# Impact of transition metal redox on next-generation Li-rich cathodes for Li-ion batteries

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"Ninety percent of all experiments fail. This is a fact. Every scientist has proven it. But you eventually start to wonder if this high rate of failure is also you. It can't be the chemicals' fault, you think. They have no souls."

-Wang Weike

#### Abstract

Developments in lithium-ion batteries for energy storage are currently focused on improving energy density, increasing cycle life, and reducing cost to match targets set by the automotive industry. An important class of cathodes known as Li-rich layered oxides is considered promising for next-generation electrode materials. However, a poor understanding of a number of detrimental processes that occur in Ni-containing materials, for which the underlying mechanisms are not clear, has hindered their commercialization. Numerous model systems have been studied in an effort to fully understand the discrete mechanisms taking place during battery operation. Herein, we build upon the previous work on model systems by studying Li–Ni–Sb–O and Li–Ni–Te–O materials to better understand the impact of Ni in this complex class of materials. Using a combination of detailed electrochemical tests, X-ray diffraction, online electrochemical mass spectrometry, X-ray absorption near-edge spectroscopy, and Xray photoelectron spectroscopy, we find a stark contrast between the electrochemistry taking place in the bulk of particles as compared to that taking place at the surface. We find that oxidation of oxygen results in reduction of nickel, as was seen previously in Li–Fe–Sb–O, and this has a detrimental impact on the discharge capacity. However, the reductive couple occurs solely at the surface of particles in Ni-containing materials because of mitigated oxygen gas production in these materials. The consequences of this contrast between the surface and the bulk are discussed to guide further development of next-generation electrodes.

#### Résumé

Le développement de batteries lithium-ion à des fins de stockage d'énergie se concentre actuellement sur l'amélioration de la densité énergétique, l'augmentation de la durée de vie, et la réduction des coûts pour atteindre les objectifs souhaités par l'industrie automobile. Une classe importante de cathodes désignées comme oxydes lamellaires riches en lithium est considérée prometteuse pour les matériaux d'électrodes de nouvelle génération. Cependant, une faible compréhension d'un certain nombre de processus néfastes qui se produisent dans ces matériaux contenant du nickel, pour lesquels les mécanismes fondamentaux ne sont pas clairs, a entravé leur commercialisation. De nombreux systèmes modèles ont été étudiés dans le but de bien comprendre les mécanismes distincts qui se produisent pendant le fonctionnement de la batterie. Nous continuons les travaux précédents sur les systèmes modèles en étudiant les matériaux Li-Ni-Sb-O et Li-Ni-Te-O pour mieux comprendre l'impact du nickel dans cette classe de matériaux complexe. En utilisant une combinaison de tests électrochimiques détaillés, de diffraction des rayons X, de spectrométrie de masse électrochimique, de spectroscopie de structure près du front d'absorption des rayons X et de spectrométrie photoélectronique des rayons X, on trouve une divergence entre l'électrochimie globale par rapport à la surface des particules. Nous constatons que l'oxydation de l'oxygène entraîne une réduction du nickel, déjà observée dans Li-Fe–Sb–O, ce qui a un impact néfaste sur la capacité de décharge. Cependant, le couple réducteur se produit uniquement à la surface des particules dans les matériaux contenant du nickel en raison de la production d'oxygène gazeux mitiger dans ces matériaux. Les conséquences de ce contraste entre les propriétés de la surface et de l'ensemble seront presentées pour guider le développement ultérieur d'électrodes de nouvelle génération.

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### List of Abbreviations

Abbreviation	Full Name
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
AR	Anionic redox
сср	Cubic close packed
CR	Cationic redox
CV	Cyclic voltammetry
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EIS	Electrochemical impedance spectroscopy
$\mathrm{EV}$	Electric vehicle
EXAFS	Extended x-ray absorption fine structure
НОМО	Highest occupied molecular orbital
ICP-AES	Inductively coupled plasma atomic emmission spectroscopy
LNSO	Lithium nickel antimony oxide
LNTO	Lithium nickel tellerium oxide
Li-ion	Lithium ion
$\mathrm{LiPF}_{6}$	Lithium hexafluorophosphate
LSV	Linear sweep voltammetry
LUMO	Lowest unoccupied molecular orbital
$M_W$	Molecular weight
NMC	Nickel manganese cobalt oxide
OEMS	Online electrochemical mass spectrometry
Redox	Reduction and oxidation

Abbreviation	Full Name
SEI	Solid electrolyte interphase
TM	Transition metal
XANES	X-ray absorption near edge spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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### List of Symbols

Symbol	SI Units	Meaning
a	М	Activity
G	kJ	Gibb's free energy
E	J kg <sup>-1</sup>	Specific energy
$E_{eq}$	V	Electromotive force
$E^{\circ}$	V	Standard electromotive force
$E_{\lambda}$	V	Vertex potential
F	$\rm C~m^{-1}$	Faraday's constant
i	А	Current
$M_W$	mol $g^{-1}$	Molecular weight
n	-	Number of electrons transferred
$Q_{exp}$	A h kg <sup>-1</sup>	Specific experimental capacity
$Q_{theo}$	A h kg <sup>-1</sup>	Specific theoretical capacity
$Q_{irr}$	-	Irreversible capacity
R	$\rm J~mol^{-1}~C^{-1}$	Gas constant
t	S	Time
T	Κ	Temperature
$\mu_A$	$\rm J~mol^{-1}$	Chemical potential of anode reductant
$\mu_C$	$\rm J~mol^{-1}$	Chemical potential of cathode reductant
ν	V s <sup>-1</sup>	Scan rate
$V_{avg}$	V	Average voltage
$V_{OC}$	V	Open circuit voltage

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#### Author Contributions

Chapter 2 includes published work from Ting et al.<sup>28</sup>, written by the author of this thesis, Michelle Ting.

Research presented in **Chapter 3** was done under the advisement and supervision of Dr. Eric McCalla and published in Ting et al.<sup>28</sup>.

Electrochemical tests and analyses were done by Matthew Burigana, while OEMS data was collected and analysed by Leiting Zhang and Sigita Trabesinger. Synchrotron data was collected by Y. Zou Finfrock at Argonne National Laboratory, and analyzed by Michelle Ting. X-ray diffraction tests and analyses were done by Michelle Ting. All electrochemical figures were prepared by Matthew Burigana, while the remaining figures were done by Michelle Ting.

Chapter 4 includes published work from Ting et al.<sup>28</sup>, while further additions were written by Michelle Ting.

#### Chapter 1

#### Introduction

#### **1.1** Principles of Li-ion Batteries

In an effort to combat the increasing effects of climate change, current works rely heavily on harnessing renewable energy sources. However, fossil fuels offer clear advantages over renewable resources in terms of consistency and reliability since renewables often vary heavily with geographical location and weather conditions. To optimize the use of such intermittent renewable energy sources, harnessed energy must be stored in a way that is easily accessible whenever it is needed, and so the development of energy storage has been the focus of many studies. Secondary batteries, which store energy in the form of electrochemical potential that can then be converted into electrical energy, have emerged as a leading form of energy storage — once their electrochemical potential has been depleted, they can be recharged to their original chemical state, ready for discharge once more, a cycle that can be repeated for many iterations.

An application of particular current interest is the use of secondary batteries in transportation, specifically electric and hybrid electric vehicles. Over the past three decades, lithium-ion batteries (LIBs) have emerged as an important storage system due to their increased energy density, which stems from their high operating voltage ( $\sim$ 4V) in comparison



Figure 1.1: Radar plot published in 2016 illustrating the present status of Li-ion battery technology (red line) compared to the targets set by the United States Advanced Battery Consortium (USABC) for all electric vehicles with a 200-mile range (blue line). Adapted from Ref. [1]

to its predecessors, such as lead-acid (~2.1V), nickel-cadmium (~1.2V), or nickel-metal hydride (~1.2V). Though lithium-ion batteries are well-established in many commercial vehicles, further developments in energy density must be made to keep up with increasing performance demands while also keeping cost and safety in mind. Figure 1.1 shows the state of current lithium-ion technology compared to the expected targets for electric vehicles. In particular, the energy density and calendar life of current batteries must be further improved upon in the near future to facilitate the transition from conventional combustion engines to electric and hybrid electric vehicles, while simultaneously decreasing the cost. Since the cost of lithium-ion batteries depends on both the material and manufacturing costs, some companies such as Tesla have attempted to optimize the manufacturing process to decrease the cost.<sup>1</sup> However, a reduction in material costs would also have a significant impact on



Figure 1.2: Schematic diagram of the lithium intercalation–de-intercalation reaction mechanism in a rechargeable lithium-ion battery containing solid electrodes and a liquid electrolyte. Reproduced from Ref. [2] with permission from The Royal Society of Chemistry.

the price of batteries in electric vehicles. Massive research efforts are therefore underway to improve energy density and maintaining or lowering material prices. The following section will introduce the basic operating principles of lithium-ion batteries, while Section 1.2 will discuss recent material development advancements in lithium-ion cathodes.

#### **1.1.1** Fundamental Operation

Lithium-ion batteries are intercalation batteries – that is, they use the reversible insertion and extraction of lithium ions in the cathodic and anodic structure to store and release energy. In essence, the lithium ions are reversibly 'pumped' in and out from one electrode to the other, acting as a charge carrier within the electrolyte to compensate for the electrical current flow through the external circuit (Fig. 1.2). During discharge, lithium ions move from the negative electrode (the anode) to the positive electrode (the cathode) through the



Figure 1.3: Crystal structure of common lithiated electrode materials.  $\text{Li}_x \text{C}_6$  is the charged anode, while LiMO<sub>2</sub> is the discharged cathode. Lithium atoms are marked in orange, carbon atoms in gray, and the metal oxide oxtahedra (MO<sub>6</sub>) is marked in blue. Reproduced from Ref. [3].

electrolyte. Simultaneously, free electrons are released from the anode and travel through the external circuit towards the cathode. During charge, the movement of both the electrons and the ions is reversed, traveling from the cathode to the anode through their respective pathways. A porous material soaked with an electrolyte serves as a separator, preventing electronic conduction through any path other than the external circuit while also acting as a medium for ionic conduction.

Common lithium-ion cells have lithium cobalt dioxide (LiCoO<sub>2</sub>) as the cathode and graphite as the anode. Figure 1.3 shows the layered structure of the anode and cathode respectively: graphite has stacked graphene sheets in a hexagonal crystal structure, while LiMO<sub>2</sub> has alternating metal oxide slabs and lithium layers. For LiCoO<sub>2</sub>, M is cobalt and thus has cobalt oxide (CoO<sub>2</sub>) slabs made of hexagonal arrangements of MO<sub>6</sub> octahedra. These materials readily allow lithium movement within their structures, making them wellsuited for intercalation (Fig. 1.3).<sup>3</sup>

For a cell with  $LiCoO_2$  and graphite as the electrodes, the respective reactions for the cathode and anode during charge are as follows:

$$\text{LiCoO}_2 \longrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$$
 (1.1.1)

$$C_6 + xLi^+ + xe^- \longrightarrow Li_xC_6 \tag{1.1.2}$$

The amount of electrical energy transferred from an operating cell can be calculated from the products of two parameters: specific capacity, and cell voltage. The capacity is the amount of charge transferred by the cell, equal to the amount of lithium ions that are reversibly removed. The specific capacity per gram of electrode material can be calculated as follows:

$$Q = \frac{nF}{3.6 \times M_{\rm w}} \tag{1.1.3}$$

where n is the number of electrons removed per formula unit. While it is possible to calculate the theoretical capacity for any material, the experimental capacity can differ greatly from the theoretical values. For LiCoO<sub>2</sub>, the theoretical capacity assuming n = 1 is 273 mAh/g. However, in reality the reversible capacity is about 150 mAh/g<sup>26</sup>, implying that only half of the lithium within the material is available for reversible intercalation. For Li<sub>1-x</sub>CoO<sub>2</sub> with x > 0.5, experimentally the material has shown irreversible structural



Figure 1.4: Comparison of the energy vs. density of states showing the relative Fermi level of the  $\text{Co}^{4+}/\text{Co}^{3+}$  redox couple for  $\text{LiCoO}_2$ , the  $\text{Ni}^{4+}/\text{Ni}^{3+}$  redox couple for  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ , and the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  redox couple for  $\text{LiMn}_2\text{O}_4$ . Adapted from Ref. [4] under the Creative Commons license.

changes, preventing reintercalation of lithium within the cathode material which has a drastic impact on the capacity.<sup>26</sup>

The voltage of the cell is the difference in electrochemical potential between the cathode and anode. The potential of each electrode depends on the Fermi level of the material. In the cathode, this is often related to the transition metal d-bands (Fig. 1.4), while the oxygen p-bands lie at lower energies. As lithium movement occurs within the material, there is a change in the electronic structure which can affect the active redox center.

Since the energy of an operating cell depends on capacity and the operating voltage, to improve energy density in the current technology means one must either increase the amount of lithium available for intercalation, or increase the difference in redox potential. Figure 1.5 shows approximate values for common cathode and anode capacities and operating



Figure 1.5: Comparison of capacities and voltages of common electrode materials. Reproduced from [5] with permission from The Royal Society of Chemistry.

voltages. The most commonly used anode, graphite, has one of the lowest operating voltages among anode materials, with relatively good capacity in comparison to cathode materials. For example, while the capacity of graphite is approximately  $350 \text{ mAh/g}^{29}$ , conventional cathode materials have experimental capacities lower than 200 mAh/g, which limits the total capacity of the cell. In addition, since the operating voltage of most cathodes is near the top of the stability window of the electrolyte and the operating voltage of the anode is near the reduction potential of lithium, further research must focus on increasing the capacity of the cathodes. Herein, the mechanism of action behind newly developed cathode materials will be unraveled in order. Each of the three main components (electrolyte, anode, cathode) will be discussed in turn in the following sections, before discussing newly developed and next-generation cathode materials.

#### 1.1.2 Electrolyte

The electrolyte used in Li-ion batteries is mainly composed of two materials, the conducting salt, and the solvent mixture. While both the salt and the solvent should have good stability within the operating cell voltage range, there are also other requirements to consider: the electrolyte should be ionically conductive, allowing lithium migration between the cathode and anode, yet electronically insulating to ensure electron travel through the external circuit. As the electrolyte should not undergo any Faradaic processes in an ideal cell, both the solvent and salt should also be electrochemically stable against both electrodes.

The chosen solvent should allow sufficient solvation of lithium ions such that ionic transport is not a significant contributor to resistance, and should not be chemically active against either the cathode or anode. Since lithium-ion batteries have a 4V operating window, organic, aprotic solvents are widely used.<sup>30</sup> Given that these solvents must readily dissolve lithium salts, commonly used solvents such as ethylene carbonate (EC) are chosen due to their highly polar nature, high lithium solubility and resulting conductivities.<sup>31,32</sup> Generally, EC is mixed with other solvents such as propylene carbonate (PC) or dimethyl carbonate (DMC), as ethylene carbonate has a higher melting point (39°C)<sup>33</sup> than the usual operating temperature of a battery.

The most widely used commercial salt,  $\text{LiPF}_6$ , is recognized for its solubility and inertness with respect to the metallic cell components and the separator. However, above 70°C it is thermally unstable and causes rapid exothermic degradation of the cell, and any contact with water causes the formation of HF<sup>34?</sup> which readily degrades cell components. Other types of electrolyte salts and solvent mixes are used for a variety of applications, but the minimum requirements are unchanged: high salt solubility to ensure good ion mobility, and electrochemical stability. In particular, the voltage range at which the electrolyte will not undergo oxidation or reduction, known as the stability window, is of critical importance. If the electrode is at a potential that exceeds this window, the electrolyte will undergo a reaction with the electrode. This can cause the buildup of an interfacial layer that affects the electrochemical performance of the cell, as well as degrading the electrolyte and ultimately shortening the lifespan of the battery. Most conventional carbonate electrolytes are relatively stable up to 4.5 vs. Li, which limits the development of higher voltage cells.

#### 1.1.3 Anode

Many current anodes are made of graphite with a capacity of 372 mAh/g<sup>29</sup> as well as an operating voltage of 0.1V vs. Li/Li<sup>+</sup> with high lithium mobility and high conductivity. The operating voltage of 0.1V is sufficiently high enough to prevent the formation of plated lithium, which could result in dendrite growth, a significant safety hazard.<sup>35</sup> Rather than plating lithium on the surface, carbon-based anodes allow the intercalation of lithium ions within layers of carbon which allows significantly less inactive lithium formation.<sup>36</sup>

To increase the energy density of a cell by improving the anode, one would either increase the capacity that is already double that of the cathode (Fig. 1.5), or decrease the potential, which cannot be done without plating lithium. In this thesis, we focus rather on the cathode, where potential gains are more important.

#### 1.1.4 Cathode

The main advantage of lithium-ion batteries over other secondary batteries is their high operating voltage. Since the electrochemical potential of most cathode materials is > 3.5V vs. Li/Li<sup>+</sup>, the energy transferred by lithium-ion cells is much higher compared to previous batteries. In comparison to the anode, the cathode has lower capacities (Fig. 1.5) and the electrolyte window limits the voltage at which the cell can operate. Therefore, the priority here is on the development of higher capacity cathodes in the pursuit of higher energy density.<sup>29,37–39</sup>

One of the most common types of cathode materials are layered oxides based on  $LiCoO_2$ , which enjoyed massive early commercial success due to its high energy density. However, in addition to the high cost, toxicity, and geopolitical issues surrounding the use of cobalt<sup>26</sup>, this material could only supply half of its theoretical capacity as discussed previously, which limited its energy density. To improve on both the cost-effectiveness and energy density, further development gave rise to the study of layered oxides that replaced cobalt with other transition metals to yield materials such as  $LiNiO_2$  and  $LiMnO_2$ . Many variations of these materials have been extensively studied over the past few decades<sup>40–43</sup>, and the development of these cathode materials will be discussed in detail in the next section.



Figure 1.6: Voltage curves upon first charging of commonly used layered oxides. Lithium atoms are marked in red, metal oxide octahedrons in green with oxygen atoms marked in blue. Reproduced from [6]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

### 1.2 Advancements in Layered Oxide Cathode Materials

As discussed previously, the electrochemical potential of a material depends largely on its Fermi level: in most lithium-ion cathode materials, the electronic structure and density of states of the transition metal levels dictate the redox potential of the cathode. As lithium ions are extracted from the cathode material and the transition metal undergoes oxidation, the density of states will determine how far the Fermi level shifts down thereby increasing



Figure 1.7: Structure of  $LiCoO_2$ , space group R3m. Reproduced from Ref. [7] under the Creative Commons license.

the voltage of the material. The trend results in the profile of the charge-discharge curve (Fig. 1.6). Since the reduction or oxidation of the electrode affects the electronic structure and thus the energy levels, at different states of charge the potential will depend on the energy level of the active redox pair, which can be tuned through material composition.

#### **1.2.1** Stoichiometric Layered Oxides

Stoichiometric layered oxides are of the form  $\text{LiMO}_2$ , where M is a combination of transition metals of interest. Structurally, these materials form alternating layers of lithium and transition metal oxides and can be represented in the R $\bar{3}$ m space group (Fig. 1.7), where the transition metal sits in the 3a site, the lithium atoms are in the 3b site, and the oxygen ions are in a cubic closed-packed arrangement on the 6c site. Due to their structure, these materials have high capacity and cycling rates as the lithium layer serves as both lithium storage and a 2D pathway for lithium movement. The Fermi level of these materials is generally located in the narrow 3-*d* band (Fig. 1.4).<sup>44</sup> Since the 3-*d* band depends on the transition metal, the substitution of various transition metals affects the operating potential of the cell. In addition, if there is good overlap between the 3-*d* transition metal band and the 2-*p* oxygen band, oxygen can then be electrochemically active at high enough potentials — as in the case of  $LiCoO_2$ .

While  $LiCoO_2$  is the most common cathode material, due to cobalt's relative scarcity and toxicity compared to other transition metals, the addition and substitution of alternative 3-*d* transition metals is favoured in cathode development.

Nickel is a popular substitute, as it has better cycling capacity (since it can oxidize from Ni<sup>2+</sup> to Ni<sup>4+</sup>) and a higher cell voltage but suffers from mixed occupancy during synthesis, where nickel occupies lithium structural sites and thereby blocks lithium diffusion pathways as well as causing site defects that prevent local lithium reintercalation.<sup>45–47</sup> In addition, while nickel initially has a high capacity as it can oxidize between the Ni<sup>2+</sup>/Ni<sup>3+</sup> and Ni<sup>3+</sup>/Ni<sup>4+</sup> redox pairs, Ni<sup>3+</sup> can migrate into the lithium vacancies and cause irreversible capacity loss over repeated cycling. Spinel LiMn<sub>2</sub>O<sub>4</sub> is another possible substitute that is cheaper and safer than LiCoO<sub>2</sub>. However LiMnO<sub>2</sub> has issues with phase transformations to spinel-like phases during cycling, as well as Mn<sup>2+</sup> dissolution into the electrolyte especially at higher temperatures.<sup>48</sup>

The use of a mixture of transition metals can counter the disadvantages of a single transition metal. The most common of these mixed transition metal oxides are NMC's of the form  $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ . A common composition is  $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ , usually written as NMC 111. Many studies have been devoted to characterizing different compositions
Compound	Specific capacity (mAh/g)		Operating Voltage
	Theoretical	Experimental	(V vs. $Li/Li^+$ )
LiCoO <sub>2</sub>	274	148	3.8
LiNiO <sub>2</sub>	275	150	3.8
LiMnO <sub>2</sub>	285	140	3.3
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	280	160	3.7
$\mathrm{LiNi}_{0.8}\mathrm{Co}_{0.15}\mathrm{Al}_{5}\mathrm{O}_{2}$	279	199	3.7
Li <sub>2</sub> MnO <sub>3</sub>	458	180	3.8
$ Li[Li_{(1-2x)/3}Ni_xMn_{(2-x)/3}]O_2 $	$\sim 300$	$\sim 250$	3.8

Table 1.1: Characteristics of various cathode compounds. Specific capacity is denoted as theoretical/experimental/typical in commercial cells.<sup>26,27</sup>

in an effort to optimize capacity and cycling stability. In NMC 111, cobalt can reduce the mixed lithium and nickel population percentage<sup>49</sup>, while manganese in its 4+ state is electrochemically inactive and stabilizes the structure.

Table 1.1 details the specific capacities and voltage range of various researched cathode materials. While these nickel- and manganese-based materials have an increased theoretical capacity, experimentally these materials deliver approximately 50% of their expected capacity, and the reversible capacities rarely exceed 180 mAh/g, furthering the need for the development of a new class of higher capacity material.

#### 1.2.2 Li-rich Layered Oxides

In 2002, Dahn published work on lithium-rich layered oxides.<sup>27</sup> These materials were in the form  $\text{Li}[\text{Li}_x M_{(1-x)}]O_2$  where a fraction of the transition metal atoms are replaced with lithium



Figure 1.8: The initial charge-discharge curves of Li-rich NMC and NMC111 coin cells at C/25 (black line indicates Li-rich NMC ( $Li_{1.252}Mn_{0.557}Ni_{0.123}Co_{0.126}Al_{0.0142}O_2$ ) and red line indicates NMC111). Reproduced from Ref. [8] with permission from Elsevier.

atoms.

These lithium-rich materials showed much higher capacities in comparison to their stoichiometric predecessors, with capacities in excess of 250 mAh/g (Fig. 1.8). Structurally, these materials are similar to their stoichiometric predecessors with alternating layers of pure lithium, and mixed lithium and transition metal (usually manganese, nickel, and cobalt) occupancy in the transition metal layer. Rather than  $R\bar{3}m$ , the space group is most commonly the monoclinic C2/m due to the ordering of lithium in the transition metal layer.<sup>50</sup>

One of the defining features of these materials is a voltage plateau observed around 4.5V during the first charge, and a significant loss of capacity after the first cycle (Fig. 1.9). This characteristic behaviour is related to the high capacities seen in these materials. While there



Figure 1.9: Variation of potential on Li extraction and then reinsertion on the first and subsequent cycles. Sample is cycled at 50 mA/g. The first charge, shown in red, is composed of three regions. Cycling is stable from cycle 2 but exhibits voltage fade. Reproduced from Ref. [9] with permission. Copyright 2016 Springer Nature.

was some initial debate on the mechanism behind this increase in capacity (such as  $\text{Li}^+/\text{H}^+$  exchange<sup>51</sup>), the excessive capacity is most commonly attributed to the addition of anionic redox to conventional cationic redox. These materials also suffer from large capacity loss in the first charge and subsequent voltage fade – that is, where the average voltage produced by the cell decreases during cycling (Fig. 1.9).<sup>52</sup>

Therefore, while lithium-rich oxides offer great advantages in terms of capacity and thus energy density, there are severe limitations that prevent their immediate commercialization. This has prompted a huge research effort to understand and mitigate the disadvantages<sup>52-56</sup> as discussed in the following section.

# **1.3** Mechanisms in Li-rich Oxides

In stoichiometric layered cathode materials, it was shown that the redox center was generally the transition metal, where the theoretical capacity was limited by changes in the transition metal oxidation state.<sup>57</sup> However, layered lithium-rich metal oxides exhibit much higher capacities than can be explained by cationic redox alone. For example, the material in Figure 1.9 should only have a capacity of 121.5 mAh/g based on the Ni<sup>2+</sup>/Ni<sup>4+</sup> and the  $Co^{3+}/Co^{4+}$  redox pair. Thus studies have turned towards oxygen redox, an example of anionic redox, to account for the excess capacity. While many mechanisms were proposed, the current accepted theory involves two main processes: First, that oxygen loss occurs at the surface as O<sub>2</sub> gas and second, that the bulk of the material undergoes reversible oxygen redox.<sup>58-60</sup> The oxygen loss at the surface causes the formation of oxygen vacancies within the structure and allow other transition metal ions to migrate within the material, a process known as *densification*.<sup>61-63</sup>

However, to directly elucidate the mechanism by which oxygen oxidation affects the cathode performance has proven difficult to do with some of the more commonly used spectroscopic methods, such as X-ray diffraction or X-ray absorption spectroscopy, which lack the resolution and sensitivity to measure local oxygen oxidation states.<sup>64</sup> In addition, the underlying mechanism of anionic redox in NMC materials has proven relatively difficult to study due to coupling with cationic redox activity, cation migration, structural transformations, and gas release.<sup>65</sup> Therefore, rather than directly studying lithium-rich NMC, model systems that had similar structures and properties were developed. 4-d and 5-d transition

metal oxides that had similar charge-discharge profiles but only a subset of the processes seen in NMC's were developed thus allowing de-coupling of the complex processes occuring in lithium-rich NMC's.

Sathiya et al. designed Li<sub>2</sub>MO<sub>3</sub> (M=Ru, Mn, Ti, Te, etc.) materials that exhibited the same step-wise discharge and first-cycle plateau as lithium-rich NMC's with no O<sub>2</sub> gas release.  $^{66-68}$  With a variety of electron microscopy and X-ray techniques, changes in the oxygen oxidation states can be measured both directly by observing the bonding environment of the oxygen atom, and indirectly through the local oxidation state of the transition metal.  $^{66,67}$  They demonstrated that the reversible redox activity in peroxo-like species (O<sup>2-</sup>/O<sub>2</sub><sup>n-</sup>) was responsible for the capacity seen in lithium-rich oxides.  $^{68}$ 

Further studies showed reduced O-O interlayer distances in models by probing cationic oxidation states in  $\text{Li}_{2-x}\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_2$  and in  $\text{Li}_2\text{Ir}_{1-x}\text{Sn}_x\text{O}_3$ .<sup>69,70</sup> While the Ru-based systems all showed significant cationic migration, the replacement of  $\text{Ru}^{4+}$  with  $\text{Ir}^{4+}$  increased the covalency of the M-O bond which prevented transition metal migration into the lithium vacancies.<sup>70</sup> This was further studied in  $\beta$ -Li<sub>2</sub>IrO<sub>3</sub><sup>71</sup> which maintains remarkable structural stability during cycling. Using a combination of transmission electron microscopy (TEM) and neutron diffraction it was also shown that O-O dimers form in the oxygen sublattice and these were found to be roughly  $\text{O}_2^{3-}$  in the fully charged state. Additionally, depending on the overlap between the oxygen 2-*p* and transition metal *n*-*d* band, the oxygen loss and plateau length could change drastically.

While these systems showed reversible oxygen redox, both the Ru- and Ir-based model systems had oxidation processes occurring below 4.2V and thus showed no oxygen gas evolu-



Figure 1.10: DEMS data presenting  $O_2$  (red) and  $CO_2$  (black) released during cycling. The dashed red line marks the amount of oxygen released if the conversion of  $O^{2-}$  to  $O_2$  was the only contribution to the current for a) Li<sub>4</sub>FeSbO<sub>6</sub> and b) Li<sub>4.27</sub>Fe<sub>0.56</sub>TeO<sub>6</sub>. Adapted with permission from Ref. [10]. Copyright 2015 American Chemical Society. Adapted from Ref. [11]. Copyright IOP Publishing. Reproduced with permission. All rights reserved.

tion. However, since lithium-rich NMC materials operate both below and above 4.2V, other materials such as  $\text{Li}_{2-x}\text{Fe}_{0.75}\text{Sb}_{0.25}\text{O}_2^{10}$  and  $\text{Li}_{4.27}\text{Fe}_{0.57}\text{TeO}_6^{11}$  were studied using Mössbauer spectroscopy in order to probe the impact of redox dominated by  $O_2$  loss. While the latter showed no capacity below 4.2V, the Li-Fe-Sb-O system was studied in detail as it showed activity both above and below 4.2V,<sup>10</sup> making it a good model system that approaches next-generation cathode candidates in terms of electrochemistry complexity. Surprisingly,  $\text{Li}_4\text{FeSbO}_6$  showed that iron was first oxidized to 4+ at mid-charge, then *reduced* back to 3+ during the rest of charge as  $O_2$  gas was released. This prevents iron from being reduced during discharge, limiting the amount of reversible capacity available.

Since the Li-Fe-Sb-O studies, there have been no reports studying model systems showing this reduction of the transition metal during end of charge. It is thus important to look for other model materials that progress towards lithium-rich NMC's, our system of interest. The next logical step is to replace iron with nickel in the Li-Fe-Te-O and Li-Fe-Sb-O materials, since NMC materials rely heavily on nickel in an effort to stabilize nickel-rich layered oxides. This work therefore serves to understand the impact of replacing cobalt with nickel in lithium-rich NMC's. In addition, certain commercialized layered materials such as Li[Ni<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>]O<sub>2</sub> already use nickel as the main redox center of the material.<sup>72</sup> Therefore, in this thesis both Li-Ni-Te-O and Li-Ni-Sb-O materials are studied in an attempt to clarify the impact of nickel substitution on reversible and irreversible oxygen redox, as well as the effects of nickel oxidation during cycling.

## **1.4** Structure of the Thesis

Chapter 2 describes the synthesis of the materials studied in this thesis. Given the difficulty of directly measuring both cationic and anionic redox, this chapter also details the methods and techniques used to determine changes in the cathode material during cycling. In turn, Chapter 3 presents and interprets data compiled on the effects of oxygen and metal redox for the Li-Ni-Te-O and Li-Ni-Sb-O materials. Finally, Chapter 4 considers the impact of this work in the context of further developing NMC materials for commercial purposes, as well as detailing the path for future works.

### Chapter 2

## **Experimental Methods**

This chapter details the various synthesis and characterization methods used in this thesis. Our goal here is to understand the structural and chemical changes occuring in the samples during electrochemical cycling to a specific state of charge, thus X-ray characterization is done *ex-situ* after cycling to the desired voltage, while online electrochemical mass spectrometry (OEMS) is done *in-situ*. Two lithium-rich Ni-M-O systems are studied herein, Li-Ni-Sb-O and Li-Ni-Te-O.

## 2.1 Material Synthesis

Three materials are studied in this thesis, all of which have previously been published in the literature:  $\text{Li}_4\text{NiTeO}_6^{67}$  (denoted herein as LNTO),  $\text{Li}_{1.15}\text{Ni}_{0.47}\text{Sb}_{0.38}\text{O}_2^{23}$  (L<sub>1.15</sub>NSO), and  $\text{Li}_{1.10}\text{Ni}_{0.53}\text{Sb}_{0.37}\text{O}_2^{23}$  (L<sub>1.10</sub>NSO). The cathode material was made by ballmilling (Retsch) stochiometric amounts of NiO (Sigma) and either Sb<sub>2</sub>O<sub>3</sub> (Alfa Aesar) or TeO (Alfa Aesar), along with lithium carbonate (Sigma) in 5% stoichiometric excess to account for lithium loss during heating. Since these materials are air-sensitive during synthesis, the material is prepared in a glovebox and the stainless steel milling jar (Form-Tech Scientific) sealed in argon gas. The mixed precursor was then heated to 800°C or 900°C in a box furnace for LNSO

and LNTO respectively according to literature at a rate of 5°C/min.<sup>22,67</sup> Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used on the synthesized material to confirm the elemental composition of the material matched the literature values.

## 2.2 Electrochemical Measurements

Any electrochemical measurements herein are done using Swagelok cells assembled under argon since both the electrolyte and metallic lithium are sensitive to water and oxygen. Figure 2.1 shows the cross section of a Swagelok cell with aluminium and stainless steel plungers for the cathodic and anodic current collectors respectively. To improve the electrical conductivity of our material it was then ballmilled with 20 wt. % carbon black (Sigma) for 10 minutes.<sup>73</sup> Prepared material was then measured with PXRD to ensure crystallinity based on peak broadening and compared against the literature values. Once the active material is placed on the aluminium plunger, two layers of a GF/D Microfiber filters (Whatman) are used as the separator before 1M LiPF<sub>6</sub> in 1:1 EC:DMC (SoulBrain MI) electrolyte is dripped on to its surface. Once the metallic lithium anode and a stainless steel current collector is placed, a spring is added to ensure proper contact between cell components, and the stainless steel plunger is added. Perforated nuts are used to keep the plungers in place, while Teflon rings and a Mylar sheath is added to prevent short-circuiting the cell.

Galvanostatic cycling on a Neware BTS 3000 cycler was performed at various rates and cut-off potentials (Table 2.1), where a constant current is applied to the system. This provides us with the charge-discharge curve and differential capacity (also known as a dQ/dV)

Material	Voltage Range (V)	Rate $(mA/g)$
	2.5 - 4.1	11
L <sub>1.15</sub> NSO	2.5 - 4.6	11
	2.0 - 4.95	11
	2.5 - 4.2	5.5
LNTO	2.5 - 4.6	5.5
	2.0 - 4.95	5.5
	2.5 - 4.1	7
	2.5 - 4.25	140
L <sub>1.10</sub> NSO	2.5 - 4.6	7
	2.5 - 4.6	140
	2.5 - 4.95	7
	2.5 - 4.95	140

Table 2.1: Table of cycled rates and voltage ranges for galvanostatic cycling.



Figure 2.1: A two electrode Swagelok cell, a) the schematic design, and b) picture of a 10mm diameter Swagelok-type assembled cell. Reproduced from Ref. [12] with permission.

plots, similar to those shown in Figure 2.2. These plots provide information on the electrochemical behaviour of our cathode material. In particular, we are interested in seeing the voltage plateau on charge of our materials, and the effects of the cut-off potentials on the length of the plateau and thus the cycling reversibility. First and foremost, the charge-discharge curve allows us to see the charging and irreversible capacity of the cathode material, which can also be represented by the lithium content in the material. In the differential capacity plots, peaks at certain voltages allow us to visualize at what voltage an electrochemical or intercalation events occurs such as active redox pairs.

Samples prepared for *ex-situ* measurements are cycled to a specific voltage before they are reintroduced into an argon-filled glovebox in preparation for characterization. The various



Figure 2.2: Voltage profiles of  $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$  in lithium half-cells as a function of lithium content with corresponding dQ/dV curves for the first cycle. Reproduced from Ref. [13] under the Creative Commons license.

cut-off potentials for each material used is detailed in Table 3.3. The half charge denoted here is the material charged to the end of the first potential plateau, while the full charge is the material charged to 4.90V, and the full discharge is the material charged to 4.90V then discharged again past the discharge potential plateau. For example, for the material in Figure 2.2, the half charge would be around 4.30V, the full charge would be 4.80V, and the full discharge would be around 3.25V.

# 2.3 X-ray techniques

#### 2.3.1 X-ray diffraction

X-ray diffraction depends on the formation of diffraction patterns due to the scattering of X-rays from the average structure of a crystalline material. Once collected, this diffraction



Figure 2.3: XRD patterns of a)  $\text{Li}_{1.21}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$  before and after 1, 2, and 10 cycles, inset with an image of the carbon coating layer. Reproduced from Ref. [14] with permission and b) evolution of the first XRD peak vs. lithium concentration in  $\text{Li}_x\text{CoO}_2$ . Reproduced from Ref. [15] with permission.

pattern can be fitted using Rietveld refinement using the software Rietica in order to extract information about the structural parameters (e.g. lattice parameters) that are affected as the material undergoes chemical changes.<sup>74</sup> For example, Fig 2.3 shows the changes in a) the low angle (003) peak as it disappears over cycling or b) shifts positions during cycling.

In our system, this use of this technique is two-fold: First, since the lattice parameters of our materials have been previously published it can be used to confirm the synthesis of our starting material.<sup>23,67</sup> Second, if there are changes in the average structure (either due to phase transformations<sup>48,75–77</sup>, disordering of the material structure<sup>78,79</sup>, volume changes due to lithium movement<sup>80,81</sup>) they can be recognized by changes in both the number and position of the XRD peaks.



Figure 2.4: XRD pattern and refinement of as-prepared NaMnO<sub>2</sub> in an air-sensitive holder. The broad peaks between  $10^{\circ}$  and  $30^{\circ}$  are due to the Kapton film used to seal the sample. The red lines represent the experimental data, the black line is calculated data, with the residual discrepancy in blue shown underneath. Green ticks represent the calculated peak positions. Reproduced from Ref. [16] with permission.

Cycled materials were prepared by first being re-introduced into an argon-filled glovebox before rinsing in DMC, centrifuged, and dried. After cycling, cathode materials are highly sensitive to air such that all *ex-situ* materials retrieved were held in an argon-filled air-free holder during XRD measurement.

The air-free holder consists of two stainless steel plates. One plate has a window of Kapton film which has relatively high transmittance to X-rays. Kapton shows a background bump at low angles of diffraction, which can be easily subtracted from the final spectra (e.g., Fig. 2.4). An O-ring sits between the two plates to provide a hermetic seal. As these measurements often require scans in excess of ten hours, this seal is of critical importance. Powder X-ray diffraction (PXRD) measurements were performed using a Bruker D8 Discover Diffractometer with a Cu-K $\alpha$  source. All XRD patterns were refined using the Rietveld method as implemented in Rietica.

#### 2.3.2 X-ray Photoelectron Spectroscopy

To help differentiate between surface and bulk oxidation states within our material, X-ray photoelectron spectroscopy (XPS) was used to probe only the surface of the cathode material since it has a penetration depth of 1-10nm.<sup>61,82</sup> Spectra is obtained by irradiating the surface of the material with a monochromatic X-ray while measuring the kinetic energy and intensity of the core electrons emitted by the material. The binding energy, or work function, of these electrons can then be calculated and depends on the local bonding environment of the probed element, while the intensity of the peak is related to the percent composition of the element. Since there is a dependency on the local bonding environment, XPS can be used to track changes in oxidation state based on the peak position.



Figure 2.5: Comparison of XPS core levels a) Ni 2p, b) Mn 2p, c) Co 2p for pristine undoped  $Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2$  and  $Li_{1.184}K_{0.016}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2$  cathode. Reproduced from Ref. [17] with permission.



Figure 2.6: K $\alpha$  Vacuum Transfer Module by Thermo Scientific. Vacuum is kept by an Oring (not pictured) between the sample cover and the sample base and held in place by the retaining plate and sample cover. Reproduced from Ref. [18]

Since each peak is representative of an oxidation state for the element of choice, a weighted average using the areas under each peak can be used to calculate the average oxidation state on the surface of the particles.<sup>83,84</sup> Figure 2.5 shows the binding energies of different 2p peaks for Ni<sup>2+</sup>, Mn<sup>4+</sup>, and Co<sup>3+</sup> respectively.<sup>17</sup>

Since the *ex-situ* samples are air-sensitive, these measurements were done using an air-free holder (ThermoFisher Scientific Vacuum Transfer Module) as seen in Figure 2.6. The samples are placed on double-sided carbon tape and mounted on to the sample base, and sealed in an argon-filled glovebox using the sample cover and the retaining plate before evacuation in the glovebox antechamber. XPS measurements were performed using a Thermo Scientific K $\alpha$  Spectrometer. Data was collected for the Ni  $2p_{3/2}$  peak (845-880 eV range), the Te  $3d_{3/2}$  peak, and the C 1s peak for shift calibration at 285.0 eV. Analysis was performed using both the XPSPEAK4.1 and Avantage software.

#### 2.3.3 X-ray Absorption Near Edge Structure

X-ray absorption near edge structure (XANES) is an X-ray absorption spectroscopy technique that requires synchrotron radiation. The absorption of X-rays of varying energies provides information on the oxidation state while being sensitive to the local environment. In XANES, the absorption coefficient is plotted as a function of the incident photon energy, and depends on the ionization of a core electron. Since the oxidation state is calculated as a shift in energy at a relative intensity, our focus is on the edge shift for a particular element during electrochemical cycling which can be compared to reference materials for analysis. Figure 2.7 shows the rigid edge shift of nickel in comparison to the changes in manganese and cobalt. Shifting of the edge is due to the change in oxidation, while the difference in shape arises from local environment changes.



Figure 2.7: Normalized XANES spectra and Mn, Co and Ni K-edge spectra of  $Li_{1.2}Ni_{0.5}Co_{0.1}Mn_{0.55}O_2$  collected during the initial charging process. Adapted with permission from Ref. [19]. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

XANES measurements were performed by Dr. Y. Zou Finfrock at the 20-BM-B beamline at the Advanced Photon Source, Argonne National Laboratory.<sup>85</sup> All samples were sealed between layers of Kapton tape in a glovebox, and then transferred to a helium enclosure for XANES measurements, where the K-edge of each element was measured.<sup>85</sup> Samples included references for each transition metal (Sb<sub>2</sub>O<sub>3</sub>, LiNiO<sub>2</sub>, NiO, TeO<sub>2</sub>). Data analysis was done by Michelle Ting using the Minerva, Mercury, and MATLAB software.

## 2.4 Online Electrochemical Mass Spectrometry



Figure 2.8: a) Schematic drawing of the PSI two-compartment cell. Reproduced from Ref. [20] with permission. OEMS data showing b) cell voltage vs. capacity of NMC111 (black), NMC622 (red), and NMC811 (green), and the moles of evolved gas versus state of charge for c)  $O_2$  and d)  $CO_2$  Adapted from Ref. [21].

Online electrochemical mass spectrometry (OEMS) is a common *in-situ* method for detecting volatile and gaseous decomposition products in lithium-ion batteries.<sup>86–89</sup> The cell is cycled and interrupted periodically to sample the cell headspace and replace the gas with inert gas. The sampled gas is then fed into a mass spectrometer to quantify gaseous products of the cell. This allows correlation between gas production and state of charge as shown in Figure 3.10.

All OEMS measurements were performed by Dr. Leiting Zhang and Dr. Sigita Trabesinger from the Paul Scherrer Institut (PSI) on their in-house OEMS setup, depicted in Figure 3.10a. A slurry consisting of 80% of cathode active material, 10% of conductive carbon SC65, and 10% of polyvinylidene fluoride (PVDF) binder, was coated on Al mesh with a wet thickness of 100  $\mu$ m. OEMS cells were assembled using lithium metal as the counter electrode, one piece of Celgard 2400 separator, and 120  $\mu$ L of 1M LiPF<sub>6</sub> in EC:DEC (3:7 w/w) as the electrolyte. The OEMS setup operates with a quadrupole mass spectrometer (QMS 200, Pfeiffer) for partial pressure measurements. For partial pressure and gas evolution rate analysis, 0.7 mL of gas are extracted from the headspace (~3.2 mL) of the cell and replaced by pure argon.

### Chapter 3

# Redox in Li-Ni-TM-O Systems

This chapter will present and discuss work done on three materials based on published work:  $Li_4NiTeO_6$  (denoted herein as LNTO),  $Li_{1.15}Ni_{0.47}Sb_{0.38}O_2$  ( $L_{1.15}NSO$ ), and  $Li_{1.10}Ni_{0.53}Sb_{0.37}O_2$  ( $L_{1.10}NSO$ ).<sup>22,23,67</sup> Techniques and methods from the previous chapter are used to elucidate and correlate redox activity to the electrochemistry of the materials. This chapter is adapted from Ting et al.<sup>28</sup>.

# 3.1 X-ray Diffraction and Electrochemical Characterization

All samples were synthesized as single phase materials, determined from PXRD (Fig. 3.1), and LNSO and LNTO were refined in the R $\bar{3}$ m and C2/m space groups respectively. Although pristine L<sub>1.10</sub>NSO shows superstructure peaks in the 20° - 30° range that are not present in the refinements, both the space group and the lattice parameters values of all three pristine materials are consistent with the literature (Table 3.1).<sup>23,67</sup> Furthermore, as can be seen in Table 3.2, the ICP results for the pristine materials coincide with available literature results.<sup>22</sup> The L<sub>1.15</sub>NSO sample was found to be slightly richer in Li than the target composition, indicating that not all excess Li was lost during synthesis — again, in good



Figure 3.1: a) Cu K $\alpha$  PXRD pattern of pristine Li<sub>1.10</sub>Ni<sub>0.53</sub>Sb<sub>0.37</sub>O<sub>2</sub> with R $\bar{3}$ m Rietveld refinement, b) for L<sub>1.15</sub>NSO refined with the space group R $\bar{3}$ m space group, and c) LNTO with the C2/m space group. Blue points represent experimental data, the red line is the calculated Rietveld pattern, and the residual is plotted in green.

Material	a	b	С	β (°)
L <sub>1.15</sub> NSO 10mA/g $R\bar{3}m$				
Pristine	2.988(7)	_	14.60(4)	_
Half Charge	2.966(6)	_	14.58(4)	_
Full Charge	2.962(9)	_	14.46(4)	_
Full Discharge	2.990(6)	_	14.57(3)	_
LNTO 10mA/g C2/m				
Pristine	5.155(9)	8.87(1)	14.60(4)	110.4(1)
Full Charge	5.10(3)	8.78(5)	14.60(4)	109.1(3)
Full Discharge	5.15(1)	8.85(2)	14.60(4)	110.1(2)
LNTO 2mA/g C2/m				
Pristine	5.155(8)	8.87(1)	5.14(1)	110.35(9)
Half Charge	5.107(1)	8.774(1)	5.142(1)	109.68(7)
Full Charge	5.113(3)	8.760(6)	5.118(2)	109.12(2)
Full Discharge	5.13(2)	8.82(2)	5.149(2)	109.03(4)
References				
LNSO <sup>23</sup>	2.983	_	14.568	_
LNTO <sup>67</sup>	5.158	8.881	5.1366	110.241

Table 3.1: Lattice parameters a, b, and c in Å extracted from ex-situ XRD patterns of LNSO and LNTO.

Target Material	ICP (this study)	Average Ni Oxidation	Literature ICP <sup>22</sup>
$Li_4NiTeO_6$ (LNTO)	$Li_{4.11}Ni_{0.94}Te_{0.95}O_2$	+2.33	
$Li_{1.10}Ni_{0.53}Sb_{0.37}O_2$	$Li_{1.10}Ni_{0.58}Sb_{0.32}O_2$	+2.24	$Li_{1.02}Ni_{0.54}Sb_{0.38}O_2$
$Li_{1.15}Ni_{0.47}Sb_{0.38}O_2$ (LNSO)	$Li_{1.24}Ni_{0.40}Sb_{0.36}O_2$	+2.40	$Li_{1.22}Ni_{0.46}Sb_{0.37}O_2$

Table 3.2: Composition of pristine materials as determined by ICP-AES. Oxygen content determined by assuming oxidation states of  $Te^{6+}$ ,  $Sb^{5+}$ , and  $Ni^{2,3+}$  while average nickel oxidation is calculated based on the ICP measurements from this study

agreement with the literature.<sup>22,23,67</sup> Similarly, LNTO is also slightly higher in Li content by approximately 2.5% above the target composition.



Figure 3.2: Electrochemical cycling of LNSO at 11 mA/g (a and c) and LNTO at 5.5 mA/g (b and d). The different colors refer to cells cycled to different upper cutoff voltages.

The voltage profiles and dQ/dV plots for both  $L_{1.15}$ NSO and LNTO (Fig. 3.2 and Fig. 3.3) show remarkable similarities to those seen for Li<sub>4</sub>FeSbO<sub>6</sub>.<sup>10</sup> Not only are the results in good agreement with both material references<sup>22,23,67</sup>, but in our work the data has been extended to broader potential windows (up to 5.0V). There is an important features that points to the possible formation of oxygen gas evolution during cycling based on previous work in Li<sub>4</sub>FeSbO<sub>6</sub>: the decreasing reversibility of the redox plateau in the vicinity of 4.0 V vs. Li (3.9 V for LNSO and 4.1 V for LNTO (Fig. 3.2)) as the charge cutoff increases. This feature can most clearly be seen as a shrinking of the dQ/dV peak during discharge.

The low voltage plateau seen between 1.5 and 2.0 V in LNTO only (Fig. 3.3) is tentatively



Figure 3.3: Cycling for LNTO. a) Electrochemistry for LNTO with various voltage cutoffs including a lower cutoff of 1.5 V. b) Yellow: an LNTO sample that was charged to 4.9 V, taken into an argon-filled glovebox, rinsed in dimethyl carbonate and re-assembled into a new cell before discharge to 1.5 V. Orange: LNTO sample that was started on discharge, down to 1.5 V.

attributed to the role of oxygen gas in the cell after charging to high potentials (4.9 V). This is based on the fact that this peak nearly disappears when the charged sample is rinsed in dimethyl carbonate and re-assembled into a new cell, and it is therefore not solely electrochemistry taking place in the active material. Furthermore, the cell that began on discharge showed very little capacity below 2.0 V (about 10 mAh/g), which is again consistent with the conclusion that oxygen gas formation during charge gives rise to this discharge plateau. Since such low potentials are of no interest for Li-ion cathodes and more direct methods of observing oxygen gas (OEMS) are used further in this study, this redox activity was not further studied. In addition,  $Li_{1.10}NSO$  also showed a decline in the discharge capacity (Fig. 3.4) when cycled to high voltage, and this effect is diminished at higher cycling rates. Thus, all three materials studied here show electrochemistry consistent with oxygen gas release reducing the nickel redox: the release of oxygen gas is limited by diffusion,



Figure 3.4: Electrochemistry of  $Li_{1.10}Ni_{0.53}Sb_{0.37}O_2$ . The first electrochemical cycle at a) 7 mA/g and b) 140 mA/g with different cutoff voltages. The extraction of 1 lithium per formula unit corresponds to 231.5 mAh/g. The corresponding dQ/dV plots are shown for c) 7 mA/g and d) 140 mA/g.

such that when rapid cycling minimizes the time spent at high potential, less oxygen gas is released.

Both  $L_{1.10}$ NSO and  $L_{1.15}$ NSO were studied here due to the constrast of the published electrochemistry from Ref. [23] and Ref. [22] — specifically, whether the discharge capacity of LNSO increases at higher rates. However, our work found no such contrast (Fig. 3.5a), and therefore only  $L_{1.15}$ NSO was selected for further study below. It should also be noted that the strange rate performance seen previously in  $L_{1.15}$ NSO in Ref. [22] is not observed here (Fig. 3.5a and 3.5b). This is attributed to the fact that the materials here were neither nanosized nor carbon-coated.

Recent studies of LNSO were first considered within the context of percolation theory, assuming disorder of the cation network during charge as seen in  $Li_{1,211}Mo_{0.467}Cr_{0.3}O_2$  ma-



Figure 3.5: a) First ten discharge capacities from this study compared to those in Ref. [22,23] for LNSO cycled over a large range of rates and b) first cycle charge (empty circles) and discharge (filled circles) capacities from this study compared to those in Ref. [22,23]

terial. Further *in-situ* XRD showed no disordering of the cationic network during charge; in fact very little structural changes occur in these materials during cycling. Further studies of battery performance with this material showed capacities of about 150 mAh/g, thus they are not comparable to next-generation materials and have no benefit compared to current state-of-the-art LiCoO<sub>2</sub> or Li[Ni,Mn,Co]O<sub>2</sub>. However, the authors found a peculiar rate performance as the materials had lower capacities at slow cycle rates, higher capacities at intermediate rates and decreased capacity again at very high rates. This strange behaviour warrants further attention. Figure 3.5 show the rate performance from the current study in comparison to those published previously.<sup>23,67</sup> Whereas previous works show a maximum discharge capacity for LNSO at a rate of around 220 mAh/g, no such maxima is seen in our work. Cycled under identical conditions, our synthesized material has typical rate behaviour: a high capacity at low rate, staying more or less constant as the cycling rate increases until a relatively sharp drop-off occurs at currents above 44 mA/g. In contrast, the previous data 'optimum' rate. We therefore attribute the strange rate performance seen previously to the differences in electrode preparation. Here, we only mix the active material with sufficient carbon black to enable electronic conductivity in the material.

# 3.2 Ex-Situ X-Ray Diffraction Studies

Given the similarity of electrochemical features seen for all three materials here as compared to those of Li–Fe–Sb–O, both  $L_{1.15}$ NSO and LNTO were selected for *ex-situ* in-depth study to better understand the role of Ni substitution in the materials. *Ex-situ* samples were obtained for each material as follows: charging to 4.3 V (half charge), charging to 5.0 V (full charge), and charging to 5.0 V followed by discharging to 3.6 V (full discharge). First, ex-situ XRD patterns of  $L_{1.15}$ NSO and LNTO (two different rates) were collected to determine to what extent structural changes are taking place during electrochemical cycling. Two different rates were used for LNTO in an attempt to increase the amount of oxygen gas released by giving the material more time at high potentials. Figure 3.6 shows the XRD patterns for pristine, fully charged, and fully discharged samples. All patterns can be indexed in the space group of the pristine material, except for one small peak, visible in the fully discharged LNTO sample at 2 mA/g. The refined lattice parameters obtained from Rietveld fits are reported in Table 3.1 and Figure 3.8 gives calculated unit cell volumes. In all cases, the unit cell decreases in size during charge and increases again (almost reversibly) during discharge. Thus, whereas  $Li_4FeSbO_6$  had a dramatic transformation from an O3 to an O1 structure during charge, its



Figure 3.6: XRD of *ex-situ* pristine (blue), charged to 5V (red), and discharged to 3.6V (yellow) samples for a)  $L_{1.15}$ NSO cycled at 10 mAh/g, b) LNTO cycled at 10 mAh/g and c) LNTO cycled at 2mAh/g.



Figure 3.7: Electrochemical cycling of the *ex-situ* samples. 50-85 mg of active material was used in all cases. 4.1V was used as the cutoff for the half-charged  $L_{1.15}$ NSO sample while 4.3V was used for the half-charged LNTO.



Figure 3.8: Unit cell volumes calculated from the results show in Table 3.1

Label	Charge (V)	Discharge (V)
L <sub>1.15</sub> NSO $10 \text{mA/g}$		
Half Charge	3.97	_
Full Charge	4.90	_
Full Discharge	4.90	3.87
LNTO 10mA/g		
Half Charge	4.31	_
Full Charge	4.90	_
Full Discharge	4.90	3.87
LNTO 2mA/g		
Full Charge	4.90	_
Full Discharge	4.90	3.65

Table 3.3: Table of rates and cut-off potentials used for each *ex-situ* sample.

nickel counterpart had a robust O3 structure that is maintained during the entire first cycle. No other trend was found in the XRD refinements (for example, the nickel content on the Li layer was poorly constrained by the data and was found to insufficiently impact the quality of the fits for it to be considered reliable). Nonetheless, the differences seen here in the structural evolution during cycling, when compared to those of iron-containing materials, demonstrate the importance of nickel in preventing the shearing of atomic planes, resulting in transformations from O3 to O1 structures.

## 3.3 Online Electrochemical Mass Spectroscopy

OEMS data (Fig. 3.10 and Fig. 3.9) for both LNTO and LNSO were collected to determine the extent of gas evolution during battery operation. At the cycling rate of 10 mA/g (Figure 3.10), a gas evolution rate of 1554 nmol min<sup>-1</sup> g<sup>-1</sup> would be required if oxygen evolution was the only mechanism contributing to the current. For both samples O<sub>2</sub> generation rate is below 7 nmol min<sup>-1</sup> g<sup>-1</sup> whereas that of CO<sub>2</sub> is nearly identical in both data sets and is not higher than 80 nmol min<sup>-1</sup> g<sup>-1</sup>. The CO<sub>2</sub> can be due to either electrolyte decomposition and/or O<sub>2</sub> gas released from the active material reacting with a carbon source (either carbon black or the electrolyte solvents).<sup>90</sup> Thus, even if all CO<sub>2</sub> detected is due to released oxygen gas reacting with the conductive carbon, the upper bound on the amount of oxygen produced accounts for only 5% of the current. By contrast, previous work in Li-Fe-Sb-O found that O<sub>2</sub> accounted for about 50% of the current for most of the first charge, and in Li-Fe-Te-O it accounted for about 90% of the current for most of the first charge.<sup>11</sup>

We therefore conclude that  $O_2$  gas evolution is greatly mitigated by structural stabilization because of the presence of nickel, seen specifically in Figure 3.9 and Table 3.4 based on the the cumulative oxygen and  $CO_2$  evolution during the first charge. Even if it is assumed that the current is solely generated by the reaction of oxygen with carbon species, all results lead to the conclusion that only a small amount of oxygen gas is evolved in the nickel-containing materials, such that we can speculate that it occurs at the surface of the active material particles only. Comparing the gassing of the two different cycling rates used for LNTO, oxygen evolution at faster cycling rates is diminished, consistent with insuffi-

Motorial	$O_2$ loss	$\rm CO_2 \ loss$	Max. $O_2$ loss	Theoretical
Materiai	$(\mu { m mol}/{ m mol})$	$(\mu mol/mol)$	(mol/mol)	(nmol/min/g)
$Li_{1.10}NSO 10 mAh/g$	933.45	36791.67	3.77%	1554
LNTO 10 mAh/g $$	640.77	14453.50	1.51%	1554
LNTO $2 \text{ mAh/g}$	2423.56	19972.39	2.24%	1311

Table 3.4: Cumulative loss of both oxygen and carbon dioxide based on OEMS data. The maximum oxygen loss is calculated assuming that all the  $CO_2$  came from sample oxygen reacting with a carbon source. In all cases, /mol represents per mol of  $O_2$  in the pristine compound (either LNSO or LNTO). Theoretical oxygen refers to the oxygen production rate required to account for the entire current assuming 4 electrons are produced per molecule of  $O_2$ .



Figure 3.9: OEMS of LNTO cycled at 2 mAh/g. The voltage curves are shown in the top panel with the corresponding  $O_2$  and  $CO_2$  production rates in the middle and bottom panels respectively. For the oxygen gas to account for the entire current, a rate of 311 nmol min<sup>-1</sup> g<sup>-1</sup> is required.



Figure 3.10: OEMS of a) LNSO cycled at 10mA/g and b) LNTO cycled at 10 mAh/g. The voltage curves are shown in the top panel with the corresponding  $O_2$  and  $CO_2$  production rates in the middle and bottom panels respectively. For the oxygen gas to account for the entire current, a rate of 1554 nmol min<sup>-1</sup> g<sup>-1</sup> is required.

cient time for the slow oxygen diffusion to take place within the bulk of the particles, again suggesting that primarily only surface oxygen is being evolved.

# 3.4 *Ex-Situ* X-Ray Absorption Near Edge Structure and X-Ray Photoelectron Spectroscopy

For identification of the impact of oxygen evolution on the material, the oxidation state of nickel on the surface of the particle was compared to the nickel oxidation state in the bulk. XANES was used to determine the average nickel oxidation state throughout the entire material whereas XPS, owing to its surface sensitivity, was used to probe the particle surface. XANES spectra with the Ni K-edge evolution for each of the LNSO and LNTO samples,



Figure 3.11: XANES Ni K-edge of *ex-situ* samples for pristine (blue), charged to 5V (red), and discharged to 3.6V (yellow) of a) LNSO cycled at 10 mAh/g, b) LNTO cycled at 10 mAh/g and c) LNTO cycled at 2mAh/g. The black arrow corresponds to a transition of 1.0 in nickel oxidation state on the basis of the reference materials as shown in Figure 3.12.



Figure 3.12: XANES results for the two nickel reference materials.

depending on the potential cutoff and cycling rate conditions, are shown in Figure 3.11. In all cases, the charging process results in a shift of the edge consistent with change in nickel oxidation state of >1. However, the extent of reversibility varies dramatically: the LNTO materials had very little reversibility in nickel oxidation state, particularly when cycled slowly (at 2 mA/g) – upon discharge, the nickel oxidation state did not reduce back to the pristine nickel oxidation state. This is consistent with the results from the electrochemistry, wherein the discharge plateau at around 4 V was greatly diminished by extending the cutoff potential to 5.0 V.

The bulk nickel oxidation state was determined using the position of the edge in comparison to the reference materials in Figure 3.12 and Table 3.5. The position of the Ni-edge was determined using the position where the normalized absorption was 0.2, however using different values here had very minor impact on the resulting oxidation-state values (e.g. 0.5 was also used in a few cases to verify reliability of this approach) so we deem these quantified

Material	Binding Energy	Final Oxidation	
$L_{1.10}$ NSO 10 mAh/g			
Pristine	8338.82	+2.44	
Half Charge	8339.63	+3.18	
Full Charge	8339.98	+3.51	
Full Discharge	8338.88	+2.50	
LNTO 10 mAh/g			
Pristine	8338.94	+2.55	
Full Charge	8340.41	+3.90	
Full Discharge	8339.33	+2.91	
LNTO 2 mAh/g			
Pristine	8338.94	+2.55	
Half Charge	8339.98	+3.51	
Full Charge	8340.26	+3.76	
Full Discharge	8339.85	+2.39	
Li <sub>0.95</sub> Ni <sub>1.05</sub> O <sub>2</sub>	8339.32	+2.90	
NiO	8338.34	+2.00	

Table 3.5: Quantified nickel oxidation state based on the XANES nickel edge positions. Binding energy is the position of the edge at 20% relative intensity. These oxidation states are the calculated averages based on three measurements of the sample, where cell-to-cell variation in specific capacity results in an uncertainty of the calculated oxidation state of no more than 0.03.


Figure 3.13: Overall changes in Ni and O oxidation states at different points of the electrochemical cycling for LNSO cycled at 10 mA/g (top), LNTO cycled at 10 mA/g (middle), and LNTO cycled at 2 mA/g (bottom). The numbers within the blue circles correspond to the overall oxidation states within the whole particles (i.e., not solely the core), whereas the numbers within the yellow circles correspond to the surface nickel oxidation on the basis of the XPS data.

oxidation states to be robust.

The pristine materials show nickel oxidation states to be +2.44 and +2.55 for L<sub>1.15</sub>NSO and LNTO, respectively, in adequate agreement with those of +2.40 and +2.33 inferred from the ICP results in Table 3.2. These are calculated as the average oxidation state based on 3 XANES measurements on the same sample. Interestingly, all three materials show nickel oxidation states well above +3 in the half and fully charged states. It is of note that the nickel in the LNTO, charged at 2 mA/g, has a lower oxidation state than that seen with 10 mA/g

rate, despite the higher total capacity, as this is consistent with the reductive couple acting during oxygen gas production. In all cases, the change in nickel oxidation does not account for all of the capacity seen in the electrochemical testing. Therefore, the extra capacity is attributed to oxygen redox (either reversible or irreversible), permitting us to calculate the average oxidation state of oxygen which is included in the mechanism scheme in Figure 3.13. In the two materials cycled at 10 mA/g, the changes in the oxygen oxidation state are reversible, whereas in the LNTO cycled at 2 mA/g (which shows the greatest oxygen loss on the basis of the OEMS data in Table 3.4), the average oxygen oxidation state does not return to +2.0 during discharge. Also, for both  $L_{1.15}$ NSO and LNTO the nickel oxidation state changes by about 1.0 during discharge, whereas in the slowly cycled LNTO the nickel oxidation state change accounts only for 0.37. Thus, in this study, the reversibility of the nickel redox is directly impacted by the oxygen gas released, even though the amount of oxygen gas is relatively small.

To contrast the behaviour of nickel in the bulk and the surface of the particles, we also performed XPS on these same samples (Figure 3.14 and Figure 3.15). In the literature, there is one study which examines  $\text{Li}_4\text{NiTeO}_6^{67}$  in which the pristine material begins with Ni<sup>2+</sup> and Te<sup>6+</sup>. Though the authors claim that nickel was reversibly oxidized from Ni<sup>2+</sup> to Ni<sup>4+</sup>, this was based solely on the position of a peak seen in the XPS data of the charged materials, which was 1.1 eV higher than the pristine. Since that paper was published, a number of publications in Li[Ni,Mn,Co]O<sub>2</sub> has shown that the peak appearing 1.1 - 1.6 eV higher than the Ni<sup>2+</sup> is in fact Ni<sup>3+</sup>,<sup>91,92</sup> while Ni<sup>+4</sup> has a shift closer to 4 eV as compared to the Ni<sup>2+</sup> peak.<sup>93</sup> We therefore attribute any peak that is 1.1 - 1.6 eV above Ni<sup>2+</sup> to Ni<sup>3+</sup>. Thus, the



Figure 3.14: *Ex-situ* Ni XPS spectra of LNSO and LNTO charged at 10 and 2 mA/g, respectively. Dashed lines represent the peak positions attributed to  $Ni^{2+}$ ,  $Ni^{3+}$ , and  $Ni^{4+}$  as labeled.



Figure 3.15: *Ex-situ* Ni XPS spectra of LNTO cycled at 10 mA/g. Dashed lines represent the peak positions attributed to Ni<sup>2+</sup>, Ni<sup>3+</sup>, and Ni<sup>4+</sup> as labeled.

Material	Ni <sup>2+</sup>		Ni <sup>3+</sup>		Ni <sup>4+</sup>		Average Ovidation
	B.E. (eV)	Molar Fraction	B.E. (eV)	Molar Fraction	B.E. (eV)	Molar Fraction	Average Oxidation
LNSO 10 mA/g $$							
Pristine	855.12	78.0%	856.56	21.5%	858.50	0.4%	2.22
Half Charge	855.15	36.8%	856.84	56.0%	858.50	7.2%	2.70
Full Charge	855.01	35.3%	856.34	63.7%	858.33	1.0%	2.66
Full Discharge	855.00	57.7%	857.05	37.0%	858.50	5.3%	2.48
LNTO 10 mA/g							
Pristine	855.00	94.3%	856.56	5.7%	_	—	2.06
Full Charge	855.16	23.4%	857.08	60.1%	858.50	16.4%	2.93
Full Discharge	855.16	35.4%	857.02	58.1%	858.50	6.5%	2.71
LNTO 2 mA/g							
Pristine	855.00	94.3%	856.60	21.5%	_	_	2.06
Half Charge	855.16	29.7%	856.75	56.0%	858.50	18.2%	2.89
Full Charge	855.16	38.9%	856.97	63.7%	858.50	12.2%	2.73
Full Discharge	855.81	50.4%	856.42	37.0%	858.50	0.0%	2.50
Literature							
Ref. [91]	854.40		855.60		_		
Ref. [92]	854.55		855.59		_		
Ref. [93]	854.36		_		859.64		

Table 3.6: Quantified nickel oxidation states based on the fits. The average oxidation state is a weighted average of the 3 possible states (+2, +3, and +4).

idea that LNTO reversibly cycles nickel between +2 and +4 must be entirely revisited given that this conclusion relied on the XPS data with insufficient reference materials existing at the time for clear attributions of each peak.

In our study, the peak at the lowest binding energy, around 855.1 eV, is attributed to  $Ni^{2+}$ . In all *ex-situ* materials, a peak at about 856.5 eV can be seen (attributed to  $Ni^{3+}$ ), with a third peak sometimes contributing a shoulder in the vicinity of 858.5 eV (attributed to  $Ni^{4+}$ ). These peak attributions were used for all fits in Figures 3.14 and 3.15. Parameters extracted are summarized in Table 3.6.<sup>91–93</sup> All XPS patterns were therefore fit with these



Figure 3.16: Representative SEM images of the pristine LNTO and LNSO samples showing large secondary particles on the order of 5-10  $\mu$ m.

three peaks as well as an additional satellite peak centered near 861 eV. At half charge, the appearance of Ni<sup>3+</sup> and Ni<sup>4+</sup> peaks at 856 and 858 eV, respectively, can be resolved from the data, and at full charge the Ni<sup>4+</sup> peak visibly decreases. Interestingly, Ni<sup>2+</sup> is present in significant amounts in all samples and the reversibility of the nickel redox is extremely limited here, in sharp contrast to the XANES results, probing the bulk. To quantify the trends seen in the XPS data, we show in Table 3.6 weighted averages of the nickel oxidation states for each sample; these values are also shown as the surface nickel oxidation state in Figure 3.13. It is of note here that large 5–10  $\mu$ m secondary particles make up these samples, as indicated in Figure 3.16, implying that the depth probed by the XPS does in fact represent only a very small fraction of the total volume.

The mechanism, based on our results and presented in Figure 3.13, reveals a number of important points to consider and allows understanding the consequences of the use of nickel in the Li-rich oxides. First, the surface nickel has systematically a lower oxidation state than that seen in the bulk of the particle, and this effect is especially strong after

oxygen gas has been evolved (e.g., the LNTO sample fully charged at 2 mA/g has surface nickel with an average oxidation state 1.04 lower than that of the bulk). The fact that a large amount of Ni<sup>2+</sup> is still detected at the surface, even in the fully charged materials, suggests that the reductive couple is quite strong here; it is simply mitigated by how little oxygen gas is released. This is most clearly seen in the fully discharged LNTO, cycled at 2 mA/g, where nickel has an average oxidation state of Ni<sup>2.5+</sup>, even though the bulk shows  $Ni^{3.39+}$ , whereas that of the fully discharged  $L_{1.15}NSO$  shows near perfect agreement between the surface and bulk states with values of  $Ni^{2.48+}$  and  $Ni^{2.50+}$ , respectively. This reductive coupling mechanism has also been identified in Li–Fe–Sb–O, where Fe was reduced all the way back to its pristine state of  $Fe^{3+}$ , when sufficient oxygen gas release occurred. Here, the reduction is more mitigated, primarily affecting the nickel at the surface. Nonetheless, in LNTO, this process also results in the nickel remaining trapped in a high oxidation state within the bulk, even after discharge. This demonstrates that a relatively small amount of oxygen release can have a dramatically detrimental impact on the overall electrochemistry in nickel-containing cathodes, as the changes occurring at the surface prevent reversibility within the bulk.

#### Chapter 4

## **Conclusions and Future Work**

# 4.1 Conclusions

Herein, the electrochemical performance of two nickel-containing model lithium-rich layered oxides ( $Li_4NiTeO_6$  and  $Li_{1.15}Ni_{0.47}Sb_{0.38}O_2$ ) were studied to gain insights into the performance of next-generation layered oxides that rely heavily on a high nickel content. A number of conclusions are of importance in this context:

1) Nickel can be oxidized from  $Ni^{2+}$  to  $Ni^{4+}$  at high potentials (4.5V and above) at which point oxygen redox (both reversible and irreversible) becomes significant.

2) Oxygen redox results in nickel not being oxidized all the way to  $Ni^{4+}$ . This occurs with both reversible oxygen redox as seen in  $L_{1.15}NSO$  or irreversible oxygen redox as in LNTO, strongly suggesting that the reductive couple acting in materials such as  $Li_4FeSbO_6^{10}$  does, in fact, also occur in nickel-containing materials. However, in Li-Ni-Sb-O and Li-Ni-Te-O, oxygen loss occurs primarily at the surface of particles as demonstrated through XPS and XANES data.

3) Oxygen gas evolution is dramatically reduced when nickel is used in the model material compared to the iron-containing materials studied previously. Furthermore, though the spectator cation (whether it is tellerium or antimony) has an important impact on the ironcontaining model systems (seen in the electrochemistry for Li-Fe-Sb-O and Li-Fe-Te-O), few differences are found between  $L_{1.15}$ NSO and LNTO here. This suggests that further substitution of tellerium and antimony with manganese or cobalt to form Li-rich NMC materials may not eliminate the negative mechanisms elucidated herein.

4) The sharp contrast seen here between XPS and XANES data is of high significance. XPS results are not representative of the oxidation states in the particle's bulk for Nicontaining cathodes, unlike materials that do not undergo oxygen gas release during cycling, such as Li-Ru-Sn-O.<sup>94</sup>

5) Protecting the surface of particles in nickel-containing oxides is crucial to material longevity, given that oxygen oxidation at the surface reduces nickel, and bulk nickel loses reversibility by remaining trapped in an oxidized state.

Such a dramatic contrast between the electrochemistry at the surface and the bulk has not been seen previously in model Li-rich oxides. Thus, the current study brings an extra dimension to the model systems that have been studied to date to fully understand the behaviour of Li-rich NMC's that rely heavily on nickel and oxygen redox. As these materials are of extreme interest as next-generation battery cathodes, the deepened understanding of the role of nickel provided in this work will guide further efforts to bring this class of materials to commercialization.



Figure 4.1: Voltage versus capacity and dQ/dV plots for  $LiNi_{1/6}Mn_{2/3}O_2$  cycled at 30°C with specific current of 10 mA/g The red line in the dQdV curve represents the first cycle. Of note is the increasing dQ/dV peak at 3.0V showing the phase evolution over long-term cycling. Adapted from Ref. [24] with permission.

## 4.2 Future Works

Future work would continue unraveling the mechanisms of Li-rich NMC's by replacing antimony and tellerium with manganese or cobalt in these lithium-rich model materials and measuring its effects on anionic redox. In addition, since our model materials show little to no structural changes, unlike Li-rich NMCs, the effects of such transformations on long term cycling and material degradation in lithium-rich materials should also be explored. A challenge to further investigating these transformations is choosing a suitable material to study.

Previously, the Li-Mn-Ni-O pseudoternary system was investigated by McCalla et al. in which the layered region of the composition space features a 'bump' in the single-phase boundary.<sup>24</sup> The solid solution materials in this region contain vacancies to allow Ni<sup>2+</sup>



Figure 4.2: Specific discharge capacity versus cycle number for half-cells of compositions in the Ni:Mn series cycled from 2.5V to 4.9V. Reproduced from Ref. [25] with permission.



Figure 4.3: Differential specific capacity of  $\text{Li}_{0.586}$  from cycles 1 to 50 in 10 cycle increments. A rate of 5 mA/g was used for the first cycle, while subsequent cycles were run at 20 mAh/g. b) Specific capacity of  $\text{Li}_{0.586}$  after 5, 50, 100, and 150 cycles. Once again, the peak evolution at 3.0V is the increasing  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox couple due to spinel-like phases evolving over long-term cycling. Adapted from Ref. [25] with permission.

and  $Mn^{4+}$  oxidation states with deficient lithium, such that the material can be defined as  $Li[Li_{(1/3)-x}Ni_{x/2}\Box_{x/2}Mn_{2/3}]O_2$  for  $0 < x < \frac{1}{3}$  where  $\Box$  denotes vacancies. Though these materials are not Li-rich, they behave similarly to lithium-rich materials: exhibiting oxygen redox at high voltage, irreversible capacity loss, and oxygen redox. Thus, these lithium-richlike materials could be used to study the underlying mechanisms of lithium-rich materials.

In addition to this material's lithium-rich-like behaviour, Figure 4.1b shows the evolution of the  $Mn^{3+}/Mn^{4+}$  peak around 3.1V on discharge, which can be seen evolving with subsequent cycles. The activation of the  $Mn^{3+}/Mn^{4+}$  redox couple is generally associated with the conversion of layered to spinel-like structures. Furthermore, the metal vacancies seen in this appear to promote the structural transformations, as seen in Fig. 4.1b where voltage fade is significant. Though the role of these metal vacancies are not fully understood, the composition is still a good model for studying both the effects of oxygen redox on transition metals and long-term structural transformations through EXAFS (for local structural changes) and XRD (for bulk structural changes).

Similar materials with varying levels of lithium content were also studied<sup>25</sup>, some of which show a dramatic increase in capacity during material cycling as seen in Figure 4.2. In these materials that had both spinel and layered phases, electrochemical data also show an increase in manganese redox activity at 3.0V (Fig. 4.3a). While these materials are not specifically lithium-rich, the mechanism behind the behaviour of these multiphase materials includes fundamental structural transformation and should help elucidate changes in Li-rich materials. The structural study of these materials during long-term cycling could allow us to understand the capacity growth in this material in comparison to similar lithium-rich materials, which show significant voltage decay. As such, these materials would be of interest for further study in continuation of the work done herein and the dramatic transformations will make it easier to identify the mechanisms at play.

Given that some of the materials discussed above in this work suffer from detrimental electrochemical effects due to structural phase evolution, a method of preventing structural changes within the material would be of interest. It has been theorized that the insertion of dopants into the lithium and transition metal sites of the material hinders phase transitions during cycling – however, the actual mechanism is not well known. The effect of low concentration metal substitution on structural stability and oxygen redox has been studied with dopants, with reports describing significant improvements to cycle life and voltage fade<sup>95–99</sup> in lithium-rich materials. As such, the local structure of these metal substitutions would be of interest for the purposes of future commercialization of lithium-rich cathode materials.

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