Mn}^{3+/4+}$ redox couple (< 0.1 V hysteresis), high voltage O oxidation is accompanied by low voltage O reduction

giving rise to a large voltage hysteresis (approximately 1 V). This behaviour is frequently observed among O-redox cathode materials which typically exhibit a high voltage charging plateau followed by a lower voltage S-shaped discharge profile.¹⁻⁷ As a result, it is widely believed that O-redox and voltage hysteresis are intrinsically and inescapably linked phenomena. However, the results presented in this chapter challenge this widely held belief.

There are currently only two known examples of intercalation cathode materials which show a reverse high voltage plateau associated with O reduction.^{8,9} In this chapter a new example, P2-type $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ is presented and investigated in depth. Structurally and compositionally, it is very similar to P2-type $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ studied in Chapter 4 but instead it exhibits strikingly different reversibility of the high voltage O-redox plateau. By comparing and contrasting these two compounds the root cause of these divergent electrochemical behaviours is identified thus untangling the closely intertwined phenomena of voltage hysteresis and oxygen redox.

5.2 Experimental

$\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ was prepared by solid-state reaction between stoichiometric amounts of Na_2CO_3 (Sigma 99%), Li_2CO_3 (Aldrich 99.0%) and MnO_2 (Aldrich 99.0%) with a 5 wt. % excess of Na and Li to account for evaporation. The precursors were mixed for 2 hours at 400 rpm in a Retsch PM100 planetary ball-mill and then pressed into 13 mm diameter pellets. The reaction was carried out at 800 C for 10 hours under flowing O_2 gas with a heating rate of 10 C min⁻¹ and a cooling rate of 2 C min⁻¹. The material was then transferred into an Ar-filled glovebox without exposure to air.

Electrodes were prepared by mixing 80 wt. % active material, 10 wt. % conductive Super P carbon and 10 wt. % polytetrafluoroethylene (PTFE) polymer binder in a mortar and pestle and then rolling out thin ~100 μm free-standing films. Electrochemical testing was carried out in 1 M NaPF_6 (99.0% Kishida) in propylene carbonate (PC) (>99.0% BASF Selectilyte) electrolyte versus a Na metal

anode. Galvanostatic charge-discharge was carried out in CR2032 coin cells using a Maccor Series 4000 at a rate of 10 mA g⁻¹.

X-ray diffraction data for refinement of the pristine crystal structure were collected at the Advanced Photon Source, Chicago using monochromated X-ray radiation $\lambda = 0.4128$ Å. The GSAS-II software package was used for Reitveld refinement.^{10,11} X-ray diffraction data of cycled electrodes was collected on an in-house 600W Rigaku MiniFlex x-ray diffractometer housed in a N₂-filled glovebox using unmonochromated Cu K α radiation and parallel beam geometry. Mn L-edge XAS and low resolution RIXS were collected at BL27SU, Spring8 synchrotron, Japan. O K-edge XAS and high resolution RIXS data were collected at i21, Diamond Light Source (DLS), Harwell, Oxford.

Elemental composition analysis was carried out using a Perkin Elmer Optima 8000 ICP-OES. Electrodes were digested in 1 mL aqua regia and diluted with 0.2 M nitric acid for analysis in solution phase. Operando Electrochemical Mass Spectrometry (OEMS) measurements were carried out using a modified electrochemical cell from EL-CELL with gas inlet and outlet ports linked to a Bronkhorst mass flow controller and benchtop Thermo Fischerquadrupole mass spectrometer respectively.

ADF-STEM data were collected by Dr Juan Lozano on an aberration corrected JEOL ARM 200F operated at 200 kV and equipped with a Gatan GIF Quantum 965 ER. Sets of fast-acquisition multi-frame images were recorded and subsequently corrected for drift and scan distortions using SmartAlign.¹²

5.3 Results and Discussion

5.3.1 Structural Characterisation

Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ was prepared as outlined in Section 5.2. Slow cooling (2 C min⁻¹) of the sample from 800 C was essential to ensure the ribbon ordering scheme was well crystallised. At high temperatures the honeycomb ordered structure is favoured even with low Li contents.

Powder x-ray diffraction (PXRD) data were used to refine the structure of Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ which can be well fitted to the P6₃/mmc space group, the

simplest space group to describe P2 structures, Figure 5.1 and Table 5.1. This space group does not account for in-plane ordering of Li and Mn in the TM layer which manifests as unique superstructure peaks within the regions $2\theta = 2.5 - 3.9$ degrees and $4.6 - 8.2$ degrees which were excluded from the refinement. To account for the peaks observed within the excluded regions of the diffraction pattern, unit cells containing ribbon ordered layers of Li and Mn were constructed each with a different stacking sequence of ordered layers, and the diffraction patterns of each one were calculated. This arrangement seemed the most logical possibility considering the 1:4 ratio of Li:Mn and minimisation of coulombic charge repulsion. For each model, the unit cell parameters were calculated from the refined $P6_3/mmc$ unit cell such that the interlayer spacing and relative atomic positions were identical. As can be seen in Figure 5.2, the most intense peaks observed can all be described by the $P21/c$ space group. The weaker peaks, such as those at 3.3 and 3.7 can all be accounted for by each of the other two models described by space groups $C2/m$ and $Cmcm$, indicating that some minor regions of the material have different stacking.

To confirm the presence of ribbon ordering within the TM layer ADF-STEM imaging was performed on pristine $Na_{0.6}[Li_{0.2}Mn_{0.8}]O_2$. As shown in Figure 5.3 the images are consistent with the refined model from the diffraction data and confirm that the ribbon ordered layers are predominantly offset with respect to one another as captured by the $P21/c$ space group. This is the first time that the ribbon ordering arrangement has been definitively shown in alkali-rich layered cathode materials and represents a rare departure from the honeycomb ordering scheme which is the most commonly observed superstructure ordering by far.

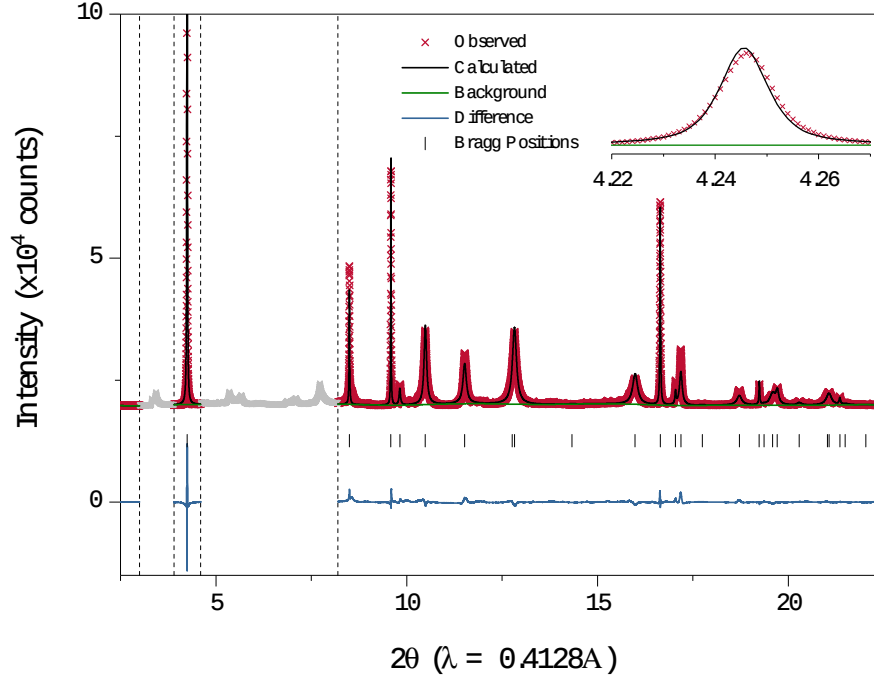


Figure 5.1: Rietveld refinement of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. The superstructure region (greyed, $2\theta = 2.5 - 3.9$ degrees & $4.6 - 8.2$ degrees), was excluded from the refinement. Diffraction data were collected at the Advanced Photon Source (APS) Synchrotron, Chicago through their mail-in service using monochromated X-ray radiation $\lambda = 0.4128 \text{ \AA}$.

Atom	Wyckoff Positions	x	y	z	Occupancy	U_{iso}
Li	2a	0	0	0	0.2	0.0016(3)
Mn	2a	0	0	0	0.8	0.0016(3)
Na	2b	0	0	1/4	0.310	0.0587(16)
Na	2d	2/3	1/3	1/4	0.290	0.0587(16)
O	4f	2/3	1/3	-0.0871(2)	1	0.0131(6)
$a = 2.8516(1) \text{ \AA}$, $c = 11.1403(2) \text{ \AA}$, Space Group: $P6_3/\text{mmc}$.						
$R_w = 19.2 \%$, $R_{\text{exp}} = 3.28 \%$						

Table 5.1: Table of XRD Rietveld refinement parameters for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$.

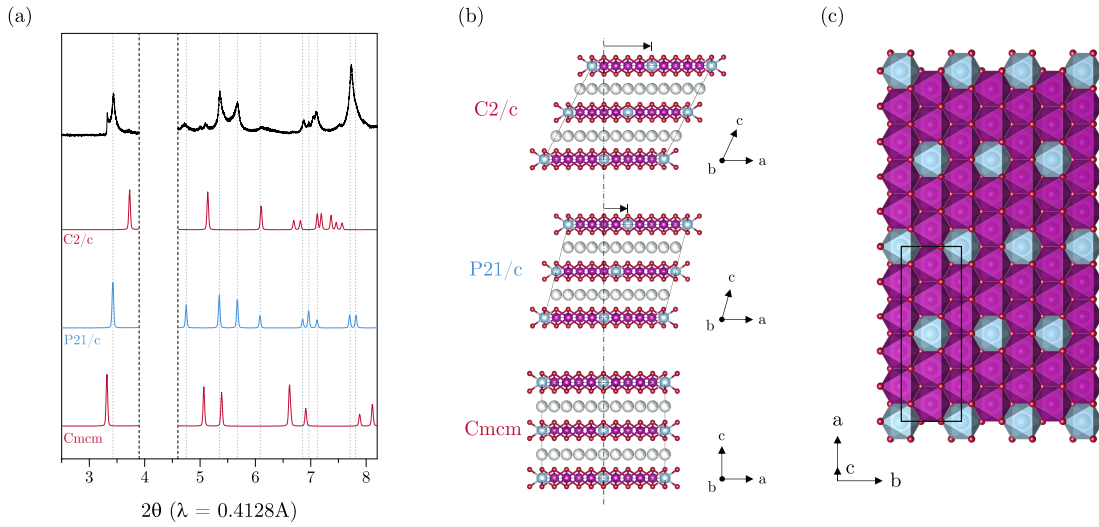


Figure 5.2: (a) Superstructure region of XRD data for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ excluded from refinement. Below, modelled diffraction patterns for different stacking sequences. (b) Unit cells of each possible stacking arrangement. The pattern for singly offset layers (space group P21/c) best describes the observed diffraction peaks although there is also some evidence of aligned layers (space group cmcm). (c) in-plane 'ribbon' ordering of Li and Mn within the TM layer in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$.

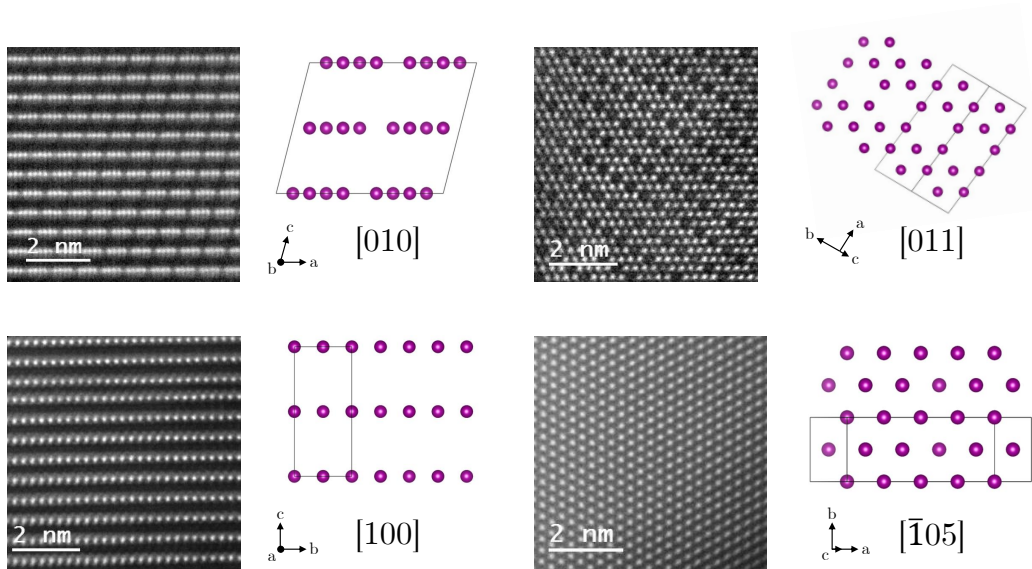


Figure 5.3: (a) ADF-STEM images of pristine $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ and structural models in matching orientations (space group P21/c). Manganese (purple) gives rise to the strongest contrast difference in the images. Lighter elements lithium (blue), sodium (green) and oxygen (red) are virtually not seen. The models were constructed using VESTA, some atoms and bonds are omitted for clarity. ADF-STEM images were obtained by Dr Juan Lozano. The material was prepared by me.

Structurally, $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ share very similar characteristics making them ideal for side-by-side comparison. Both crystallise in the P2 structure type with Na exclusively in the AM layers and Li and Mn exclusively in the TM layers. The Na content of each composition is chosen such that each material possesses Mn in the +4 oxidation state, thus ensuring that each operates predominantly on O-redox. The primary difference between them is the in-plane ordering scheme of Li and Mn, but what impact, if any, does this have on the electrochemical performance and O-redox chemistry?

5.3.2 Electrochemical Characterisation

The electrochemical behaviour of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ was examined versus a Na metal negative electrode. The first cycle charge-discharge load curves are shown in Figure 5.4. Upon discharge (in blue), $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ can be almost fully sodiated through a low voltage process involving reduction of Mn^{4+} to Mn^{3+} . This TM-redox mediated process occurs with very little voltage hysteresis.

Upon charging (in red), the voltage rises steeply and quickly transitions into a plateau region at an average voltage of 4.3 V. This region corresponds to approximately 0.4 moles of electrons per formula unit beyond Mn redox. On subsequent discharge, in stark contrast to the large voltage hysteresis and sloping voltage profile of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ a high voltage reverse plateau is observed at 4.1 V before the load curve slopes gradually down to 2.0 V and nominally recovers a Na content similar to that of the pristine. This strikingly reversible high voltage plateau is a rare example of truly reversible O-redox without voltage hysteresis and represents a remarkable exception to the general rule that voltage hysteresis is an inevitable consequence of O-redox.

5.3.3 Spectroscopic Characterisation

To probe the electronic changes occurring on Mn and O during the first charge/discharge cycle of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$, *ex situ* Mn L-edge XAS and O K-edge RIXS measurements were conducted. TM L-edge spectroscopy is considered to be a better measure

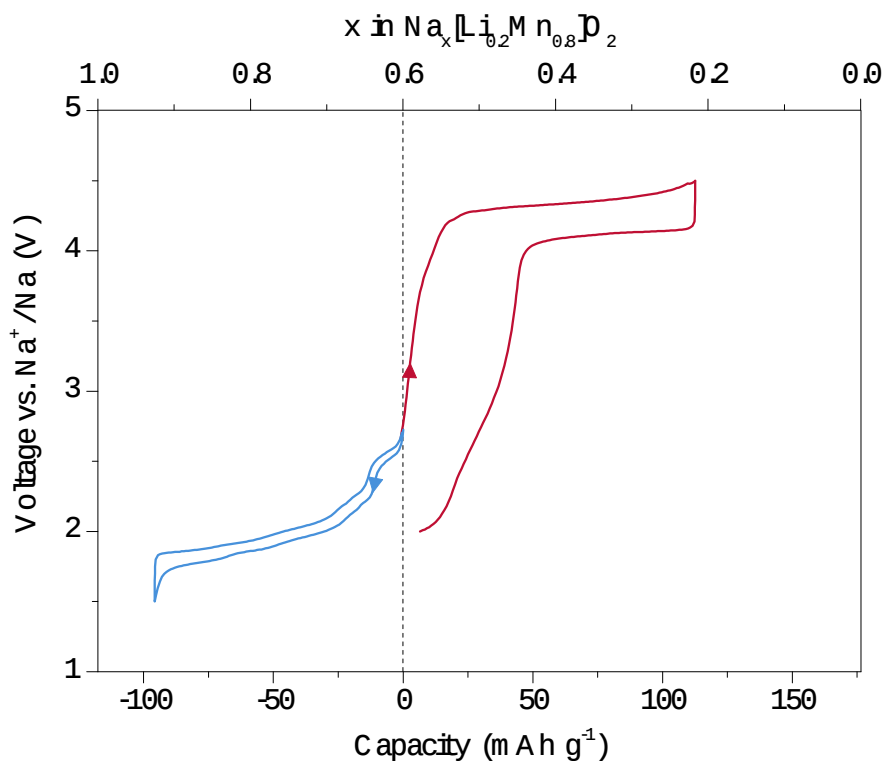


Figure 5.4: The first cycle load curve of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ cycled at 10 mA g^{-1} . Blue: discharged to 1.5 V then charged to 2.6 V. Red: charged to 4.5 V then discharged to 2.0 V.

of the TM oxidation state than the K-edge, yielding a superposition of fingerprint spectra unique to each valence state of the metal that is present.^{13,14} The K-edge, on the other hand, is much more sensitive to the ligand field environment and substantial changes to the edge shape and energy can be observed from distortions to the coordination sphere around the metal or from changes in TM-Ligand covalency.¹⁴ The Mn L-edge data were collected in inverse Partial Fluorescence Yield (iPFY) mode, which is the best mode for obtaining spectra that are representative of the bulk of the electrode and are free from self-absorption effects (see Chapter 2 for more detail).¹⁵

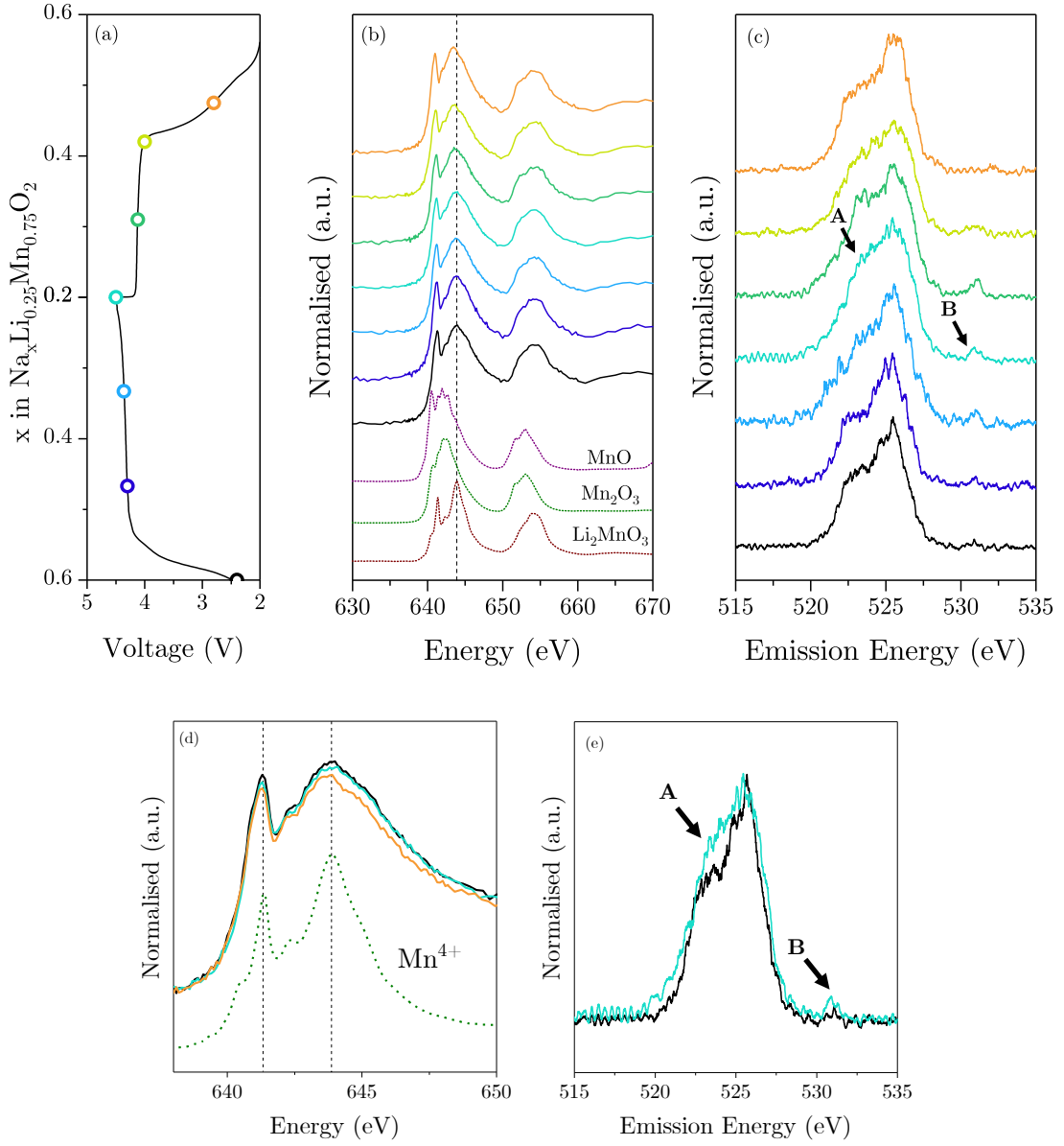


Figure 5.5: (a) The first cycle load curve of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ with states of charge chosen for *ex situ* analysis. (b) *Ex situ* Mn L-edge XAS data as a function of state of charge. Reference spectra for MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}) and Li_2MnO_3 (Mn^{4+}) are shown below. (c) O K-edge XAS data as a function of state of charge. The reference spectrum for Li_2MnO_3 is shown below. (d) Close-up of Mn L-edge XAS data. (e) O K-edge RIXS data highlighting changes in spectral weight between pristine and charged states of charge.

From the Mn L-edge data, presented in Figure 5.5 (b), it is clear that no change in Mn oxidation state from +4 occurs throughout the charge and discharge cycle of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. Oxidation of the oxide ions must therefore take place. The RIXS

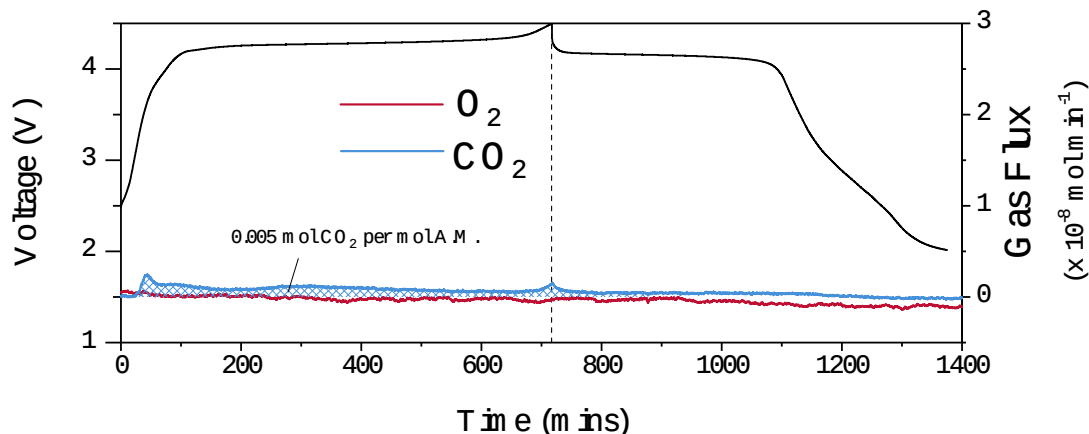


Figure 5.6: The first cycle load curve of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ monitored by *operando* mass spectrometry. Negligible O_2 gas was evolved. 0.005 moles of CO_2 per mole of active cathode material was evolved.

data collected at the O K-edge, shown in Figure 5.5 (c), illustrate that similar changes occur to the electronic states on O in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ to those observed for both $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. Measured at low resolution the vibrational progression of peaks at low energy loss (0 - 2 eV) is not resolved and instead appears as a broad shoulder to the elastic peak. High resolution RIXS data are presented later in the chapter showing that the new features are in fact identical to those observed for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ and indeed for Li-rich materials such as $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_3]\text{O}_2$ and $\text{Li}_2\text{Ir}_{0.75}\text{Sn}_{0.25}\text{O}_2$.^{7,16–18}

5.3.4 Oxygen Loss

To investigate the possibility of oxygen loss occurring in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$, OEMS was employed. The results presented in Figure 5.6 show no traces of O_2 and only a negligible release of CO_2 (0.005 moles of CO_2 for 0.4 moles of electrons stored on O). O loss therefore does not explain the capacity seen on charge.

5.3.5 Structural Change

To more closely compare the electrochemical behaviour of these two compounds, equivalent charge-discharge data for the first 10 cycles are presented in Figure 5.7 (a) and (b). The high voltage plateau that is initially seen on discharge for

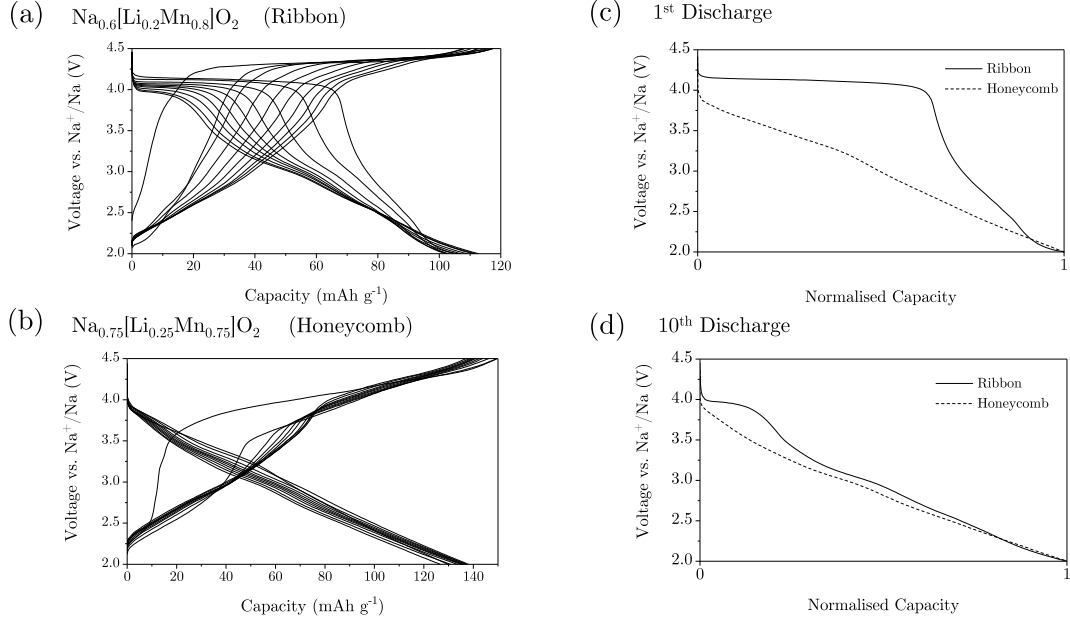


Figure 5.7: The first ten charge-discharge load curves of (a) $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ and (b) $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ cycled between 2.0 V and 4.5 V at 10 mA g^{-1} . (c) first and (d) tenth discharge load curves overlaid for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$.

$\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ gradually disappears and is instead replaced by lower voltage sloping capacity such that the Coulombic efficiency remains constant but the energy density falls. In contrast, for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, the initial charging plateau is followed immediately by a sloping discharge profile which does not appear to evolve substantially with cycling. Directly overlaying the normalised discharge profiles between $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ highlights the pronounced difference in voltage behaviour for O reduction on the first discharge, (c), that accompanies the different in-plane ordering schemes. After ten cycles the discharge profile for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ closely resembles the sloping curve for that of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, (d), implying that the reduction process occurring on discharge at this point is very similar and that whatever structural change occurred during the first charge in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ has now predominantly taken place in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ too.

In order to probe the local structural changes that take place in ribbon ordered $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ and honeycomb ordered $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, ^6Li NMR was employed at different states of charge. Given that lithium forms part of each TM

layer superstructure arrangement, it should be a sensitive indicator of any changes that occur to the ordering schemes. The results, presented in Figure 5.8 show, broadly, that a similar structure transition happens in both cases. Initially, the lithium occupies ordered sites in the TM layer giving rise to a signal centred at 1850 ppm for the honeycomb structure and 2150 ppm for the ribbon structure. The linewidth of the signal for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ appears to be substantially wider than that of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ due to an increased array of unique local environments compared with the latter in which lithium sits in very uniform environments.¹⁹ This is likely to be due to the off-perfect stoichiometry of the $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ composition which does not have quite the correct Li:Mn ratio to give complete honeycomb ordering and so possesses some site defects.

After charging to 4.5 V the original signals disappear and are instead replaced by new signals at substantially lower chemical shifts of 600 ppm and 720 ppm. This change is characteristic of Li occupying sites in the AM layer of octahedral geometry indicating that both P2 structures have transitioned to O2-type.²⁰ On discharge the original peak is recovered for each material consistent with a return to P2-type stacking. Strikingly, the lithium environments for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ are just as sharp and well defined as before showing retention of the TM ordering scheme. For $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, however, the peaks appear to be substantially broadened in the discharged sample. This broadening can be accounted for by fitting an additional peak (purple) of much broader line width centred at a lower chemical shift of 1800 ppm representing lithium in even more diverse and disordered environments. The isotropic chemical shift is characteristic of the number and geometry of through-bond interactions between Li and paramagnetic Mn (i.e. Li-O-Mn through-bond interactions).^{21,22} Generally speaking, the more Mn atoms in the immediate coordination sphere of Li, the stronger the paramagnetic interaction felt by the lithium nucleus and the larger the chemical shift. Thus the appearance of new lithium environments at slightly lower chemical shift in the discharged $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ sample can be attributed to a clustering of lithium within the TM layer to create regions of the TM layer that are locally lower in Mn and higher

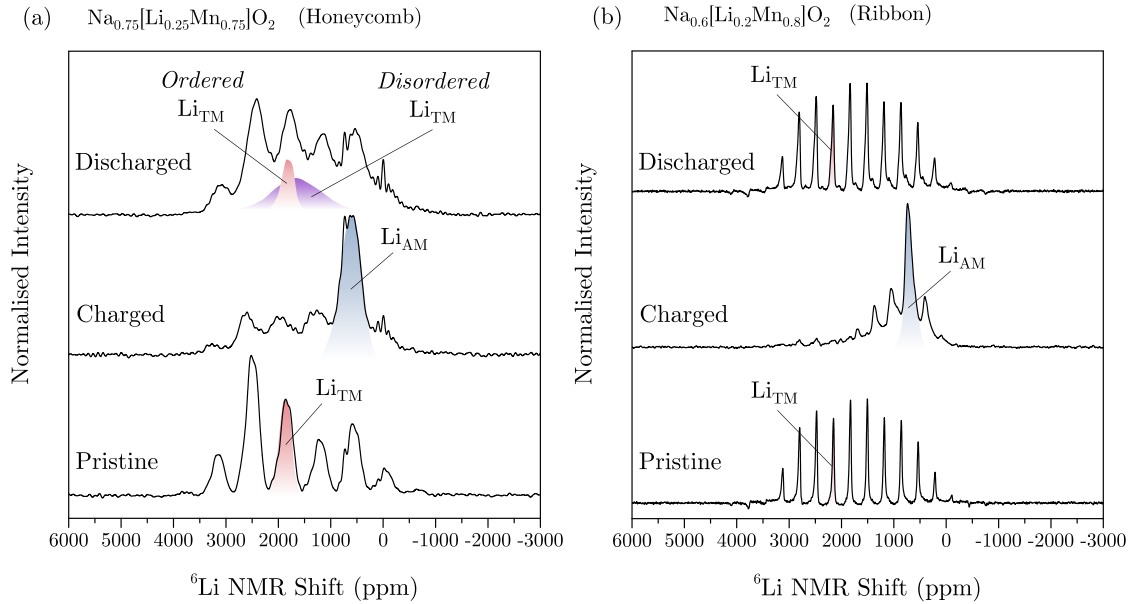


Figure 5.8: ^6Li NMR data of (a) honeycomb ordered $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and (b) ribbon ordered $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. Shaded peaks represent the isotropic shifts which were determined by repeating the measurement at different rotor spinning speed. These sample dependent peaks remain invariant with spinning speed whereas the remaining peaks change shift and are therefore spinning side bands. Spectra were collected, processed and fitted by Dr Liyu Jin. The materials were prepared by me.

in Li than the honeycomb ordering scheme. The NMR data thus provides the first evidence that the ribbon ordering scheme is retained after one charge-discharge cycle, whereas the honeycomb ordering is disrupted.

To further investigate the local structural changes, an ADF-STEM imaging study was performed on *ex situ* samples. The results, presented in Figure 5.9, show images taken along the $[010]$ direction which is the best zone-axis for observing any changes to the in-plane ordering scheme. As depicted in (c) when the ribbon and honeycomb ordered layers are viewed from the side, they give rise to 4-atom and 2-atom dumbbells respectively. Due to the offset stacking of the ordered TM layers along the c axis, neither ordering scheme can be seen along the zone-axis perpendicular to the ab plane since the Li atoms do not align into columns. During the first cycle there is a clear difference in the behaviour of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$, (a), and $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, (b). While the ribbon ordering is predominantly retained, the 2-atom dumbbells can no longer be distinguished and hence the honeycomb

superstructure is almost completely lost. After 10 cycles, the ADF-STEM image for the $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ crystal structure shows a more severe loss of ribbon ordering. In some areas, the 4-atom dumbbells can still be observed, but the majority of the image shows little contrast difference between the columns of Mn atoms within each layer indicating an almost completely disordered TM layer.

These structural changes to ribbon ordered $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ are further confirmed by x-ray diffraction data, Figure 5.10. At first glance, the diffraction patterns for the $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ structure after 1, 10 and 20 cycles appear remarkably similar to the pristine with retention of all peaks belonging to the P2 crystal structure. On closer inspection, the low angle peaks arising from the in-plane ribbon ordering scheme (highlighted in the inset) diminish and are virtually not seen by the twentieth discharge. This is clear evidence for the loss of ribbon superstructure over extended cycling. Furthermore, hkl dependent peak broadening is also observed. While the 002 and 004 peaks remain sharp and intense, the 010 and 110 peaks broaden significantly and reduce in intensity. This is indicative of increased strain within the ab plane (TM layer) as a result of increased in-plane disorder.

All of these experimental data show a clear correlation between the high voltage reduction process and the presence of superstructure. For $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$, ribbon ordering is predominantly retained during the first cycle and hence the high voltage plateau on charge is accompanied by a plateau on discharge. Over prolonged cycling the plateau is gradually lost along with the superstructure ordering. In contrast to the slow erosion of the ribbon ordering, the honeycomb structure is lost immediately on the first charge and is never recovered. Correspondingly, no evidence of a high voltage plateau is seen at all on first discharge indicating the fast and irreversible nature of this structural change for the honeycomb structure.

5.3.6 The Origin of Voltage Hysteresis

Given the clear relationship between superstructure and voltage loss from experiment, a number of key questions arise:

1. What is the driving force for the loss of superstructure ordering?

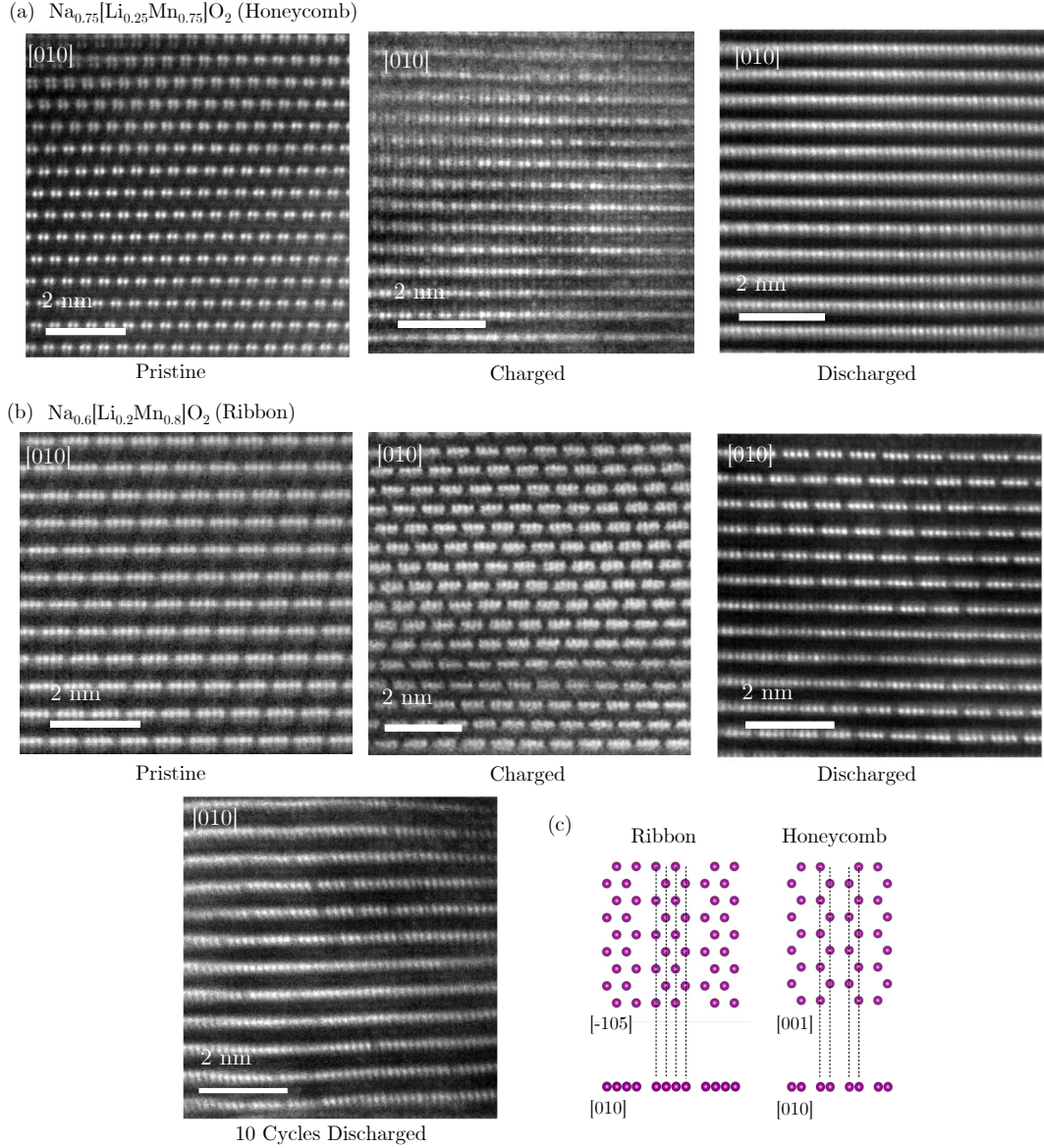


Figure 5.9: (a) ADF-STEM images of pristine, charged and discharged $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ along the $[010]$ zone-axis. (b) ADF-STEM images of pristine, charged and discharged $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ along the $[010]$ zone-axis. $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ after 10 charge/discharge cycles is also shown. Manganese gives rise to the strongest contrast difference in the images. Lighter elements lithium, sodium and oxygen are virtually not seen. (c) Structural models showing a layer of manganese atoms in a ribbon or honeycomb ordered arrangement. Each ordering scheme is viewed perpendicular and parallel to the ab plane to illustrate how each unique ordering gives rise to 4-atom (Mn-Mn-Mn-Mn) and 2-atom (Mn-Mn) dumbbells when viewed along the $[010]$ zone-axis. The models were constructed using VESTA. ADF-STEM images were obtained by Dr Juan Lozano. The materials were prepared by me.

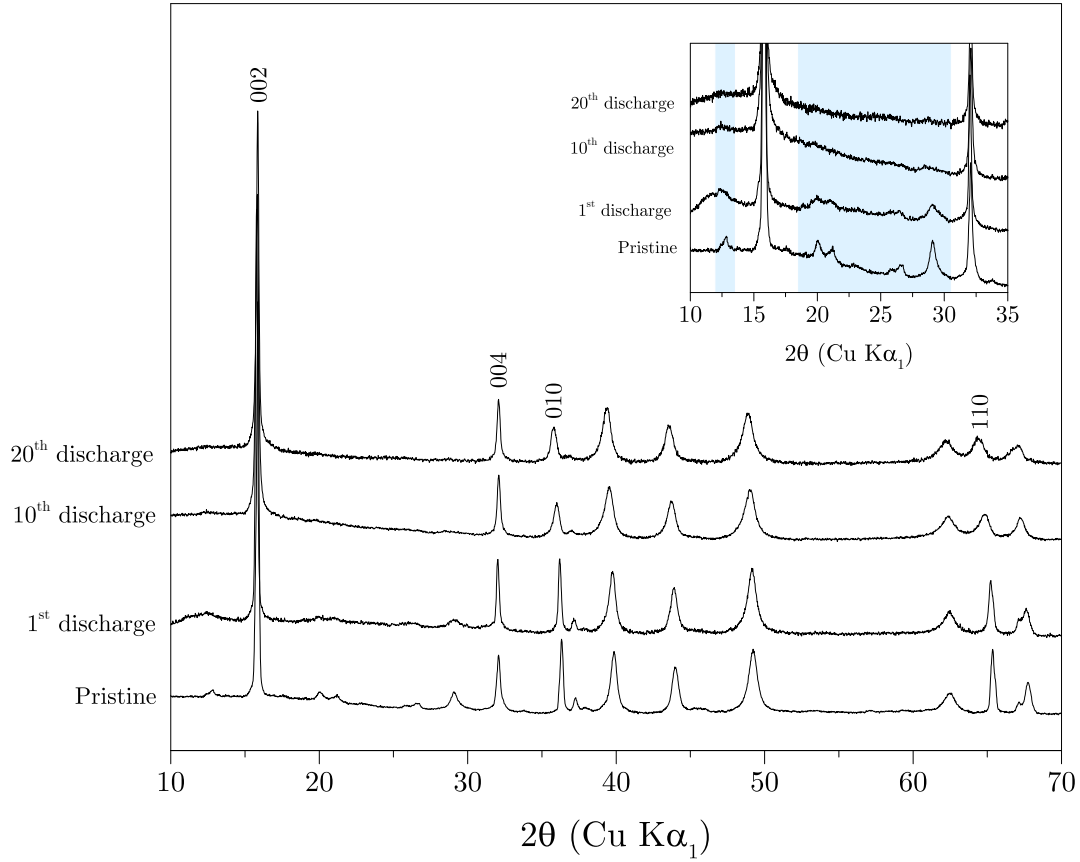


Figure 5.10: *Ex situ* X-ray Diffraction patterns of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. Diffraction data were collected using a monochromated laboratory $\text{Cu K}\alpha$ X-ray source. Peaks are indexed to the $\text{P6}_3/\text{mmc}$ space group which does not account for in-plane ordering

2. Why is the ribbon ordering scheme more resilient to disorder than the honeycomb?
3. Why does the order-disorder transition trigger such a large voltage hysteresis in honeycomb ordered structures?

To address these questions, it is important to consider the electronic changes that accompany these structural changes since the two are closely interrelated in determining the potential of the positive electrode during cell operation. Having established that neither $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ nor $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ exhibit oxygen loss or deviate from Mn in the +4 oxidation state, the substantial difference in voltage profile that is observed during the first cycle must be accompanied by clear differences between the electronic states associated with oxygen in each case. In

other words, the oxygen redox process in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ on the first cycle must be distinct from that in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$.

RIXS

Once again, high resolution RIXS data was obtained to study the nature of oxidised oxygen in each material. The results, presented in Figure 5.11, show the appearance of the same two energy loss features on charge as previously seen for $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$ in Subsection 3.3.5, which then disappear in the discharged sample. Importantly, the relative intensity of these new features is significantly lower for the $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ sample than for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ despite a similar number of electron holes on oxygen in each (0.2 h^+ and 0.25 h^+ respectively). These features bear very close resemblance to those observed for gaseous O_2 as measured by molecular spectroscopists.^{23,24} The progression of low energy loss peaks arises directly from electronic transitions between different vibrational energy levels of the O-O diatomic as shown in (c). The incident photon, specifically $531\text{ eV} \pm 0.5\text{ eV}$ in energy, excites $1s$ core electrons belonging to O in O_2 in its ground state to empty $2p$ orbitals. In the core-excited state, the O_2 molecules exhibit a dissociative potential well.²⁵ The lifetime of this transitive state is sufficiently longer than the electronic relaxation back to the ground state such that photon scattering is observed. This electronic relaxation can occur to a number of different possible vibrationally excited states of ground-state O_2 thus giving rise to inelastic scattering and a progression of sharp energy loss peaks.

Further confirmation that the RIXS features arise from molecular O_2 and not a different diatomic of oxygen (such as peroxide $(\text{O}_2)^{2-}$ or superoxide $(\text{O}_2)^{-}$) comes from analysing the peak spacing. Since each energy loss peak arises from a transition to a different vibrational energy level, the difference between them can be directly related to the spacing of the energy levels and hence the identity of the vibrating diatomic.²⁵ As shown in (c), the spacing between the elastic and first inelastic peak is 0.192 eV (equivalent to a 1550 cm^{-1} vibration). This value closely matches the

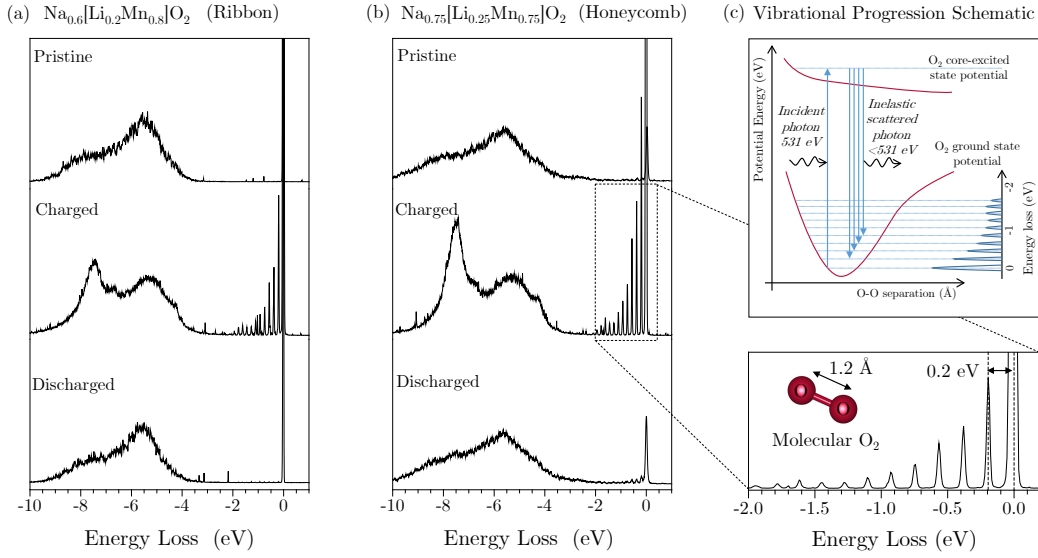


Figure 5.11: (a) *Ex situ* RIXS spectra for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ collected at 531 eV excitation energy. (b) *Ex situ* RIXS spectra for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ collected at 531 eV excitation energy. (c) Schematic illustrating the origin of the vibrational progression of energy loss peaks observed from oscillating molecular O_2 .

fundamental vibrational frequency of molecular O_2 , 1556 cm^{-1} measured by Raman spectroscopy.²⁶ In contrast, the vibrational frequency of peroxide is 743 cm^{-1} .²⁷

From these data it is apparent that molecular O_2 is formed during oxygen oxidation on charge in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ and to a lesser extent in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. The ultra high vacuum conditions under which the measurements are taken ensures that the electrodes are fully out-gassed, implying the O_2 must be trapped or bound within the bulk of the electrode. Prolonged beam exposure tests revealed negligible variation in the intensity of these peaks from 30 seconds to 9 minutes suggesting that it is not a result of O loss induced by irradiation effects. Since no O loss is observed from OEMS experiments and no evidence of the O_2 RIXS feature remains after discharge, the O_2 must therefore be reversibly formed and reduced in the bulk providing a viable redox mechanism for charge storage on oxygen.

The markedly lower intensity of the O_2 RIXS feature for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ compared with $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ suggests that O_2 is less dominant in the O-redox process for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. However, if oxidised oxygen does not

primarily take the form of O_2 , what then is the nature of oxidised oxygen in $Na_{0.6}[Li_{0.2}Mn_{0.8}]O_2$?

O K-edge XAS

The answer to this question is revealed by the O K-edge XAS spectra for $Na_{0.6}[Li_{0.2}Mn_{0.8}]O_2$. The data presented in Figure 5.12 show that, besides the usual increase in intensity at 531 eV, which is common to all 3d TM based O-redox materials and has just been shown to arise from molecular O_2 , a new feature is seen immediately before the onset of the pre-edge at 528 eV. RIXS spectra taken at this energy for $Na_{0.6}[Li_{0.2}Mn_{0.8}]O_2$ do not show evidence of any energy loss features, therefore diatomic species can be ruled out as the origin of these new empty electronic states. Instead, since these unoccupied states lie just above the Fermi Energy (E_F), they can be attributed to stable electron holes on a relatively undistorted network of O^{2-} ions. This is entirely consistent with the experimentally observed retention of ribbon ordering after one cycle whereby the local environment around oxygen is largely preserved. As a result of the suppression of structural change and hence reversible redox of the oxide sub-lattice, the high voltage electrochemical plateau is reversed on discharge and O-redox without voltage hysteresis is realised.

Discussion

The origin of voltage hysteresis, therefore, resides in the formation of molecular oxygen, whose empty states (π^* spin down) are offset much higher in energy relative to the Fermi Level (E_F) than the oxygen electron-hole (h^+) states. These high energy states are consequently reduced at much lower potentials on discharge contributing to voltage hysteresis. To understand how O_2 formation is linked to the loss of superstructure, (Density Functional Theory) DFT modelling was employed. All DFT calculations were performed by Dr Miguel Pérez-Osorio. Energetics calculations show that for a TM layer with oxidised oxygen and TM vacancies, in-plane TM disordering is favoured only when molecular O_2 is formed; different ordering arrangements without O_2 are comparable in energy, i.e. within about 50 meV per formula unit of each other. Formation of this species is found to

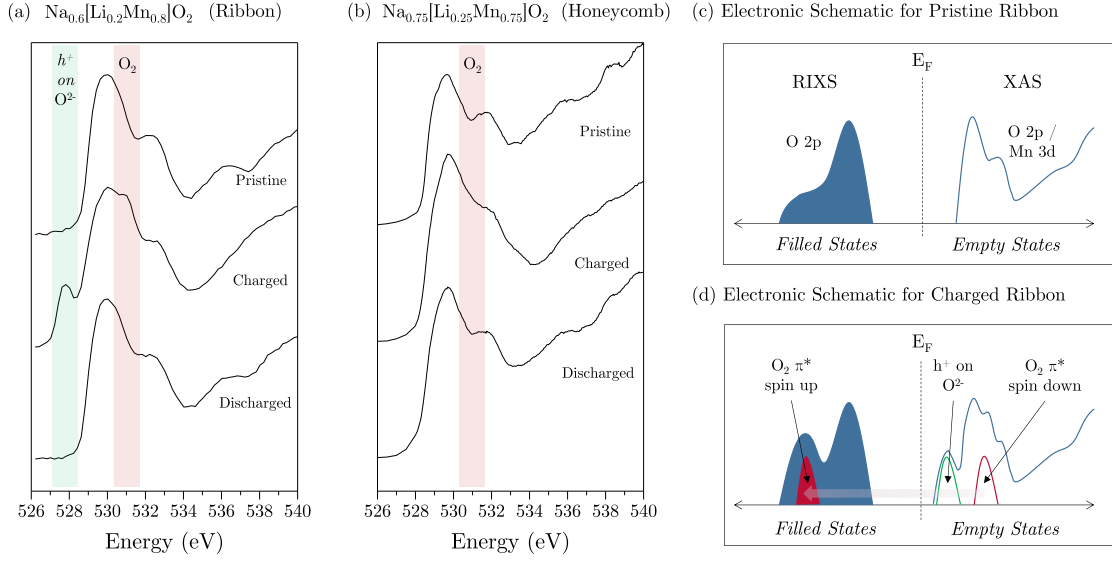


Figure 5.12: (a) *Ex situ* XAS spectra for (a) Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ and (b) Na_{0.75}[Li_{0.25}Mn_{0.75}]O₂ highlighting the unique features from oxidised O in the charged samples. (c) Schematic illustrating the electronic structure around the Fermi level in pristine and charged Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂. The empty states (green) appearing before the onset of the O pre-edge represent electron-hole (h⁺) states on O²⁻ which are reduced at high voltage on discharge. The empty states (red) appearing in the middle of the O pre-edge arise from the empty π* states of molecular O₂ and are coupled to filled π* states observed in emission spectra. This emission feature is only observed when electrons are excited into the empty π* states at 531 eV indicating they belong to the same species.

significantly lower the energy of this structure relative to the one with an ordered TM layer by about 250 meV per formula unit implying a strong electronic driving force from O-O dimerisation. This result provides the key link unveiling oxygen oxidation as the root cause of the loss of superstructure.

On charging honeycomb ordered O-redox materials, all oxide ions are in identical local environments and are equally susceptible to oxidation. The degeneracy of these electronic states can be broken by in-plane TM migration which changes the number of TMs coordinating O. Consequently, some O will become more coordinated (O-Mn₃) while others less so (O-Mn₁ and O-Mn₀). These less coordinated O can be substantially stabilised through dimerisation to form O-O bonds upon which electron holes will preferentially localise until O is fully oxidised i.e. molecular O₂. It is this electronic stabilisation which drives TM migration and the irreversible loss of superstructure ordering in honeycomb structures.

On discharge, as Li repopulates the TM layer, the disorder is retained such that local Li-rich clusters are observed, as evidenced by ^6Li NMR. The reduction of O_2 by filling the anti-bonding π^* and σ^* orbitals lengthens the O-O bond until it returns to roughly 2.6 Å and O^{2-} is reformed. The disordered discharged state is calculated to be significantly higher in energy than the honeycomb ordered pristine state due to the increased charge repulsion within the TM layer, however relaxation of the structure is inhibited by the presence of Li in the TM layer. This effect, in combination with the stabilisation of the charged phase afforded by disorder and O_2 formation, corresponds to a voltage drop on discharge that can be computed as 1 V from DFT, in agreement with the observed electrochemistry. This mechanism is summarised in Figure 5.13.

RIXS data show that molecular O_2 formation is more prolific for honeycomb ordered $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, which does not show any high voltage O reduction on discharge, than ribbon ordered $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$. In the case of the ribbon ordering scheme, which shows a reversible high voltage O-redox plateau on charge and discharge, TM migration is suppressed preventing O_2 formation and stabilising electron holes on an undistorted O sub-lattice. These unique electron-hole states manifest as a new pre-edge feature at the O K-edge at 528 eV. However, as is evident over prolonged cycling, the high voltage discharge plateau is gradually lost and after 10 cycles the ribbon ordering is almost completely lost as evidenced by ADF-STEM and PXRD. This implies that the charged ribbon ordered structure with oxidised O is metastable relative to the more stable disordered state with molecular O_2 . DFT calculations show that ribbon ordering does not offer any thermodynamic stabilisation against O_2 formation compared with the honeycomb ordering and hence the stabilisation that is observed must be of kinetic origin. One possible explanation for this is that more TM migration events are required to allow O_2 formation in the ribbon than the honeycomb ordered system and hence it is less likely to occur when the TM vacancies are ordered in the ribbon arrangement.

This understanding can be widely applied to other layered O-redox materials. All known honeycomb ordered O-redox materials, including $4d$ and $5d$ based systems

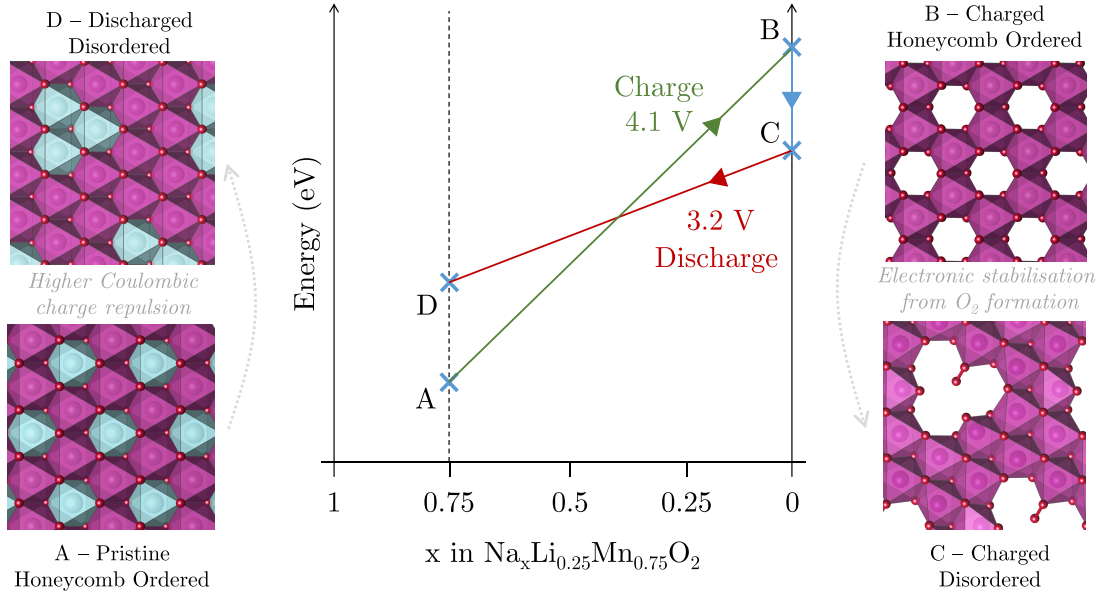


Figure 5.13: Schematic illustrating the structural and electronic origin of voltage hysteresis on the first cycle for $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$. Images show the evolution in local structure occurring within the TM layer at different states of charge. Purple represents Mn, blue Li and white, TM layer vacancies. In the pristine state, A, the TM layer is honeycomb ordered and all oxide ions are in identical local environments surrounded by 2 Mn and 1 Li (O-Mn_2). During charge Li is removed from the TM layer to leave behind a honeycomb ordered arrangement of TM vacancies, B. in-plane Mn migration disrupts the ordering, lowering the energy of the structure, C. This migration is driven by the formation of O_2 which breaks the degeneracy of the O states providing substantial electronic stabilisation. On discharge Li repopulates the TM layer blocking any further Mn migration thus freezing in the disorder, D. The gradient of the energy versus composition pathways between these structures gives rise to the voltage of that transition.

such as $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ and $\text{Li}_2\text{Ir}_{0.75}\text{Sn}_{0.25}\text{O}_3$, exhibit voltage hysteresis.^{1–7} Commonly, a flat voltage plateau is followed by an S-shaped discharge curve which then persists as S-shaped for multiple cycles. In all cases, the honeycomb superstructure is irreversibly lost on the first cycle and, in all cases where the measurements have been made, the signature RIXS feature of O-redox appears.^{7,16–18,28,29} Through employing high resolution RIXS, this work unveils the true origin of this new spectral feature and clarifies the redox mechanism associated with O-redox in these materials. O_2 formation is the electronic driving force for TM migration and, together with the increased Coulombic repulsion, explains why the 1 V drop in voltage seen on the first cycle. The ribbon ordering scheme suppresses TM migration and O_2 formation

to an extent, thereby preserving the degeneracy of the O states. This gives rise to high voltage O oxidation and reduction which persists for up to 10 cycles but eventually succumbs to low voltage O-redox as the ordering is gradually eroded. Similar behaviour is reflected in related compounds P3-type $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ and $\text{Na}_2\text{Mn}_3\text{O}_7$ which also possess ordering schemes unique from the honeycomb.^{8,9,30}

5.4 Conclusion

O-redox without voltage hysteresis can be realised if structural disordering and O_2 formation in the bulk of the electrode can be prevented. Honeycomb ordering in the TM layer of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ appears to be completely unstable in the charged state and will preferentially disorder in favour of O_2 formation which provides substantial electronic stabilisation. This promotes the voltage drop on the discharge. Ribbon ordering, however, affords some stability to the oxide sub-lattice allowing the formation of metastable electron holes on degenerate, undistorted O^{2-} ions. The ribbon ordering scheme is predominantly retained on the first cycle giving high voltage plateaus on charge and discharge in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$, but over prolonged cycling is gradually lost resulting in a sloping, low voltage load curve, much like $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$. The origin of the improved structural stability of ribbon versus honeycomb ordering is therefore likely to be kinetic as O_2 formation is still thermodynamically favoured and will eventually prevail.

The results in this chapter lay out new criteria for the discovery of high voltage O-redox cathode materials. To maintain a stable high voltage O-redox plateau on charge and discharge, ordering schemes distinct from the honeycomb arrangement must be sought. By further dispersing the excess alkali-ions throughout the AM layer, the kinetic barrier to O_2 formation is increased offering greater stability to the metastable electron hole states. Pillaring might also be considered an effective strategy to inhibit disorder by maintaining an interlayer spacing too high to favour out of plane TM migration.

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6

New O-redox Materials with Disordered Rocksalt Structure

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6.1 Introduction

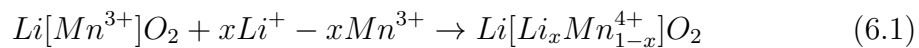
Fully harnessing the dual benefit of Mn and O-redox to access high capacities at high voltages is a demanding materials chemistry challenge. These materials must have:

- A corresponding amount of Li-ions that can be exchanged alongside charge compensation.

- A crystal structure that can withstand large variations in lithium content and oxidation state accompanying charge and discharge.
- High Li diffusivity to allow for high power output during cell operation.
- A sufficient number of ionic interactions (i.e. $\text{Li}^+\text{-O-Li}^+$ configurations) to promote O-redox.
- Suppression of, or resistance to, Jahn-Teller (JT) induced distortion arising from cycling Mn between the +3 (JT active) and +4 (JT inactive) oxidation states.
- Suppressed irreversible O-loss.

Layered crystal structures are limited in their ability to meet these stringent conditions. LiMnO_2 , where Mn is in the +3 oxidation state, only possesses a sufficient amount of Li to activate Mn +3/+4 redox and no ionic $\text{Li}^+\text{-O-Li}^+$ configurations to trigger O oxidation. In practice, LiMnO_2 cannot be directly prepared as a layered phase due to Jahn-Teller distortion around Mn which favours corrugated TMO_2 layers,¹ instead ion-exchange of NaMnO_2 must be performed.^{2,3} Nevertheless, these structures are generally unstable during cycling, again due to JT distortion which triggers the formation of spinel phases and enhanced electrode dissolution.³⁻⁶

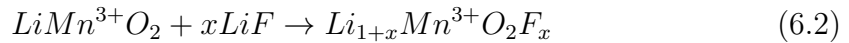
Introducing Li-excess into LiMnO_2 is a favourable strategy to promote O-redox. One way to achieve this is by replacing Mn with Li in the TM layer, according to Equation 6.1. This increases the amount of Li available for exchange and also creates $\text{Li}^+\text{-O-Li}^+$ configurations which place the electronic bonding states of O at higher energies and at more readily accessible voltages.⁷ However, this necessarily reduces the amount of available Mn redox reservoir since the oxidation state must necessarily increase to charge balance the substitution of monovalent Li^+ .



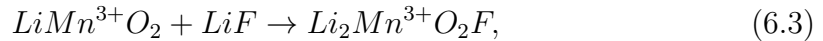
At the upper limit of Li substitution, where Mn is exclusively in the +4 oxidation state, $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_3$, is reached (more commonly known as Li_2MnO_3) with a

honeycomb ordered TM layer of Li and TM. In theory, this material has an exceptionally high capacity of 460 mAh g⁻¹ from complete Li extraction and should exhibit exclusively O-redox. In practice, prolific O-loss is observed from this material rendering it virtually useless as a cathode.⁸⁻¹¹

To avoid raising the Mn valence while introducing Li-excess, another strategy is to co-substitute Li⁺ and F⁻ on the cation (Li/Mn) and anion sites (O). This is equivalent to adding LiF according to Equation 6.2. The benefit of this is that the full Mn 3+/4+ redox capacity remains available and additional capacity can be provided by O-redox triggered by the Li⁺-O-Li⁺ interactions that come with Li-excess. At very high LiF contents, eventually both Mn and O will become too dilute to charge compensate the available Li. However, intermediate compositions, such as Li₂MnO₂F, with Li compensating equal amounts of Mn and O-redox (total capacity 450 mAh g⁻¹), could be envisaged, Equation 6.3. The trouble with this is that fluoride solubility in layered LiTMO₂ compounds is low and instead of distributing throughout the structure on oxide anion sites, phase segregation into LiF and LiTMO₂ is preferred at > ~5 wt. % LiF.¹²



And specifically, when $x = 1$,



Given the recent discovery that high energy ball-milling can be used as a way of synthesising metastable materials in a rocksalt-type crystal structure, such as Li₂VO₃ and Li₂VO₂F,¹³ with complete disorder on the cation (Li, V) and anion (O, F) sites, it was supposed that the same methodology could be applied to forming a metastable solid solution between LiF and LiMnO₂. This strategy proved successful and Li₂MnO₂F was synthesised as a disordered rocksalt. This chapter examines the material properties, electrochemical performance and structural evolution of this newly discovered compound.

6.2 Experimental

$\text{Li}_2\text{MnO}_2\text{F}$ was prepared by mechanochemical ball-milling reaction between stoichiometric amounts of Li_2O (Alfa 99%), LiF (Sigma 99.99%) and Mn_2O_3 (Sigma 99.9%). The precursors (typically no more than 3 g in total per jar) were mixed in a pestle and mortar before being loaded into the ball mill jar and sealed under an inert argon atmosphere. The reaction was carried out for a total of 3 x 6 hour milling periods and at each intermediate point the powder was scraped from the jar and reloaded to ensure complete homogeneity. Each 6 hour milling period was interspersed with a 10 minute rest after every 5 minutes of milling to dissipate heat. Milling was carried out at 750 rpm using a Fritsch premium line Pulverisette 7 planetary ball mill. Zirconia-walled jars with 20 mL internal volume and 80 x 5 mm zirconia balls were used. The jars were always opened inside an Ar-filled glovebox to avoid air exposure.

Electrodes were prepared by mixing 80 wt. % active material, 10 wt. % conductive Super P carbon and 10 wt. % polytetrafluoroethylene (PTFE) polymer binder in a mortar and pestle and then rolling out thin (about 100 μm thick) free-standing films. Electrochemical testing was carried out in 1 M LiPF_6 in a 50:50 ethylene carbonate (EC): dimethyl carbonate (DMC) mix (>99.0% BASF Selectilyte) electrolyte. Galvanostatic charge-discharge was carried out in CR2032 coin cells using a Maccor Series 4000 at specified rates.

All diffraction measurements were conducted on an in-house 9kW Rigaku Smart Lab x-ray diffractometer using monochromated Cu K_α radiation and parallel beam geometry. The GSAS-II software package was used for Reitveld refinement.^{14,15} Neutron total scattering data for PDF analysis were collected by beamline scientists at NOMAD, SNS, Oak Ridge National Laboratory. Refinement was performed using PDFgui and PDFfit2 software.¹⁶ XANES measurements were conducted at beamline B18, Diamond Light Source, Harwell. Data were reduced using Athena.¹⁷ Electrodes were dispersed in boron nitride, pressed into pellets and sealed from the atmosphere in clear plastic for measurement without air exposure. EXAFS data reduction was performed using Athena, part of the Demeter software package.¹⁷ Soft XAS and RIXS data were collected from BL27SU, Spring8, Japan.

TGA-MS measurements were conducted on an in-house Netzsch Jupiter STA 449 F3 thermogravimetric analysis instrument coupled with a Netzsch Aeolos QMS 403 D mass spectrometer. Elemental composition analysis was carried out using a Perkin Elmer Optima 8000 ICP-OES to determine Li and Mn content. Electrodes were digested in 1 mL aqua regia and diluted with 0.2 M nitric acid for analysis in solution phase. Operando Electrochemical Mass Spectrometry (OEMS) measurements were carried out using a modified electrochemical cell from EL-CELL with gas inlet and outlet ports linked to a Bronkhorst mass flow controller and benchtop Thermo Fischer quadrupole mass spectrometer respectively.

Liquid state ^7Li and ^{19}F NMR measurements were carried out on solutions of $\text{Li}_2\text{MnO}_2\text{F}$ before and after synthesis in 12 M hydrochloric acid to measure Li and F content. Iodometric titration was performed to determine the oxidation state of Mn. A known mass of $\text{Li}_2\text{MnO}_2\text{F}$ was dissolved in 1.0 M hydrochloric acid with an excess of potassium iodide and a few drops of starch indicator and titrated against a known concentration (~ 0.03 M) of sodium thiosulphate solution. The sodium thiosulfate concentration was standardised using titration against potassium iodide.

SEM imaging was performed on a Carl Zeiss Merlin high resolution field emission gun SEM instrument. ADF-STEM data were collected by Dr Juan Lozano on an aberration corrected JEOL ARM 200F operated at 200 kV and equipped with a Gatan GIF Quantum 965 ER. Sets of fast-acquisition multi-frame images were recorded and subsequently corrected for drift and scan distortions using SmartAlign.¹⁸ BET surface area analysis was carried out using a 3Flex Physisorption instrument from Micromeritics.

6.3 Results and Discussion

6.3.1 Structural Characterisation

$\text{Li}_2\text{MnO}_2\text{F}$ was prepared as outlined in Section 6.2. Powder x-ray diffraction (PXRD) data were used to refine the structure of $\text{Li}_2\text{MnO}_2\text{F}$, which can be well described by the $\text{Fm}\bar{3}\text{m}$ space group as a cubic rocksalt crystal structure, Figure 6.1 and Table 6.1. From the diffraction data it is evident there is very little long range order due to the

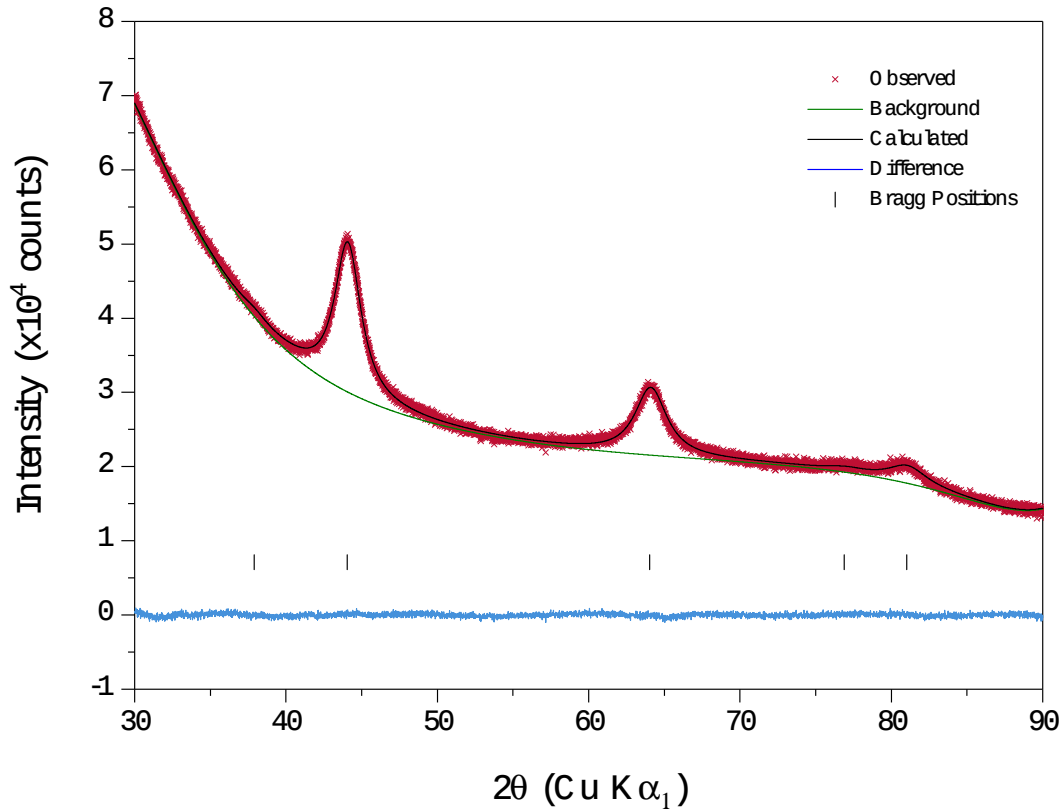


Figure 6.1: Rietveld refinement of $\text{Li}_2\text{MnO}_2\text{F}$. Diffraction data were collected using a monochromated laboratory $\text{Cu K}\alpha$ X-ray source.

Atom	Wyckoff Positions	x	y	z	Occupancy	U_{iso}
Li	4a	0	0	0	2/3	0.01
Mn	4a	0	0	0	1/3	0.01
O	4b	1/2	1/2	1/2	2/3	0.01
F	4b	1/2	1/2	1/2	1/3	0.01
$a = 4.109(1) \text{ \AA}$, Space Group: $\text{Fm}\bar{3}\text{m}$.						
$R_w = 0.40 \%$, $R_{\text{exp}} = 0.39 \%$						

Table 6.1: Table of XRD Rietveld refinement parameters for $\text{Li}_2\text{MnO}_2\text{F}$.

lack of sharp, intense diffraction peaks. Instead, the peaks that are observed have a very broad peak shape indicating the size of the ordered domains is small. From Scherrer analysis the width of the ordered domains can be estimated at around 5 nm, i.e. this material is nano-crystalline. Strain broadening will also contribute to the peak width but has been neglected here. Separating the contributions of size and strain broadening in this case is difficult due to the small number of Bragg peaks.

To extract further structural information from this poorly crystalline material,

local probe techniques are required. One such technique, Pair Distribution Function (PDF) analysis, allows the extraction of atom-atom pair lengths as a function of increasing separation distance using x-ray or neutron scattering data.^{19,20} This provides unique insight into the local arrangement of atoms relative to each other from which structural refinements can be carried out to determine the bulk crystal structure. Typically, scattering data is composed of Bragg scattering, which relates to long-range periodicity, and diffuse scattering, which relates to short-range order and whose intensity is typically several orders of magnitude less than Bragg. By measuring the total scattering (i.e. Bragg and diffuse) with high enough intensity, Q range and resolution it is possible to capture all of this information and perform PDF analysis to plot out the distribution of atom-atom pairs in the crystal structure.

Neutron total scattering data was collected for $\text{Li}_2\text{MnO}_2\text{F}$ and the PDF extracted. Since x-rays are hardly scattered by Li, neutron scattering data was preferred to enable refinement of the lithium position. The data, plotted in Figure 6.2 over two different r lengths (a) and (b) show a series of peaks and troughs which each correspond to a unique atom-atom distance in the structure. Since the scattering lengths of the anions are positive (O^{2-} , $b = 5.803$ fm, F^- , $b = 5.654$ fm) and the cations are negative (Li^+ , $b = -1.9$ fm, Mn^{3+} , $b = -3.73$ fm), the troughs correspond to negative scattering from cation-anion pairs and the peaks correspond to positive scattering from anion-anion or cation-cation pairs. For instance, the first trough at 2 Å corresponds to a superposition of all nearest neighbour pair interactions (i.e. the Li-O, Li-F, Mn-O, Mn-F bonds), the first peak at 3 Å corresponds to the next nearest neighbour pairs (Li-Li, Li-Mn, Mn-Mn, O-O, O-F, F-F) and so on.

Structure refinement was performed over an r range of 1.5 to 20 Å using the same crystal structure parameters as from the XRD refinement, Table 6.1, and the resulting fit is shown in Figure 6.2 (a). In order to account for attenuation of peak intensity with increasing r, which is a result primarily of the loss of coherence between pairs beyond the edge of the nano-crystallites, a damping function was applied and refined to obtain a better fit. Thermal vibrations of the atoms, which leads to peak broadening, were also taken into consideration by refinement of the U_{iso}

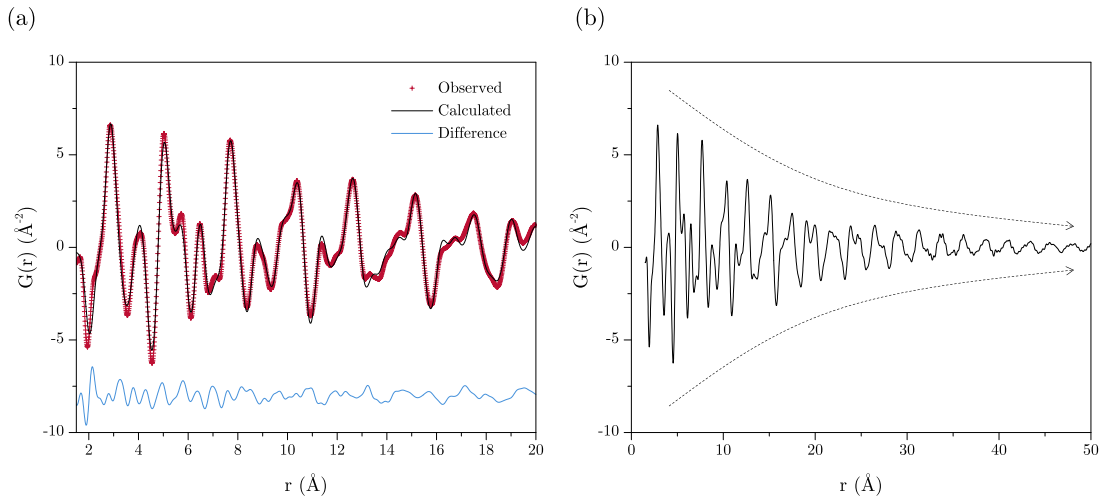
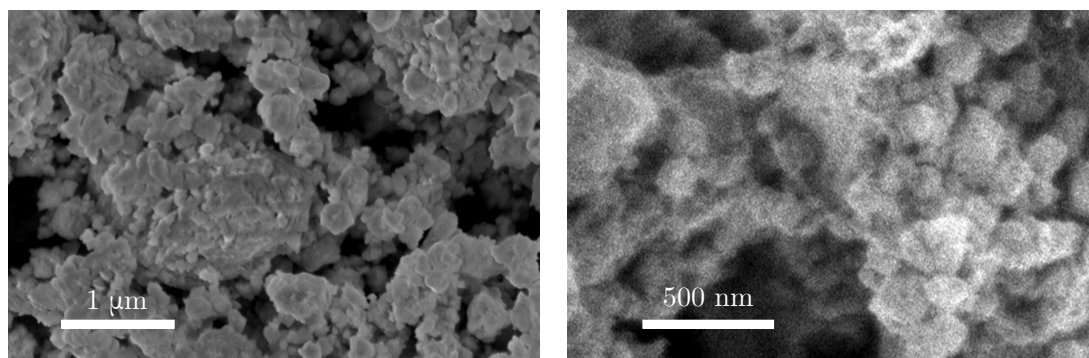


Figure 6.2: (a) Refined neutron PDF data of $\text{Li}_2\text{MnO}_2\text{F}$ over an r -range of 1.5 to 20 $\text{\AA}$. (b) Full range of neutron PDF data, the almost complete attenuation in signal up to 50 $\text{\AA}$ indicates that the ordered domain size is approximately 5 nm. Neutron data were collected from NOMAD and refinement was performed using the PDFgui interface.

value which was constrained as a single, equal value for all elements. This analysis shows that the local structure can be well described by a single phase rocksalt crystal structure with disordered Li/Mn occupancy and O/F occupancy of the cation and anion lattice sites, respectively. Furthermore, by 50 $\text{\AA}$ the PDF intensity diminishes more or less completely to nothing indicating that the size of ordered domains is approximately 5 nm, in close agreement with the Scherrer analysis.

With a good understanding of the atomic crystal structure, Scanning Electron Microscopy (SEM) imaging and Brunauer-Emmett-Teller (BET) surface area analysis were conducted to understand the macro-scale particle morphology. The images obtained, Figure 6.3, show that, despite the nano-scale crystallite size, the particle size is orders of magnitude greater ranging in diameter from 0.1 to 0.5 μm . The surface area from BET, $13.4(1) \text{ m}^2 \text{ g}^{-1}$ indicates an average particle size of 0.15 μm , assuming spherical particles.

Finally, to accurately confirm the composition of the pristine material, various chemical analysis techniques were employed as summarised in Table 6.2. ICP-OES confirmed no change in the Li:Mn ratio before and after milling. Similarly, solution state ^{19}F and ^7Li NMR show that the Li:F ratio remained unchanged. The only

**Figure 6.3:** SEM images of pristine $\text{Li}_2\text{MnO}_2\text{F}$ powder.

Technique	Measurement	Precursors	Ball-milled
ICP-OES	molar ratio Li : Mn	2.03(3)	1.99(3)
^{19}F and ^7Li NMR	molar ratio Li : F	0.99(2)	0.95(2)
Redox Titration	Mn oxidation state	+3.00(1)	+3.27(1)
Target Composition : $\text{Li}_2\text{MnO}_2\text{F}$			
Actual Composition : $\text{Li}_2\text{MnO}_{2.14}\text{F}$, or, $\text{Li}_{1.9}\text{Mn}_{0.95}\square_{0.15}\text{O}_{2.05}\text{F}_{0.95}$			

Table 6.2: Table of results for composition analysis for pristine $\text{Li}_2\text{MnO}_2\text{F}$.

obvious discrepancy is found in the Mn oxidation state which was determined from Iodometric redox titration to be +3.27, where it was expected to have stayed +3.00. Given all other elements were confirmed present in the expected amounts, this must be due to a slightly higher O content in the material. Since no other impurities were detected from Neutron PDF, which is sensitive to even amorphous components, this oxidation of the sample must have occurred as a result of ingress of a small amount of O_2 into the ball-mill jar during the milling process. The structure can therefore be most accurately described as a defect rocksalt with a small number of cation vacancies of composition $\text{Li}_{1.9}\text{Mn}_{0.95}\square_{0.15}\text{O}_{2.05}\text{F}_{0.95}$. Despite the compositional deviation, for simplicity the compound is labelled as $\text{Li}_2\text{MnO}_2\text{F}$ throughout.

6.3.2 Electrochemical Characterisation

The electrochemical behaviour of $\text{Li}_2\text{MnO}_2\text{F}$ was examined versus a Li metal negative electrode. As shown in Figure 6.4, $\text{Li}_2\text{MnO}_2\text{F}$ exhibits sloping voltage profiles on charge and discharge indicative of a single phase reaction mechanism. Charging up to 4.8 V vs. Li^+/Li , almost 70 % of the Li in the material can be extracted.

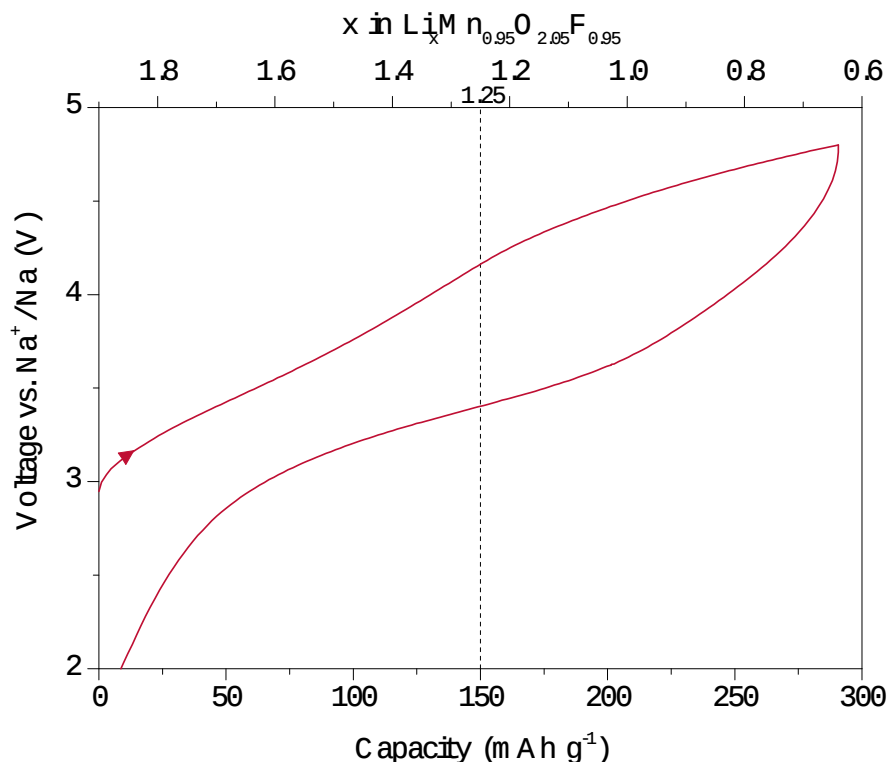


Figure 6.4: The first cycle load curve of $\text{Li}_2\text{MnO}_2\text{F}$ cycled at 22.4 mA g^{-1} ($C/10$). The cell was charged to 4.5 V then discharged to 2.0 V.

Furthermore, a substantial amount of charge is extracted beyond that which can be compensated by Mn oxidation alone, (150 mAh g^{-1}) marked on the figure as a dotted line. After this point the load curve changes appearing to become gradually more shallow extending for a further 140 mAh g^{-1} . On discharge, almost all of the capacity from charge is returned, 280 mAh g^{-1} , at an average voltage of 3.4 V vs. Li^+/Li . This corresponds to an energy density of 950 Wh kg^{-1} , comparable with the Li-rich materials, $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$, 950 Wh kg^{-1} , and $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$, 880 Wh kg^{-1} , but without the presence of Ni or Co.^{21,22}

To confirm that the charging process was predominantly due to lithium extraction from $\text{Li}_2\text{MnO}_2\text{F}$ and not electrolyte oxidation, ICP-OES compositional analysis was conducted on cathode materials extracted at different states of charge. Table 6.3 shows the expected values of the lithium content from charge counting the electrochemical response and the measured values from ICP-OES. The Li content was calculated from the Li:Mn ratio obtained from measurement assuming no

	Pristine	Charged to 4.8 V	Discharged to 2.0 V
Expected Li content	1.90	0.65	1.85
Measured Li content	1.85(2)	0.64(2)	1.89(2)

Table 6.3: Table of results of composition analysis for $\text{Li}_2\text{MnO}_2\text{F}$ electrodes.

dissolution of Mn into the electrolyte in the cell. The results show very close agreement between expectation and measurement indicting minimal contribution from electrolyte oxidation.

The electrochemical behaviour gradually evolves over cycling as shown in Figure 6.4. Both the charge and discharge capacities decrease until, after 50 cycles, they have decayed by approximately 40% of the initial value. By plotting the dQ/dV it is possible to see that the capacity fades predominantly around the 4.5 V region of the charge and 3.4 V region of the discharge corresponding to the capacity delivered by O-redox. Interestingly, limiting the upper cut off voltage to 4.2 V affords much better cycling stability, albeit at a significantly reduced capacity. The electrochemical capacity fading over cycling will be revisited at a later point in the chapter. For now, the focus remains on understanding the first charge-discharge cycle of $\text{Li}_2\text{MnO}_2\text{F}$.

6.3.3 Spectroscopic Characterisation

Having established that lithium is extracted from and inserted into $\text{Li}_2\text{MnO}_2\text{F}$ in line with expectation, a spectroscopic investigation was carried out to study the charge compensation mechanism accompanying charge and discharge. *Ex situ* Mn L-edge XAS was conducted in iPFY mode to probe oxidation state changes to Mn in the bulk of $\text{Li}_2\text{MnO}_2\text{F}$. O K-edge XAS and RIXS measurements were also performed to detect the possible presence of oxidised O.

Mn L-edge XAS

As shown in Figure 6.6, the L-edge spectrum for pristine $\text{Li}_2\text{MnO}_2\text{F}$ most closely resembles that of the Mn^{3+} reference compound Mn_2O_3 as expected. At the half charged state, the Mn spectra exhibit a peak shape very similar to that of Mn^{4+} in Li_2MnO_3 indicating that Mn has reached +4 by 4.2 V. After charging

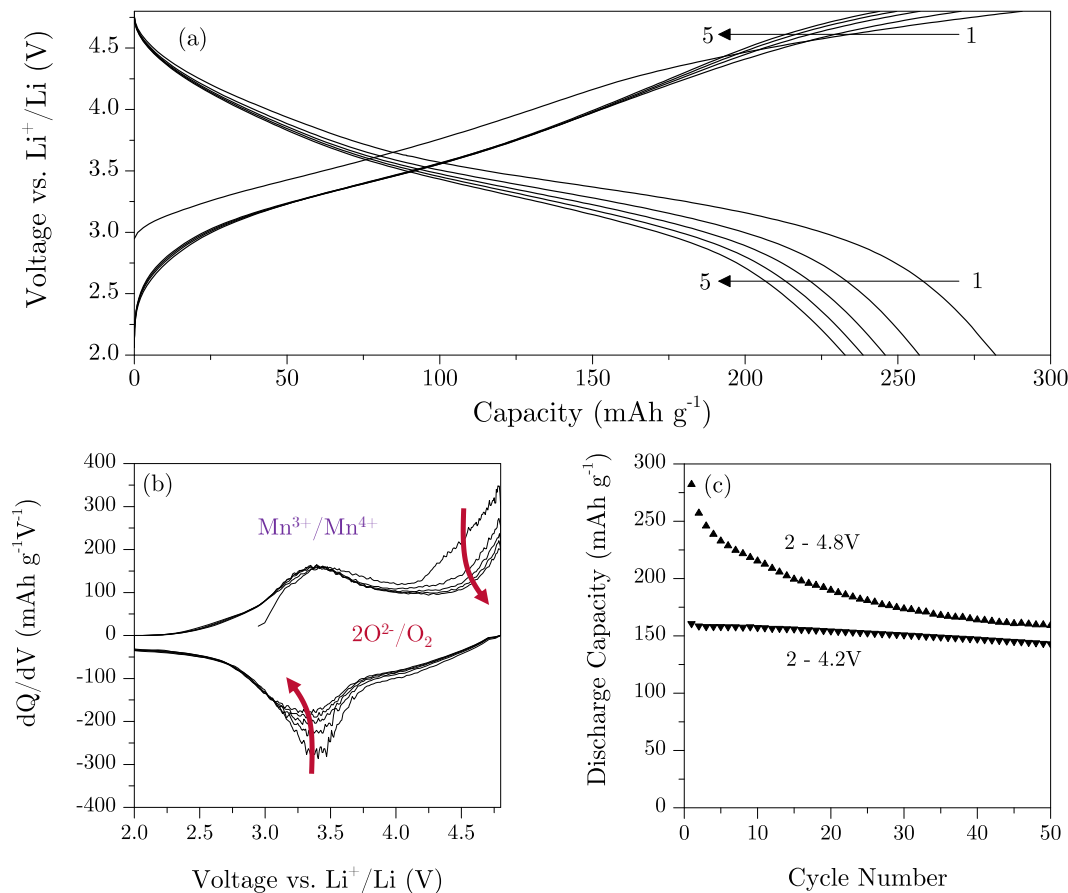


Figure 6.5: (a) Voltage versus capacity plot of the first five charge-discharge load curves of $\text{Li}_2\text{MnO}_2\text{F}$ cycled at 22.4 mA g^{-1} ($\text{C}/10$). (b) dQ/dV versus voltage plots highlighting the redox couples evolving over cycling. (c) Discharge versus cycle number plot of $\text{Li}_2\text{MnO}_2\text{F}$ half cells cycled between different voltage limits.

a further 130 mAh g^{-1} to 4.8 V, the Mn spectra remain unchanged implying a different charge compensation mechanism is taking place. On discharge, the Mn appears to remain predominantly +4 until the latter half of the load curve when it is reduced back to a similar oxidation state as the pristine material, +3. Some slight broadening of the L-edge at the halfway point indicates greater crossover on discharge of the two-redox mechanisms.

O K-edge XAS

Turning to the O K-edge XAS data at the same states of charge there are some clear changes observed. Firstly, after the initial charge to 4.2 V the O K-edge exhibits a

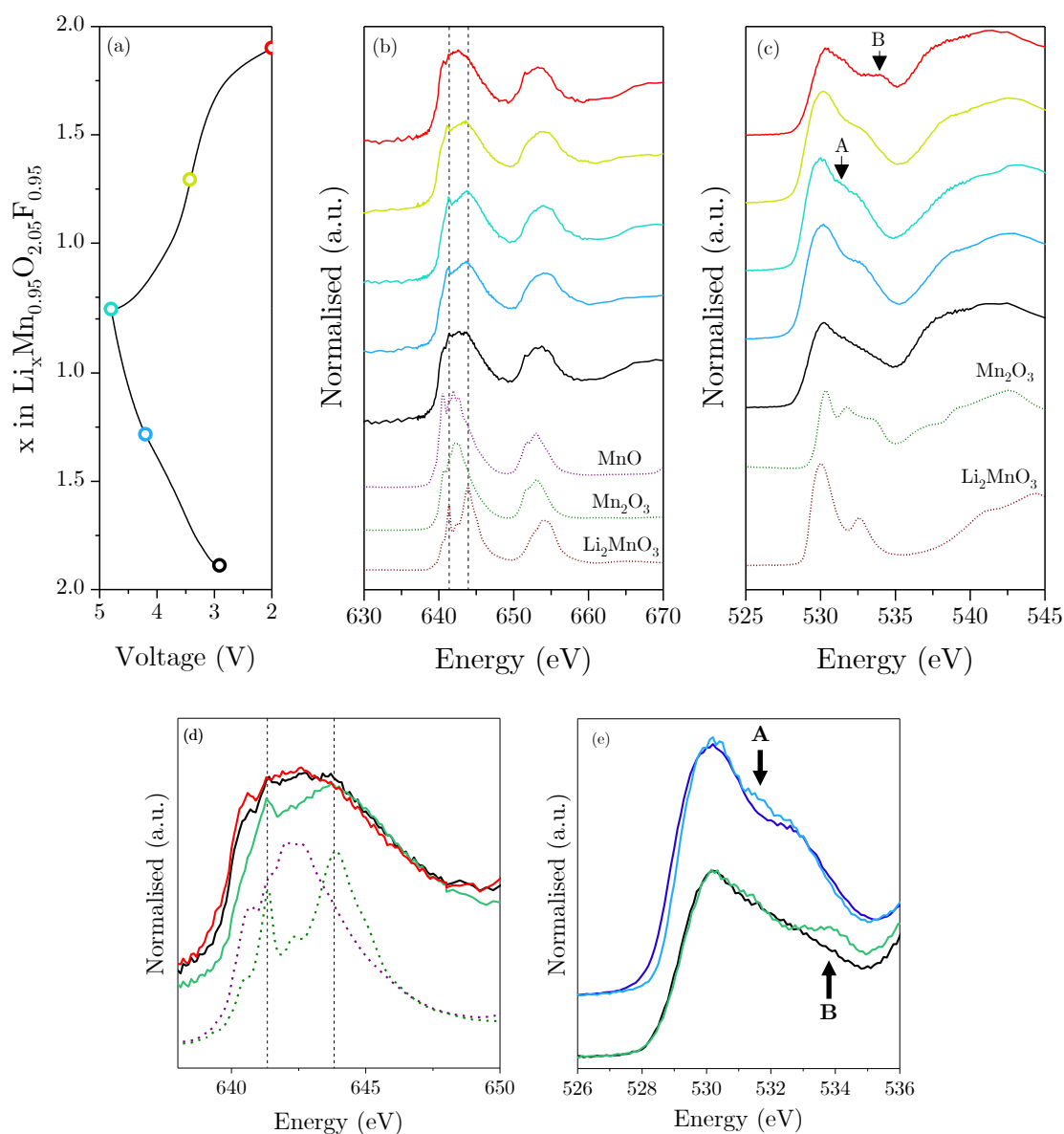


Figure 6.6: (a) The first cycle load curve of $\text{Li}_2\text{MnO}_2\text{F}$ with states of charge chosen for *ex situ* analysis. (b) *Ex situ* Mn L-edge XAS data as a function of state of charge. Reference spectra for MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}) and Li_2MnO_3 (Mn^{4+}) are shown below. (c) O K-edge XAS data as a function of state of charge. The reference spectrum for Mn_2O_3 and Li_2MnO_3 are shown below. (d) Close-up of Mn L-edge XAS data. (e) O K-edge XAS data highlighting changes in spectral weight between different states of charge.

shape similar to that of Li_2MnO_3 or indeed any of the +4 Mn materials studied in Chapters 3, 4 or 5. Then on charging to 4.8 V a new feature appears at 531 eV labelled A. From earlier chapters this feature has been determined as originating from oxidised O, specifically molecular O_2 , suggesting that the same O-redox process is occurring here. Feature A disappears by the halfway point on discharge. After full discharge, another feature labelled B appears on top of a spectrum that otherwise resembles that of the pristine again. This feature can be attributed to carbonate (CO_3^{2-}) which usually give a peak in the O K-edge at 534 eV that must form at the surface of the electrode.²³ The implication of this is that there is likely to be some surface reactivity between the electrode and the electrolyte.

O K-edge RIXS

To confirm the participation of O in the redox processes accompanying Li extraction and insertion in $\text{Li}_2\text{MnO}_2\text{F}$, O K-edge RIXS data were collected. As seen from the data presented in Figure 6.7 the now familiar signature of O-redox can be clearly seen when exciting at 531 eV. An increase in the elastic peak intensity and the appearance of an inelastic scattering feature at 524 eV show that molecular O_2 is formed in the bulk of $\text{Li}_2\text{MnO}_2\text{F}$ at the end of charge. O oxidation only occurs after $\text{Li}_2\text{MnO}_2\text{F}$ is charged to 4.2 V, since no such features are seen in the 4.2 V spectrum, indicating a clear separation between the Mn 3+/4+ oxidation (low voltage) and O oxidation (high voltage).

6.3.4 Oxygen Loss

To evaluate the possibility of oxygen loss from $\text{Li}_2\text{MnO}_2\text{F}$, an OEMS experiment was performed. The results show a very small release of O_2 from the electrode upon charging, <0.005 mol O_2 per mole of cathode. Some CO_2 is also released corresponding to 0.03 moles per mole of cathode material. This could arise from reactions at the electrode-electrolyte interface, potentially from surface oxidised O, however the amount observed is too small to contribute substantially to the charging process.

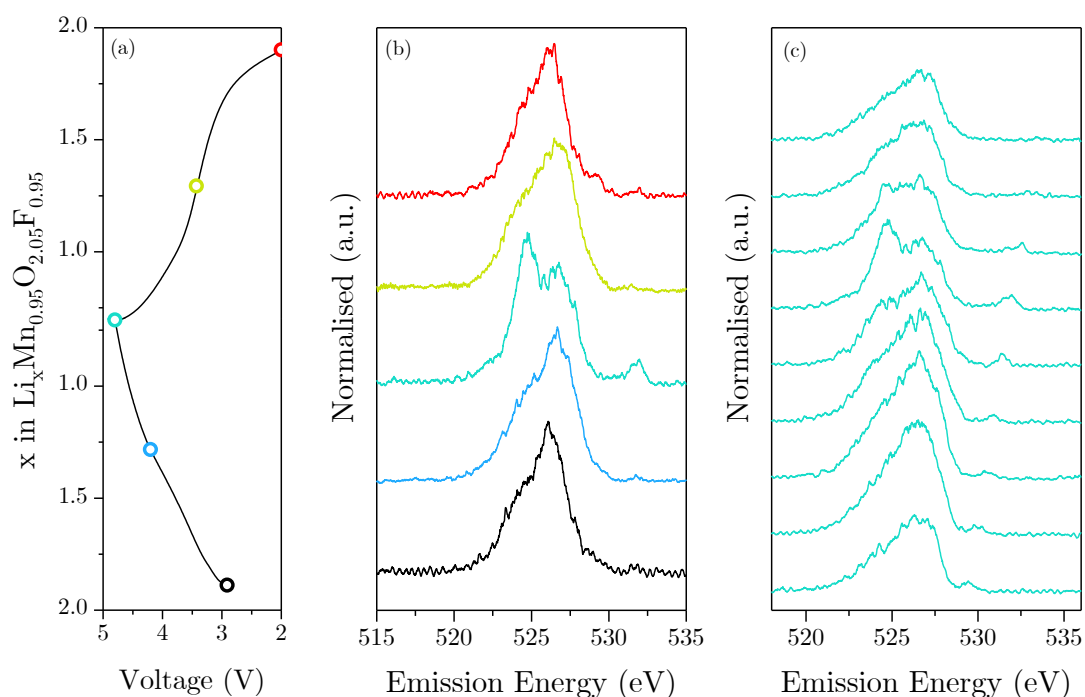


Figure 6.7: (a) The first cycle load curve of $\text{Li}_2\text{MnO}_2\text{F}$ with states of charge chosen for *ex situ* analysis. (b) Low resolution RIXS spectra at 531 eV excitation energy of $\text{Li}_2\text{MnO}_2\text{F}$ at different states of charge measured at Spring8, Japan (c) Low resolution RIXS spectra of $\text{Li}_2\text{MnO}_2\text{F}$ charged to 4.5 V at excitation energies chosen at 0.5 eV intervals between 529 eV and 534 eV measured at Spring8, Japan.

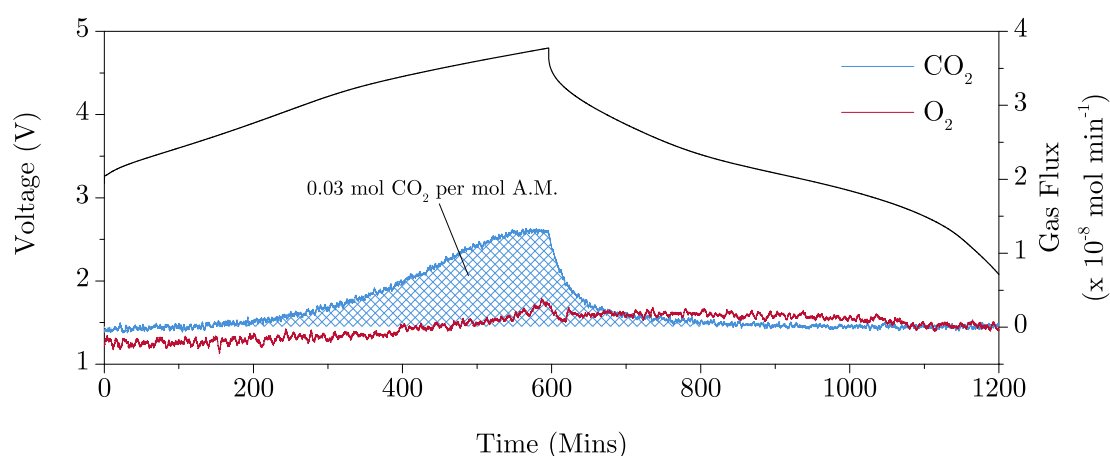


Figure 6.8: The first cycle load curve of $\text{Li}_2\text{MnO}_2\text{F}$ monitored by *operando* mass spectrometry. Negligible O_2 gas was evolved. 0.03 moles of CO_2 per mole of active cathode material was evolved.

In light of the understanding from Chapter 4, it is perhaps surprising that only trace amounts of O-loss are recorded. Given the random distribution of Li and Mn around O, there will potentially be plenty of underbonded O at or near the electrode surface (i.e. any configurations around O with >3 coordinating Li). The suppression of O-loss seen for $\text{Li}_2\text{MnO}_2\text{F}$ is likely to be due to the presence of F^- anions which reduce the number of neighbouring O atoms thereby disrupting the formation of O-O bonds. Another consideration is that, while the crystallite size is very small (i.e. 5 nm) the particle size (composed of many crystallites) is orders of magnitude larger ($0.5\text{ }\mu\text{m}$) and so the surface to volume ratio of the electrode will be much smaller and, in fact, comparable with conventional electrode materials.^{24,25} Surface O-loss could therefore be smaller than might otherwise be anticipated from nano-particulate electrodes.

6.3.5 Structural Change

Recalling the sloping shape of the charge and discharge profiles for $\text{Li}_2\text{MnO}_2\text{F}$, a single phase structural transformation is anticipated during Li extraction and reinsertion. This is indeed what is observed as seen from the *ex situ* PXRD data at different states of charge. As lithium is extracted during charge, the diffraction peaks gradually shift to higher 2θ values indicative of a contracted unit cell parameter and thus an isotropic contraction of the cubic crystal structure as a whole. On subsequent discharge the unit cell parameter increases as the structure expands to accommodate Li. In total, the volume expands and contracts by about 6 %. These data clearly support a single phase reaction mechanism of Li insertion and extraction in agreement with the electrochemical response.

PXRD patterns measured on electrode samples that had been cycled 50 and 100 times show the remarkable retention of long range order. This structural stability is surprising considering the rocksalt crystal structure is metastable, phase segregating upon moderate heating to LiF and layered LiMnO_2 or spinel LiMn_2O_4 . Furthermore, the rocksalt experiences quite severe degrees of delithiation in the charged state and thus a large concentration of cation vacancies. In ordered layered materials at

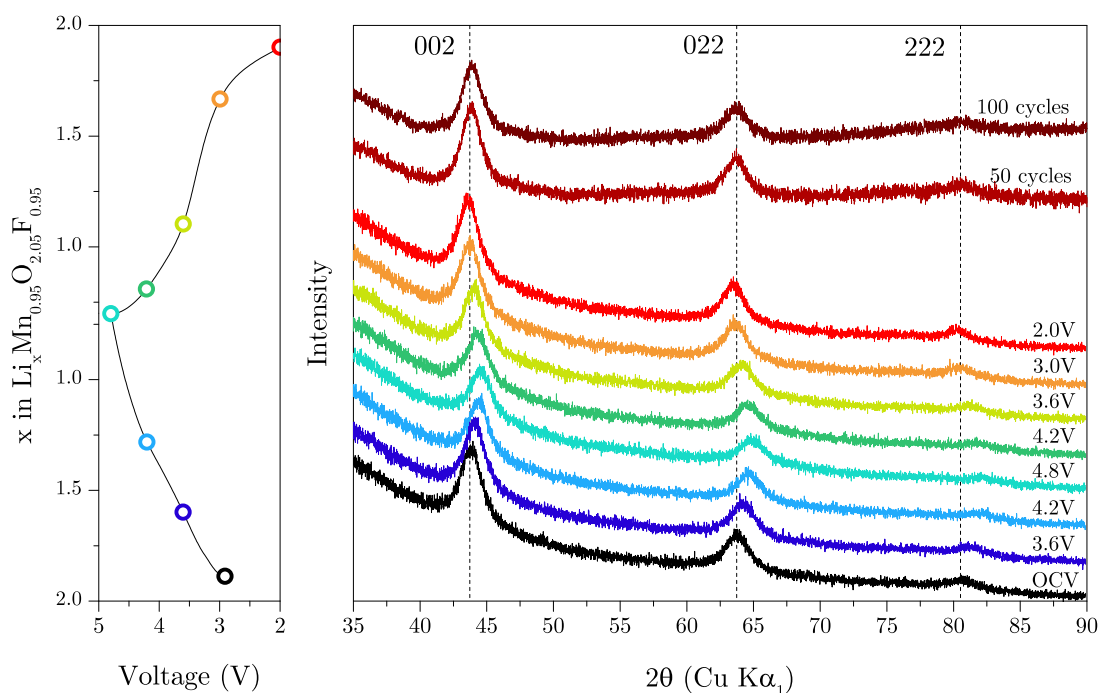


Figure 6.9: The first cycle load curve of $\text{Li}_2\text{MnO}_2\text{F}$ monitored by *ex situ* XRD. The cells were charged galvanostatically between 4.8 V and 2.0 V. The current was set at 22.4 mA g^{-1} ($\text{C}/10$) on charge and discharge.

similar states of delithiation, metal migration has been shown to occur introducing defects and disorder into the crystal structure.^{26–29} However, given that $\text{Li}_2\text{MnO}_2\text{F}$ is already very disordered and in a high entropy state, there may not be as large an entropic driving force towards further disordering the system.

Nonetheless, the density of cation vacancies in the charged structure is very high and so migration of metals is likely. One possibility is that the system is at equilibrium with Mn migrating equally in all directions and there is no net structural change. Another possibility is a gradual densification of the structure to eliminate cation vacancies thereby ejecting anions near the surface into solution in the electrolyte or as a surface interphase. This would necessarily result in an increase in the average number of nearest neighbour Mn atoms. To investigate this, Mn EXAFS data was employed on electrode materials at different states of charge and cycle number.

Mn EXAFS

Similar to PDF, EXAFS is a technique which relies on coherent scattering between neighbouring atoms in a structure.³⁰ By analysing the trailing edge of the Mn K-edge XANES spectrum, which contains oscillations resulting from scattering of x-rays from atoms immediately surrounding Mn, EXAFS allows an element-specific insight into local coordination environment around that element that typically extends out to the 3rd and 4th nearest neighbour atoms.

The EXAFS data for $\text{Li}_2\text{MnO}_2\text{F}$ are shown in Figure 6.10 (a). For comparison, the EXAFS for fully cation dense MnO, which also possesses a cubic rocksalt crystal structure, is overlaid. The primary two features that are seen at 1.4 Å and 2.4 Å correspond to scattering from the first nearest neighbour (NN) anions (i.e. O/F) and cations (i.e. Li/Mn) respectively. Since all the materials studied possess a fully dense cubic lattice of anions, all spectra can be normalised in intensity to 1 according to this peak for direct quantitative comparison. Taking the intensity of the second peak of MnO to be the upper limit of Mn densification, as all 12 neighbouring cations are Mn, and 0 intensity to be the lower limit, since Li hardly scatters x-rays at all, it is possible to extract the average number of 1st NN Mn atoms around Mn in the electrode samples.

The robustness of this analysis can be immediately tested by considering the 2nd peak intensity of the pristine $\text{Li}_2\text{MnO}_2\text{F}$ sample which corresponds to approximately 3.7 Mn. This is a pretty close match to the average value of 3.5 Mn calculated assuming a completely random distribution of Li and Mn in a 2:1 ratio among all available cation sites as determined from PDF analysis. The probability and cumulative probability distribution functions from this calculation are plotted in Figure 6.10 (b) and (c). The average number of NN Mn is extracted from the intercept of the cumulative probability function with the halfway line and is labelled.

Electrode samples were collected after the 1st and 50th cycles and their Mn EXAFS plotted. At first glance there does not appear to be any substantial change in the 2nd peak intensity even after 50 cycles. By this time, the capacity has faded by about 40% of the initial value, Figure 6.5 (c). To more closely quantify

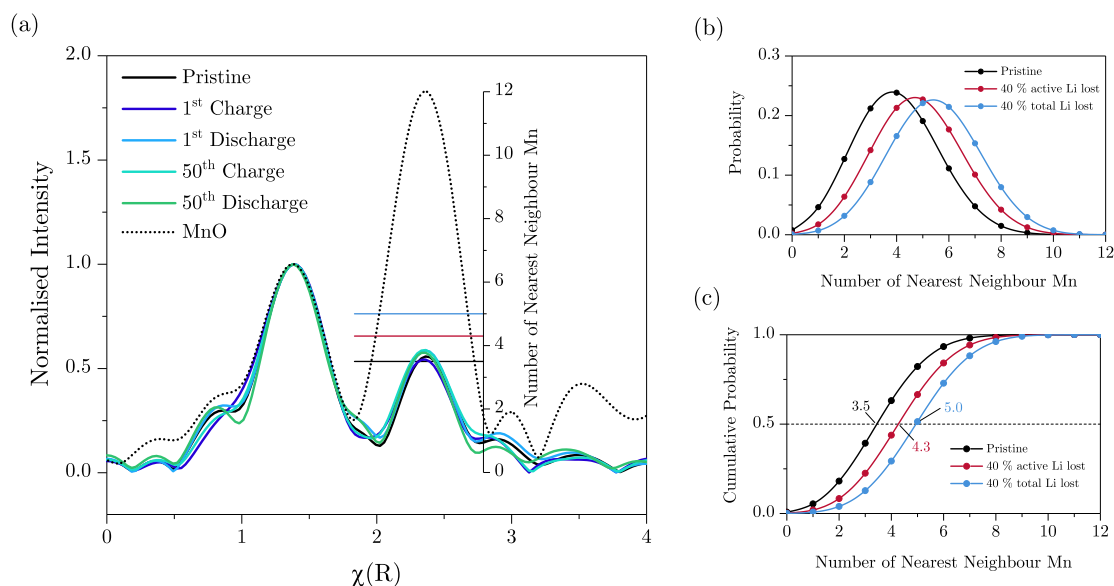


Figure 6.10: (a) EXAFS data for Li₂MnO₂F at different stages of cycling with reference data for MnO. Data are normalised to the first peak corresponding to the nearest neighbour anions. A scale bar is overlaid for the second peak corresponding to the nearest neighbour Mn. There is no obvious change in the peak height over cycling indicating the absence of Mn clustering. (b) Probability distribution curves for the number of nearest neighbour Mn assuming a random distribution in pristine Li₂MnO₂F (black), densified Li₂MnO₂F assuming loss of 40% of the active Li (red) and densified Li₂MnO₂F assuming loss of 40% of the total Li (blue). (c) Plot of the cumulative probability to determine the average number of nearest neighbour Mn. These average values are plotted as as coloured lines on the scale bar in (a).

the degree of densification that might have occurred at this point, the probability distribution functions were adjusted to account for a 40% loss of active Li (the amount of Li reversibly extracted and reinserted) and 40% loss of total Li (all of the lithium in Li₂MnO₂F). This analysis again assumes a completely random distribution of the remaining Li and Mn with no vacancies, therefore providing a lower limit which ignores any preference for phase segregation/formation (i.e. crystalline MnO) which would otherwise push up the expected value for NN Mn for the same compositions. The distributions show that, even with 40% of the total Li lost, the random cation mixing ensures the number of NN Mn stays lower than might be anticipated for such a large compositional change. Nevertheless, plotting the average values for these distributions on the scale over the EXAFS, it is clear that the 2nd peak intensity does not change by a large enough margin

for Mn migration alone to explain the capacity fade.

Cathode-Electrolyte Surface Reactivity

The evidence suggests that long- and short-range structural transformation in the bulk of the $\text{Li}_2\text{MnO}_2\text{F}$ electrode can be ruled out as the primary cause for the capacity fading that is seen over cycling. The root cause is therefore likely to be a surface localised phenomenon. Some CO_2 release is observed as a result of charging the material through the high voltage O-redox region. Furthermore, a significant carbonate signal is detected on discharge in the O K-edge XAS data. This suggests there may be some reactivity between the oxidised O at the surface of the electrode particles with the electrolyte that forms carbonate decomposition products. These are likely to be oxidised at high potentials to form CO_2 gas and deposited at low potentials as alkyl carbonates which is why they only appear in the discharged sample. In this way, the surface of the particles could be eroded over cycling through the repeated formation, deposition and stripping of carbonates thereby gradually eating away at the electrode.^{31–33}

This degradation mechanism would also involve dissolution of Mn into the electrolyte such that densification does not occur. Mn solubility in commonly used liquid electrolytes is a well-known problem which has inhibited the full commercial implementation of Mn-rich electrodes such as LiMn_2O_4 which also consequently exhibit capacity fade.^{3–6} Continued cycling between Jahn-Teller active and inactive Mn^{3+} and Mn^{4+} respectively has also been implicated in exacerbating Mn dissolution from these electrodes.⁴ However, this effect may be suppressed to an extent in $\text{Li}_2\text{MnO}_2\text{F}$ by the presence of fluoride anions which disrupt the degeneracies of the e_g and t_{2g} orbitals in the coordination sphere around Mn. The driving force for Jahn-Teller distortion is a lowering of the total electron energy that results from breaking the degeneracy of partially occupied orbitals.³⁴ In the octahedral crystal field, concerted elongation and compression of bonds breaks the degeneracy of the e_g and t_{2g} sets of orbitals lowering the energy only when either of them are part filled, Figure 6.11. For a coordination sphere comprised of O^{2-} and F^-

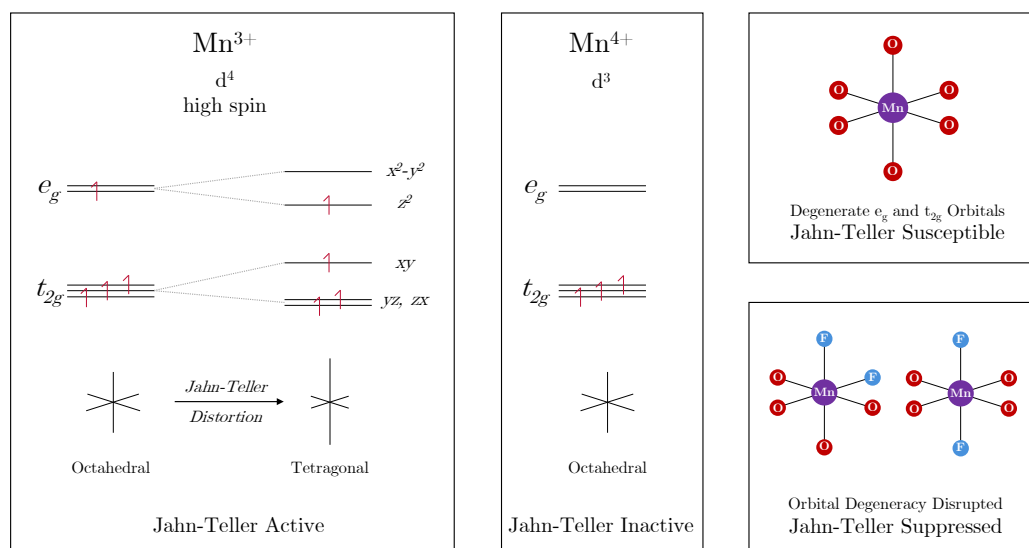


Figure 6.11: Schematic illustrating the electronic origin of Jahn-Teller distortion for Mn^{3+} in the octahedral crystal field. Partial occupation of degenerate orbitals drives structural distortion to remove this degeneracy and lower the electron energy. For $\text{Li}_2\text{MnO}_2\text{F}$, the mixing of O^{2-} and F^- anions disrupts the orbital degeneracy of the e_g and t_{2g} orbitals, suppressing Jahn-Teller distortion.

anions in various configurations, the degeneracy of the e_g and t_{2g} will already be disrupted by virtue of different bonding between Mn-O and Mn-F. Hence, there is no driving force for Jahn-Teller distortion to occur limiting the structural changes between different oxidation states of Mn.

Nonetheless, to investigate Mn dissolution in $\text{Li}_2\text{MnO}_2\text{F}$, ICP-OES was employed to measure the total amount of Mn found in the electrolyte, deposited on the anode and cell parts. Cycled cells were disassembled and the cathode extracted. All of the other cell parts were then washed with concentrated nitric acid to fully dissolve the Mn that had left the cathode and an aliquot of the solution was tested. The results indicate that around 4 % of the total Mn from the electrode had been lost after 50 cycles and 8% after 100 cycles.

While this degree of Mn loss alone doesn't appear to fully explain the observed capacity fade (4% versus 40%), the combined loss of redox active Mn and O, as well as impedance that may build up due to: a) the surface layer that develops at the

cathode-electrolyte interface; b) the decomposed electrolyte; or c) Mn deposition at the anode, could explain the observed cell deterioration.

6.3.6 Outlook for Disordered Rocksals exhibiting O-redox

Since the discovery that disordered rocksalt materials exhibit appreciable degrees of lithium insertion and extraction and that ball-milling can be used to easily access metastable phases, many new compositions have now been discovered. Strategies have generally centred around compositions involving TM elements that undergo multiple oxidation state changes to compensate for Li exchange such as $\text{Li}_2\text{VO}_2\text{F}$ ($\text{V}^{3+/4+/5+}$),^{13,35,36} $\text{Li}_2\text{MoO}_2\text{F}$ ($\text{Mo}^{3+/4+/5+}$)³⁷ or most recently $\text{Li}_2\text{Mn}_{2/3}\text{Nb}_{1/3}\text{O}_2\text{F}$ ($\text{Mn}^{2+/3+/4+}$).³⁸ While these strategies successfully deliver high capacities, typically $>300 \text{ mAh g}^{-1}$, it is at the expense of high voltage due to the need to use low metal valence states.

This work on $\text{Li}_2\text{MnO}_2\text{F}$ demonstrates that O-redox can be invoked in disordered rocksalt materials to reversibly store charge beyond the TM valence states. In $\text{Li}_2\text{MnO}_2\text{F}$, redox is restricted only to the high valence states of Mn ($+3/+4$) and the high voltage O-redox couple. This therefore allows access to both high capacity and high voltage delivering a high overall energy density. The energy density of $\text{Li}_2\text{MnO}_2\text{F}$ is comparable to that of the leading layered Li-rich materials being considered as candidate replacements in next-generation Li-ion cells under similar testing conditions (i.e. current rates and temperatures).

Beside $\text{Li}_2\text{MnO}_2\text{F}$, other disordered rocksalt materials have been found which are suspected of operating on oxygen redox and similarly provide competitive energy densities to the leading candidates in the field. Figure 6.12 shows a voltage versus capacity plot of all known O-redox disordered rocksalt materials (purple) compared with layered Li-rich (red) and conventional (green) cathode materials. Bars represent the voltage limits and the black line is the average voltage delivered on the first discharge, while the dotted lines represent the contours of equal energy density.

However, these promising metrics are tempered by some critical shortcomings. Due to the poorer conductivities of the Nb and Ti based systems, they typically need

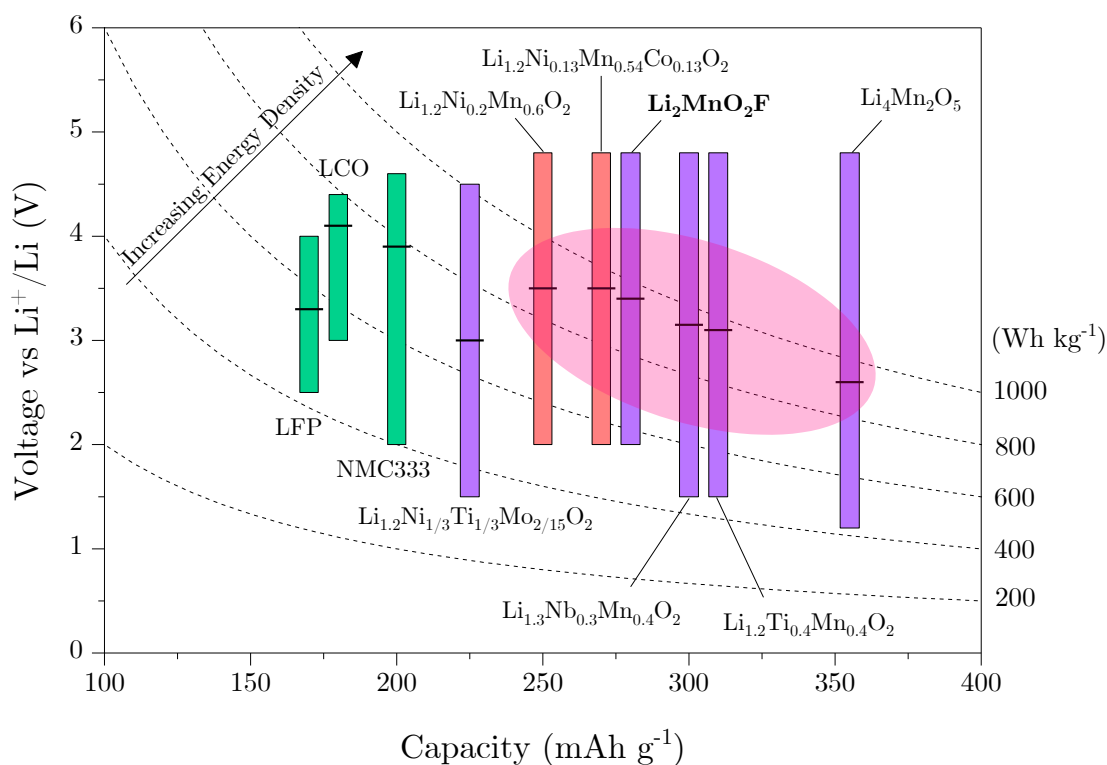


Figure 6.12: Voltage versus capacity plot for conventional positive electrode materials (green),^{39–41} layered lithium rich O-redox materials (red)^{21,22} and disordered rocksalt lithium rich O-redox materials (purple).^{42–44} Red shaded region highlights high energy density cathodes.

to be operated at elevated temperatures (50 °C) and low current rates (5 mA g⁻¹) to give good performance.⁴² $\text{Li}_4\text{Mn}_2\text{O}_5$ similarly needs charging and discharging slowly within wide voltage limits to be competitive on energy density.⁴⁴ Furthermore, all of these materials, including $\text{Li}_2\text{MnO}_2\text{F}$ exhibit severe capacity decay over cycling which needs to be understood and overcome for these materials to ever be considered as viable replacements. Nevertheless, there remains immense potential in the field of disordered rocksalt materials and particularly those exhibiting O-redox. The compositional space in the disordered rocksalt crystal system is vast and unexplored. Moreover, the results presented in this chapter for $\text{Li}_2\text{MnO}_2\text{F}$ reveal a remarkable stability to the short and long range structures of these materials which could translate to very long cycle lives if suitable electrolyte systems can be developed to inhibit interfacial reactions and Mn dissolution.

6.4 Conclusion

O-redox chemistry can be extended from ordered layered systems to highly disordered cubic rocksalt materials successfully realising high energy density materials. $\text{Li}_2\text{MnO}_2\text{F}$ was synthesised by ball-milling and found to exhibit a disordered rocksalt crystal structure with no evidence of local ordering. Chemical analysis showed a slight deviation from the expected composition on account of oxidation during synthesis. $\text{Li}_2\text{MnO}_2\text{F}$ delivers a high capacity to store charge, 280 mAh g⁻¹ at an average voltage of 3.4 V (corresponding to 950 Wh kg⁻¹). This capacity arises from both Mn and O-redox. The material exhibits negligible O-loss and no detectable structural change on a local or long-range scale over 50 cycles despite severe capacity decay. This could be due to the inherent stability of a disordered system which may be more impervious to the effects of metal migration than ordered systems or the presence of fluoride anions which disrupt Jahn-Teller effects and O-O bond formation.

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7

Conclusion

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7.1 Further Work

7.1.1 Preventing O-loss

In light of the understanding of underbonding, one strategy that could be investigated to prevent O-loss from Li-rich compositions is synthesising materials which are more cation dense in the surface region using cations that are unlikely to be de-intercalated. For instance, if Mg is introduced into the surface of Li_2MnO_3 or $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$, O-loss may be effectively suppressed by preventing the coordination around O dropping below three, such as in $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$. This could be achieved through a soft chemistry approach, such as chemical ion-exchange or low temperature annealing, to prevent Mg distributing through the bulk of the material. Alternatively, surface coatings could be employed which would

act as a physical barrier preventing O_2 evolution but allowing Li^+ transfer.

7.1.2 Promoting Reversible High Voltage O Reduction

Given the improved stability of the ribbon ordering scheme at accommodating oxidised oxygen without substantial structural rearrangement, specific compositions, structures and synthetic routes which promote new in plane ordering schemes ought to be pursued. Na-ion compounds are useful intermediate compounds for tuning in-plane ordering since the strict division between Na and Li in adjacent layers allows the TM layer composition to be carefully tweaked. Subsequently, ion-exchange reactions could be performed to make Li-ion cathode materials which would otherwise not be accessible via direct conventional solid state routes.

Substituting Mn in the ribbon structure for alternative metals with a reduced tendency for TM migration might also serve to suppress the structural rearrangement and promote longer term stability of high voltage O-redox. Compositions such as ribbon ordered $Na_{0.6}[Li_{0.2}Co_{0.8}]O_2$ in the P2-type crystal structure could be envisioned and ion-exchanged to make Li-rich cobalt oxide compounds.

A different approach to suppress TM migration could be to insert large, immobile cations into the AM layers distorting the AM layer sites to make them less favourable for TM occupation. For Li-rich compositions, this may well suppress out-of-plane TM migration but will be unlikely to prevent in-plane migration. However, this strategy could be employed in compounds without excess alkali-ions (such as $Na_{0.67}[Mg_{0.28}Mn_{0.72}]O_2$ or compounds with Li:TM ratio of 1:1) containing electrochemically inactive elements in the TM layer (such as Mg^{2+} , Al^{3+} or Ti^{4+}) to promote O oxidation over TM oxidation. While this might not offer the higher capacities promised by virtue of excess Li, this may well raise the voltage of the whole charge realising higher energy densities by operating on a reversible high voltage O-redox plateau. In these structures, in-plane ordering would be blocked and O-O dimerisation would not be able to occur.

7.1.3 Synthesising New O-Redox Active Disordered Rock-salts

The discovery of $\text{Li}_2\text{MnO}_2\text{F}$ and the apparent versatility of ball-milling as a methodology to access metastable disordered rocksalt phases (such as $\text{Li}_2\text{VO}_2\text{F}$, $\text{Li}_2\text{MoO}_2\text{F}$ and $\text{Li}_2\text{Mn}_{1/2}\text{Ti}_{1/2}\text{O}_2\text{F}$) raises the exciting prospect of new compositions within this class of compounds. Li-ion oxyfluoride materials based on Co, Ni or Fe could be possible. The Li content and the O/F ratio can be tuned appropriately to favour TM redox over O-redox or vice versa. It might be possible to remove fluorine, which is pretty toxic and expensive, and make disordered rocksalt oxides or even oxychlorides or oxysulfides which are O-redox active.

Beyond Li-ion cathodes, new Na-ion materials could be possible such as $\text{Na}_2\text{MnO}_2\text{F}$, the analogue compound to $\text{Li}_2\text{MnO}_2\text{F}$, or even $\text{Na}_2\text{FeO}_2\text{Cl}$ which could be made from NaCl and Fe_2O_3 - salt and rust! Each of these would be anticipated to operate on TM and O-redox should they be viably synthesised.

7.2 Conclusion

Invoking the redox chemistry of oxide ions is a compelling strategy to surpass the limitations imposed by transition metals on storing charge in cathode materials for rechargeable batteries. The O $2p$ band of electrons lies low in energy in transition metal oxides and thus in principle offers a means to deliver high voltage capacity yielding significant improvements in energy density, if it can be accessed within the voltage stability window of the electrolyte. However, oxidation of O results in structural instability and, in most cases, substantial structural change. Direct loss of O from the lattice can occur as O_2 or as CO_2 through reaction with the electrolyte. Furthermore, TM migration, voltage hysteresis and sluggish kinetics are all commonly associated with O-redox. This thesis summarises work undertaken to unravel the complex web of phenomena that appear to accompany O-redox and further to identify strategies that might harness O-redox effectively.

Ionicity of the O bonding environment is a critical lever for promoting access to these low lying O states at voltages within the electrolyte stability window.

Substitution of TM atoms in the TM layer for excess Li or Na introduces $\text{Li}^+\text{-O-Li}^+$ (or $\text{Na}^+\text{-O-Na}^+$) configurations which give rise to high energy *orphaned* O $2p$ orbitals that are placed nearer the top of the valence band. As seen in Chapter 3, this can also be achieved without needing to use alkali metal ions (i.e. Li- or Na-rich compositions). Instead, other elements such as Mg successfully promote O-redox, as demonstrated for $\text{Na}_{0.67}[\text{Mg}_{0.28}\text{Mn}_{0.72}]\text{O}_2$, revealing the importance of ionicity.

Another interesting consequence of Mg substitution is the suppression of O-loss, which is otherwise observed without exception among alkali-rich cathodes. In contrast to Li or Na, Mg is much less mobile in solid state materials and is retained in the cathode structure even under harsh charging conditions. When Li from the TM layer of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ is removed from the structure altogether, O-loss from the lattice is observed originating exclusively from the near surface (first 10 nm) region. The retention of Mg prevents the coordination number around O from dropping below three thereby avoiding underbonding and O-loss from the surface. This implies that surface treatments to protect against underbonding will be necessary in Li-rich compositions to mitigate O-loss.

Most layered O-redox cathodes exhibit a high voltage plateau followed by substantial voltage loss on discharge. However, these two are not inextricably linked. One notable exception is $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ which shows a remarkably reversible high voltage charge/discharge plateau which persists over several cycles. $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ is different from the vast majority of O-redox compounds since, rather than exhibiting a honeycomb arrangement of Li, such as in $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$, the TM layer is ribbon ordered. Ribbon ordering is predominantly retained over the first few cycles, whereas honeycomb ordering is almost completely lost on the first cycle correlating well with the appearance of voltage hysteresis. DFT calculations reveal that the formation of O_2 is the dominant driving force for this disorder by providing electronic stabilisation to the high energy electron holes. The presence of O_2 in the bulk of $\text{Na}_{0.75}[\text{Li}_{0.25}\text{Mn}_{0.75}]\text{O}_2$ is confirmed for the first time using high resolution RIXS which resolves the signature feature of O-redox into a vibrational progression unique to O_2 . This signal disappears

on discharge indicating the reduction of O_2 which takes place at lower voltages than the charging plateau at 4.2 V vs. Na^+/Na . Other studies have shown that the RIXS feature is present for many hundreds of cycles on charge suggesting that O can be reversibly cycled between O^{2-} and O_2 albeit at the lower voltage of around 3.2 V vs. Na^+/Na .

Furthermore, a completely new feature is seen just before the O pre-edge in charged $Na_{0.6}[Li_{0.2}Mn_{0.8}]O_2$ which is attributed to electrons holes on an undistorted network of O^{2-} ions. This preservation of the degeneracy of the O environments, by virtue of the stability of the ribbon ordering scheme, allows for the oxidation and reduction of O at high voltage with suppressed TM migration. These results untangle O-redox from voltage hysteresis showing that voltage loss is not an immutable consequence of O-redox. O_2 formation can be suppressed in ordering schemes other than the ubiquitous honeycomb ordering promoting truly reversible, high voltage O-redox. This points towards a compelling new strategy for discovering materials that could enable high voltage O-redox.

Finally, moving away from layered materials, a new disordered rocksalt material was discovered, Li_2MnO_2F , which stores charge using both the $Mn^{3+/4+}$ redox couple and O-redox. The same RIXS feature is observed for Li_2MnO_2F indicating a similar mechanism of O-redox is occurring here as for the layered compounds (reversible $O^{2-} \longleftrightarrow O_2$). The crystal structure remains remarkably stable over long term cycling, with little evidence of TM clustering or O-loss, pointing to the potential for the disordered rocksalt class of compounds to deliver disruptive new materials for high energy density battery cathodes. Nevertheless, there are critical problems for Li_2MnO_2F of capacity fade and voltage hysteresis which are as yet unexplained phenomena.

Overall, the insights provided by the results and discussion in this thesis offer renewed hope for O-redox in realising high energy density cathode materials. While the materials studied herein are unlikely to be technologically viable cathodes in their current forms, studying their behaviour in depth has established valuable fundamental understanding of the chemistry of O-redox.