NMR OF CATHODES FOR LITHIUM ION BATTERIES

SOLID-STATE NMR OF CATHODES FOR LITHIUM ION BATTERIES

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Lay Abstract

The high energy density lithium ion battery (LIB) is one of the most important energy storage devices of the modern world. It has facilitated the widespread use of lightweight portable electronic devices and electric vehicles. The necessary shift towards renewable energy use in modern civilizations relies heavily on improvements to energy storage devices, specifically the LIB, of which the lithium-housing cathode is an essential component. Therefore, understanding and tailoring the chemistry of the cathode is crucial to making technological improvements to batteries. The following research aims to deepen the understanding of the structure and function of LIB cathodes using a technique called nuclear magnetic resonance (NMR). NMR probes the nanoscale environments of lithium ions, 'tuning into the radio station of the lithium ions' in the material, so that knowledge of the location and movement of the atoms through the material is determined.

Abstract

Polyanionic and layered oxide cathodes for lithium ion batteries (LIBs) have been studied using a combination of nuclear magnetic resonance (NMR) spectroscopy and galvanostatic cycling. The pyrophosphate series of ⁶Li-enriched and ⁷Li Li₂Mn_{1-y}Fe_yP₂O₇ were synthesized, and characterized by magic angle spinning (MAS) NMR. The four crystallographic sites in Li₂MnP₂O₇ are resolved in its ⁶Li MAS spectrum, but as iron content increases across the series the resonances broaden, and in Li₂FeP₂O₇ only one resonance is partially resolvable from the other overlapped resonances. Li₂FeP₂O₇ shows the highest capacity in the series. Super-fast MAS rates of 60 kHz were obtainable using a 1.3 mm NMR probe, which enabled the effective analysis of electrochemical samples of Li₂FeP₂O₇ using NMR. Spectra of cycled samples of Li₂FeP₂O₇ reveal that one particular lithium site (Li4) is fully extracted by full charge (4.6 V).

The layered oxide cathodes studied here, Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ and Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂, possess large chemical shift anisotropies and wide isotropic regions such that, in the ⁷Li spectra, spinning sidebands overlap with the isotropic region even at high spinning rates (60 kHz). The pj-MATPASS experiment effectively removes all spinning sidebands, revealing the full isotropic region in ⁷Li spectra. NMR of cycled samples of NMC show that lithium in the transition metal layer and in the lithium layer is extracted upon charge, and a change of paramagnetic Ni²⁺ toward diamagnetic Ni⁴⁺ is reflected by resonances of the remaining lithium in the lithium in the lithium in the pj-

MATPASS spectra of the $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ series reveals an increase in intensity in the transition metal layer region of the spectra as the amount of lithium (x) increases. Spectra of cycled lithium-rich $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$ show that structure is unaffected by reversible cycling between 2.5-4.4 V, whereas cycling between 2.5-4.8 V gives rise to irreversible loss in signal intensity.

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Only when we realize we 'know nothing' can we learn to know something.

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List of Abbreviations and Symbols

- i. AM active material
- ii. B₀ static magnetic field
- iii. CB carbon black
- iv. CSA chemical shift anisotropy
- v. dB decibels
- vi. DFT density functional theory
- vii. EC/DMC ethylene carbonate/dimethyl carbonate
- viii. EELS electron energy loss spectroscopy
- ix. LCO LiCoO₂
- x. LIB lithium-ion battery
- xi. LFP LiFePO₄
- xii. LMO LiMn₂O₄
- xiii. MAS magic angle spinning
- xiv. MAT magic angle turning
- xv. MATPASS magic angle turning phase adjusted spinning sideband (pj projection)
- xvi. µs microsecond
- xvii. NMC Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂
- xviii. NMP n-methyl-2-pyrrolidone
- xix. NMR nuclear magnetic resonance
- xx. PVDF polyvinylidene fluoride
- xxi. rf radio-frequency
- xxii. SOC state of charge
- xxiii. TM transition metal
- xxiv. T₁ longitudinal relaxation
- xxv. T₂ transverse relaxation

1.0 Introduction

1.1 Motivation for Lithium Ion Batteries

Environmental sustainability is a particularly acute challenge for modern civilizations. Rising carbon dioxide emissions, environmental degradation, and resource scarcity have unveiled the necessity for change in the way we consume energy. We must be able to diversify our energy sources and develop ways of eliminating excessive use of non-renewable sources of energy. The traditional internal combustion engine, as one example, must be supplemented by the fully electric or hybrid electric vehicle on the roads in and between today's increasingly-populated cities. A paradigm shift from non-renewable fossil fuels to renewable energy relies heavily on the development of energy storage devices. The high energy density lithium ion battery (LIB), depicted in Figure 1-1 (a), is currently the most effective mobile energy storage device. Among battery systems it is the clear winner in volumetric and gravimetric energy densities, as shown in Figure 1-1 (b).¹ It has facilitated the production of electric vehicles, and offers potential for storage of sustainable energy from devices like wind turbines and solar cells during off-peak energy consumption.



Figure 1-1. (a) A depiction of a lithium ion cell. (b) Plot of volumetric and gravimetric energy densities of a variety of battery systems, adapted from reference [1].¹

There is much excitement about the promise of electric vehicles and LIBs in helping to drastically reduce dependence on foreign oil, reduce emissions, and store power generated during off-peak hours. However, there remain substantial economic and environmental barriers to the realization of LIB-powered electric vehicles as a 'green' solution to existing modes of transportation and energy consumption. These barriers are present at all levels of battery production and existence: the extraction of raw resources, manufacturing, charging and recycling/disposal. The two main types of raw material sources for lithium are minerals, where the production of lithium metal is energy intensive, and sea-water brines, where the concentrations of lithium are very low but concentrating lithium may only require the use of solar energy.² In both cases, exploitation of lithium is economically challenging. Furthermore, the infrastructure for mass amounts of lithium ion battery recycling is non-existent and it is difficult to predict what the environmental and economic costs of disposal or re-use of batteries would be. Lastly the environmental impact of LIBs is dependent on the source of energy production which provides the electricity for the plug-in vehicle. As a result, there would be a large advantage of using electric vehicles in regions with low carbon electricity generation, but there would be no benefit to using electric vehicles in areas with coal-based electricity generation.³ These examples illustrate some of the major problems associated with implementing large-scale use of LIBs and warrant the continuous improvement in LIB technology both on the industrial scale as well as through fundamental scientific research. LIBs need to be better in order to seriously contribute to a more sustainable future.

The cathode greatly influences the working voltage, capacity, and lifetime of a LIB cell. It also constitutes a majority of the cost of the cell. Thus much of the focus of battery research involves exploring novel materials and understanding the mechanisms of cathode function in the cell. The first commercial LIB (SONY 1991) hosted LiCoO₂ (LCO) as its cathode, which is still used extensively to power portable electronic devices like laptops.² As shown in Table 1-1,⁴ LIBs that power modern commercial electric vehicles employ cathodes similar to the original lithium-donor, LCO. John Goodenough and coworkers introduced three types of materials that encompass all cathodes used in modern LIBs, and a large portion of the LIB cathode research done today. Those being the layered-oxide LCO,⁵ spinel LiMn₂O₄ (LMO),⁶ and polyanionic materials (i.e. PO₄³⁻). Appropriately, the present work focuses on polyanionic pyrophosphates Li₂Mn_{1-y}Fe_yP₂O₇ and layered-oxide cathodes: Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ (NMC) and Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂.

Vehicle	Battery Supplier	Cathode	Anode
Nissan Leaf EV	Automotive Energy	LiMn ₂ O ₄ (LMO)	Graphite (C)
	Supply (Nissan NEC		
	JV)		
Chevrolet Volt	Compact Power (LG	LMO	С
	Chem)		
Renault	Automotive Energy	LMO	С
Fluence	Supply		
		LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	С
Tesla Roadster	Panasonic Energy	Nickel-type	
Tesla Model S	BYD	LiFePO4 (LFP)	С
BYD E6	Subaru	Li ₃ V ₂ (PO ₄) ₃ (LVP)	С
Subaru G4e	Toshiba	Li(Ni _{1/3} Mn _{1/3} Co _{1/3})O ₂	Li4Ti5O12
Honda Fit EV	Corporation	(NMC)	(LTO)

Table 1-1. Examples of electric vehicles and their lithium-ion batteries.⁴

1.2 Cathodes

Layered Transition Metal Oxides

Although LiCoO₂ is still commonly used for commercial LIB applications, there are many alternative oxides that have lower cost and improved stability. Because of the lower availability of cobalt, other transition metals such as nickel and manganese are less costly alternatives. LiNiO₂ forms the same structure as LiCoO₂, which is α -NaFeO₂ (R $\overline{3}m$ with rhombohedral lattice centering and in the trigonal crystal family).⁷ LiNiO₂ is less expensive and has a higher energy density, but is less stable than LiCoO₂.⁸ Furthermore nickel ions occupy lithium sites because of the similar sizes of the cations and nickel can impede lithiation/delithiation. Adding cobalt to LiNiO₂ limits this Li/Ni exchange⁹ and allows for the use of high nickel-content layered oxides. As the other extreme, LiMnO₂ does not form the α -NaFeO₂ structure but rather forms a monoclinic structure.¹⁰ However, with

the addition of nickel, or nickel and cobalt the α -NaFeO₂ structure is formed.⁸ The most common Li(Ni,Mn,Co)O₂ composition is Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ (NMC) which has high capacity, good rate capability and can operate at high voltages.⁸ NMC is discussed further in its own chapter of this thesis.

The overlithiation of layered oxide cathodes, leading to structures like the family studied here, Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂, have been shown to improve electrode performance.^{11–13} The more complex and often debated mechanism of lithium extraction in these lithium-rich oxides involves significant structural changes in the 1st cycle, where the highest capacities of any of the layered transition metal oxide cathodes have been observed. In addition to transition metal redox processes which accompany lithium extraction/intercalation in conventional cathode materials, these lithium-rich materials also exhibit oxygen loss and a reversible oxygen redox process which give rise to the high capacity on the first cycle and on subsequent cycles.¹⁴

Polyanionic Phosphates

Polyanionic materials, like LiFePO₄, are another promising class of cathode materials with the potential for high capacity, structural stability, low cost and environmentally benign constituents. The phospho-olivine LiFePO₄ was first proposed as a positive electrode in 1997,¹⁵ but its use was limited because of the poor electrical conductivity exhibited by polyanionic materials. With the implementation of thin carbon-coating on the particle surface in 1999, however, the approximately full extraction of

lithium from LiFePO₄ was achieved.¹⁶ This achievement enabled the commercialization of LiFePO₄, and initiated the exploration of more novel polyanionic materials for LIB applications. In addition to the low cost of raw materials, low toxicity and excellent thermal stability, LiFePO₄ possesses a safe operating voltage of 3.5 V.¹⁷ This is in contrast to the operating voltage of the layered oxide LiMO₂-type materials which require higher charging voltages, extending to above 4.3 V. The decomposition potential of LIB electrolyte (LiPF₆ in EC/DMC) is approximately 4.3-4.5 V, vs Li,^{18,19} which means that some of the capacity in layered oxides is not practically accessible, whereas in lower operating voltage cathodes like LiFePO₄ the full capacity is accessible.

The pyrophosphates (Li₂Mn_{1-y}Fe_yP₂O₇) have been explored as potential upgrades to LiFePO₄ due to their greater theoretical capacity. This increase in theoretical capacity is due to the two lithium charge carriers per transition metal centre as opposed to only one in LiFePO₄. The reversible capacity of Li₂FeP₂O₇ is ~85 mAh/g, which shows that, as of yet, only one lithium can be cycled.²⁰ The second lithium extraction is accompanied by an oxidation process at about 5 V, which is above the threshold of stability for current LIB electrolytes.²⁰ In contrast, the Mn analogue Li₂MnP₂O₇ demonstrates poor cycling behaviour, despite the gradual increase of the redox potential with higher Mn content in the pyrophosphates.²¹ The pristine pyrophosphates as well as cycled Li₂FeP₂O₇ are extensively studied by Nuclear Magnetic Resonance (NMR) spectroscopy in this thesis work, with the aim of understanding why lithium extraction in Li₂MnP₂O₇ is not favourable and how lithium is extracted from Li₂FeP₂O₇.

1.3 Galvanostatic Cycling

Galvanostatic cycling is a method used to assess electrochemical performance of LIBs. In this experiment a constant current (galvano = current, static = constant) is applied across the circuit of the cell and the changes in potential are monitored with computer software. When the cell is charged, the constant positive current increases the potential of the cell as lithium is extracted from the cathode. This is accompanied by a loss of electrons and an increase in oxidation state of the redox-active transition metal in the cathode (i.e. Fe²⁺/Fe³⁺). Inversely, when the cell is discharged the constant negative current decreases the potential of the cell as lithium is re-inserted into the cathode and the redox-active transition metal is reduced. Limits of the minimum and maximum potentials are set according to the stability range of the electrolyte and cathode/anode combinations. This allows automatic charge/discharge cycling of cells.

The working potential of a cell is the voltage of the discharge plateau in a galvanostatic curve. As shown in Figure 1-2, the discharge plateau for a typical NMC cathode is sloped about 3.7 V. The working potential as well as the mass/volume and capacity of a cell dictate the energy density of a LIB. The reversible capacity (reported in mAh/g) is a measure of how much charge (how many electrons) can be reversibly extracted and re-inserted between the cathode and anode of a cell.



Figure 1-2. Galvanostatic cycling curve; twelve cycles of NMC; 175 mAh/g total reversible capacity. Potential limits are 2.5 V and 4.5 V. Cycled at a C/20 rate. The voltage range is indicated by a green dotted line and the discharge capacity is indicated by a red dotted line

The voltage-range and capacity on discharge are important cycling characteristics to consider when comparing cathode materials. In general, smaller voltage ranges, higher discharge voltages, and larger discharge capacities are best for lithium-ion cells. Figure 1-2 shows the discharge capacity, as a red dotted line, and the voltage range, as a green dotted line, for NMC. This convention is adapted from a review by Fergus,⁸ in which different cathode materials are compared. In the review, cycling is done between 2.5-4.3 V as opposed to the higher voltage limits presented here. The voltage range is determined by the points of inflection in the discharge curve.⁸ This review compares spinel LiMn₂O₄, layered oxides LiCoO₂ and NMC, and LiFePO₄ at different charging rates. In general, layered oxides exhibit the largest voltage ranges, spinel LiMn₂O₄ is intermediate, and LiFePO₄ exhibits the smallest voltage range. At fast cycling rates (i.e. C/1) the capacity of oxides (LiMn₂O₄, LiCoO₂ and NMC) is greater than that of LiFePO₄, and LiCoO₂ exhibits the highest capacity of these cathodes. In contrast, at slower cycling rates (i.e. C/10) the highest capacities are exhibited by NMC and LiFePO₄.

NMC and other layered oxides show sloped discharge profiles indicating solid solution type lithium extraction where the voltage changes during discharge. In contrast, LiFePO₄ shows a relatively flat discharge profile where the voltage remains relatively constant during discharge, which is the result of the formation of a two-phase mixture on cycling.⁸ Similarly, a portion of the discharge curve of Li₂FeP₂O₇ is relatively flat, as seen in Figure 1-3.



Figure 1-3. Galvanostatic cycling curve; four cycles of $Li_2FeP_2O_7$ charged at 0.00852 mA (C/50 rate). Potential limits are 2 V and 4.5 V.

1.4 Experimental Design

In order to examine structural changes in cathodes as a function of cycling, the experimental design depicted in Figure 1-4 is implemented. First the cathode is synthesized, then the cell is assembled with the synthesized cathode material as the positive electrode (the details of cell assembly are outlined in each cathode chapter). The

cell is then cycled galvanostatically and held potentiostatically at the desired voltage until the current relaxes to approximately zero. The cell is then disassembled in an argon atmosphere glovebox, packed into a MAS rotor and analyzed by NMR spectroscopy. NMR Spectroscopy will be discussed in the following sections.



- Synthesize cathode

- Assemble cell
- Pack cathode in rotor
- Super fast MAS 60 kHz
- NMR spectroscopy

Figure 1-4. A depiction of the *ex-situ* cycling experiment implemented in this thesis work. First the cathode is synthesized, then the cell is assembled with the synthesized cathode material as the positive electrode. The cell is then cycled galvanostatically and held potentiostatically at the desired voltage until the current relaxes to zero. The cell is then disassembled, packed into a MAS rotor and analyzed by NMR spectroscopy.

1.5 Solid-State NMR of Cathode Materials for Lithium Batteries

This section covers key concepts that are required for an understanding of the spectroscopic techniques used in this thesis work. The concepts will be approached mostly empirically and verbally rather than theoretically and mathematically. A fundamental undergraduate-level understanding of NMR spectroscopy is assumed and so

the aim of this section is to familiarize the reader with concepts that are not covered in a typical undergraduate curriculum. Given the nature of the materials studied in this body of work – solid paramagnetic materials – and the nuclei under investigation – ^{6,7}Li – there are several concepts that must be addressed. These include solid-state NMR; paramagnetic NMR; quadrupolar coupling; and the pulse sequences used in this thesis, namely: the simple Hahn-echo²² and the complicated projection Magic Angle Turning – Phase Adjusted Sideband Separation (pj-MATPASS) techniques.²³

Magic Angle Spinning

Solid-state NMR (ssNMR) is a sensitive probe of nuclear environments of mobile Li ions (^{6,7}Li) and the structural framework (³¹P, ¹⁹F) of cathodes. In conjunction with electrochemical cycling, ssNMR provides a means for understanding mechanisms of lithium transport as well as structural changes in cathodes as a function of charge/discharge.

SsNMR differs from conventional solution NMR because the orientations of crystals in a solid give rise to different Larmor precession frequencies about an external magnetic field vector. Whereas in solution molecular tumbling averages anisotropic (orientation dependent) effects, in solids there is a lack of averaging of dipolar (through-space) coupling, quadrupolar coupling, and chemical shielding anisotropy (CSA). Chemical shielding arises from the electron current that shields a nucleus from the external magnetic field, and is given by²⁴:

$$\widehat{H}_{CS} = -\gamma \hbar \widehat{I} \cdot \sigma \cdot B_0$$

Where σ is the chemical shielding tensor, that describes how the size of the shielding varies with molecular orientation.²⁴ Heteronuclear dipolar coupling, which describes the through-space interactions of two nuclear spins, can be given by²⁴:

$$H_D = -\frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_j \hbar}{r_{ij}^3} (3\cos^2\theta - 1)$$

Where γ_i and γ_j are the gyromagnetic ratio of the nuclei, r_{ij} is the distance between the nuclei, and θ is the angle between the vector created by the two spins and the external magnetic field. When θ = 54.74 the term ($3\cos^2\theta$ -1) is equal to zero and dipolar coupling is decoupled. Dipolar coupling, quadrupolar coupling, and CSA give rise to extremely broad linewidths in static ssNMR. However, Magic Angle Spinning (MAS) mimics molecular tumbling by spinning solid samples at high speeds (e.g. 60 kHz) at an angle ~54.74° to the external magnetic field vector. At high enough spinning rates anisotropic effects are decoupled.

When the spinning rate is not high enough to completely decouple anisotropy, MAS gives rise to spectra with spinning sidebands located at the spinning frequency away from the isotropic peak. Besides the spinning sidebands, one nuclear environment in a crystal corresponds to one *isotropic* (centreband) resonance, like in solution NMR. Figure 1-5 shows a fast MAS spectrum and a static spectrum of LiNi_{0.1}Mn_{0.1}Co_{0.8}O₂. It is clear that the static spectrum, with significant anisotropic broadening, contains no information about the molecular environments in LiNi_{0.1}Mn_{0.1}Co_{0.8}O₂, but this information is uncovered with MAS.



Figure 1-5. ⁷Li static spectrum of a solid powder oxide material LiNi_{0.1}Mn_{0.1}Co_{0.8}O₂ shown in blue. The same material was spun to 60 kHz and the corresponding MAS spectrum is shown in black. A pictorial representation of a rotor spinning at the magic angle is shown in the inset.

Quadrupole Interaction

Quadrupolar nuclei have a spin greater than ½. Both nuclei studied in this body of work are examples of quadrupolar nuclei (⁶Li, I = 1 and ⁷Li, I = 3/2). Quadrupolar coupling is averaged out by rapid molecular tumbling in liquids, but this is not so for solids where orientations of nuclei are fixed. A quadrupolar nucleus is so called because it possesses a nuclear electric quadrupole moment which can interact with any electric field gradient at the nucleus.²⁴ In solids and for all nuclei which do not reside in a spherical (e.g. cubic)

symmetry, such electric field gradients exist due to the distribution of other nuclei and electrons in the vicinity.²⁴

The orientation of the molecule determines the electric field gradient and the applied magnetic field B_0 indirectly determines the orientation of the nuclear electric quadrupole moment.²⁴ Therefore, the strength of the quadrupole depends on the orientation of the molecule with respect to B_0 . Like any anisotropic interaction, Magic Angle Spinning (MAS) can eliminate quadrupolar coupling. The strength of the quadrupole moment, which is a constant for a given nuclear species and does not change with the chemical environment of the nucleus.

⁶Li vs. ⁷Li MAS NMR

⁶Li (*I* = 1) has a smaller quadrupole moment compared to ⁷Li (*I* = 3/2) and therefore its resonances are less affected by 2nd-order quadrupolar broadening.²⁵ In addition to the smaller quadrupole moment, the smaller gyromagnetic ratio of ⁶Li compared to ⁷Li is important to consider because the magnitude of the dipolar coupling scales with the gyromagnetic ratio. Quadrupolar and dipolar coupling contribute to the large spinning sideband manifolds often seen in these paramagnetic materials. The smaller dipolar and quadrupolar interactions for ⁶Li are easier to remove by MAS as compared to ⁷Li and so ⁶Li spectra have fewer spinning sidebands. This can be seen in Figure 1-6 which compares the ⁶Li and ⁷Li spectra of Li₂FeP₂O₇. Having fewer spinning sidebands can be very important when weaker resonances are overlapped by the sidebands of stronger resonances. Despite the advantages for using ⁶Li, on the basis of natural abundance ⁷Li is much more feasible and attractive. The natural abundance of ⁶Li is 7.4% whereas the natural abundance of ⁷Li is 92.6%. Therefore, in order to obtain ⁶Li spectra in a reasonable amount of time, samples must be enriched, which may or may not be feasible.



Figure 1-6. MAS NMR of ⁷Li₂FeP₂O₇ (blue) and ⁶Li₂FeP₂O₇ (black). The Li-7 spectrum was obtained at a Larmor frequency of 77.7 MHz with a MAS spinning speed of 30 kHz. The Li-6 spectrum was obtained at a Larmor frequency of 44.1 MHz with a MAS spinning speed of 25 kHz. Stars indicate spinning sidebands.

Field strength

Dipolar coupling scales linearly with the magnetic field strength, so the use of lower static magnetic fields can be advantageous.²⁵ In the work on layered oxides presented here all spectra were acquired at a 4.7 T field strength, which corresponds to a Larmor frequency for ¹H of 200 MHz. Lower fields can also help avoid overlap between

spinning sidebands and isotropic peaks in a MAS spectrum because the spectral width in ppm is independent of static field strength but the Larmor frequency scales linearly with field strength. Thus at higher field strengths the spinning sidebands of any particular isotropic resonance will necessarily be closer (in ppm units) to that particular resonance.

Hahn-echo experiment

Hahn-echo experiments are used because of the very large spectral widths associated with MAS spectra of paramagnetic solids. Hahn-echo experiments,²² as depicted in Figure 1-7, refocus magnetization in the transverse direction. This is very important for phasing because the frequency spread between the lowest and highest frequency peak in these spectra can be 400 kHz wide, for example. Essentially, without re-focusing these spectra would be extremely out-of-phase. Since echo experiments are performed with MAS, the pulse sequences must be rotor-synchronized. Thus the value of τ is chosen to be a multiple of the rotor period and the value of τ' must be one order of magnitude smaller than τ . The reason for this will be discussed shortly





The parameters for a typical ⁷Li spectrum presented in this thesis will now be listed and briefly discussed. The sweep width is 1 MHz to ensure that the excitation bandwidth covers the width of the whole spectrum. The MAS is typically 60 kHz which is close to the limit of spinning rate for the 1.3 mm probe and ensures adequate separation of spinning sidebands from the isotropic peaks in many cases. The recycle delay is 0.05 s, ensuring adequate longitudinal magnetization relaxation after each acquisition period (relaxation of longitudinal magnetization will be discussed below). The delay between the 90° and 180° pulses, τ , is 31 µs (a multiple of the rotor period) and the delay between the 180° pulse and the start of acquisition, τ' , is 5 µs. The reason that τ' is an order of magnitude smaller than τ is so that the maximum point in the signal (i.e. the top of the echo) can be seen in the acquired signal and the spectrum can subsequently be left-shifted to start at the top of the echo. Lastly, the pulse length is calibrated with the maximum allowed power for the particular probe using ⁷LiCl as a standard. For ⁷Li spectra on the 1.3 mm probe, the pulse length for a 90° pulse is typically 1 µs and the pulse power is 0.5 dB.

This simple pulse-echo technique is adequate for studying pristine and electrochemical cathode samples when the anisotropy of the sample is small enough or when the frequencies of the isotropic peaks do not exceed the MAS rate so that spinning sidebands in fast MAS do not overlap with the isotropic region. However, when these conditions are not met, the experimenter must try either ⁶Li enrichment or ⁷Li pj-MATPASS. The latter will now be discussed.

⁷Li pj-MATPASS

The projection Magic Angle Turning – Phase Adjusted Sideband Separation (pj-MATPASS) technique, first published in 2012,²³ combines the magic-angle turning (MAT)²⁶ technique by Gan and the phase-adjusted sideband separation (PASS)²⁷ technique by Levitt et al. Both of which will be briefly discussed, in turn, prior to pj-MATPASS. In MAS spectra when the chemical shift anisotropy (CSA) is large relative to the spinning rate, spinning sidebands can crowd the spectra, making resonance assignments and quantification difficult. It is the aim of the MAT, PASS, pj-MATPASS, and the original magic angle hopping techniques to eliminate spinning sidebands. In 1983 Bax et al.²⁸ introduced the magic angle hopping experiment which uses fast and accurate mechanical hopping to separate the isotropic chemical shift and CSA correlation spectrum into two dimensions. Although high resolution spectra with no spinning sidebands were obtained, the fast and accurate mechanical hopping system, which is not commercially available, limits the robustness of the technique.

MAT is a 2D method that uses continuous slow magic angle spinning as opposed to hopping, where the evolution period is divided into segments spaced by one-third of a rotor cycle.²⁶ The magnetization of the sample is stored along the external magnetic field during the time between these evolution segments while the sample is rotated 120°. For each segment, the chemical shift is the sum of the isotropic chemical shift and a contribution from the Chemical Shift Anisotropy (CSA). In each segment the CSA contribution is different because of the different orientations of the sample with respect to the external magnetic field and the net contribution from CSA for the three segments is averaged to zero. The PASS technique also employs continuous slow spinning. The "PASS" section of the 2D experiment evolves over a single rotor period $\tau_r = 2\pi/\omega_r$ and contains five 180° pulses. The intervals between the five 180° pulses are varied (giving the second dimension of the 2D spectrum) according to the solutions of numerical equations described by Levitt et al.²⁷ The varied positions of these 180° pulses average the CSA to zero, like in the MAT technique. The merit of this pulse sequence is first demonstrated on L-tyrosine hydrochloride powder, where in the ¹³C 1D MAS spectrum there is a tangled overlap of sidebands, but in the 2D PASS spectrum the sidebands are separated out in twodimensions according to their order. This means that all sidebands which are displaced from their corresponding centreband (isotropic peak) by a frequency $k\omega_r$, where *k* is an integer, are displayed along the same horizontal slice.²⁷ The 180° pulses used in this technique greatly limit the excitation bandwidth, however, which restricts PASS to samples with small anisotropy, excluding ⁷Li NMR of paramagnetic cathode materials.

In addition to the limited excitation bandwidth of PASS, the slow spinning requirement of MAT and PASS means that there is a requirement in both of these techniques for a large number of t_1 increments in the indirect dimension. However, pj-MATPASS allows for fast MAS and in the indirect dimension there is only the evolution of anisotropy which decreases the number of t_1 increments significantly. Furthermore, pj-MATPASS excludes the use of large flip-angle refocusing pulses (using five 90° pulses instead) which makes the experiment viable for samples with large anisotropy (~1 MHz) and/or isotropic peaks far exceeding the MAS rate.²³ Two samples which exhibit these

characteristics are shown in Figure 1-8; Li_2MnO_3 has an isotropic peak that exceeds the MAS rate of 60 kHz and $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$ has a large anisotropy (~120 kHz). The spinning sidebands of the spectra of these samples are removed using pj-MATPASS, uncovering valuable spectral information.

It would require a long discourse and more years of study on the part of the writer to give an explanation worthy of the mathematical and physical elegance of the pj-MATPASS technique. It will suffice to say that this pulse sequence allows for quantitative analysis of the full spectra of paramagnetic cathode materials.



Figure 1-8. ⁷Li MAT-PASS spectra (shown in black) and ⁷Li MAS Hahn-echo spectra (shown in blue) of (a) Li_2MnO_3 and (b) $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$. All spectra were acquired at a field strength of 4.7 T and samples were spun at 60 kHz. Black stars and crosses indicate isotropic peaks and red stars and crosses indicate spinning sidebands.

Paramagnetic NMR

The chemical shift range for lithium in diamagnetic materials is normally too small to resolve unique lithium sites. Contrarily, the chemical shift range of lithium in paramagnetic materials is large, enabling for the resolution of unique lithium sites. However, lithium spectra of paramagnetic materials are often complex and difficult to interpret; because of their large spectral widths and broad resonances. Despite the complexity of these spectra much work has been done to elucidate the mechanisms of chemical shift and to assign specific resonances to specific types of environments in cathode materials.^{25,29,30}

The chemical shift as well as the width of a particular lithium resonance is greatly influenced by the transfer of unpaired electron spin density from d-orbitals of the paramagnetic transition metal ion to the s-orbital of the lithium nucleus. The transfer efficiency depends on the geometrical arrangement of the transition metal with respect to the lithium atom as well as the distance between the two atoms. In oxides this transfer efficiency is maximized when the Li-O-TM bond angles are 180° and 90°, as seen in Figure 1-9.²⁵ All of the cathode materials examined in this thesis contain paramagnetic transition metal ions (Li₂Mn_{1-y}Fe_yP₂O₇, LiNi_{1/3}Mn_{1/3}CO_{1/3}O₂, and Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂), and the chemical shift mechanisms will be explained in detail for each cathode in their respective chapters. For a more detailed description of paramagnetic shift mechanisms and an expansive review of paramagnetic cathode materials see work by Grey and Lee (2003)²⁵ as well as Grey and Dupré (2004).²⁹



Figure 1-9. (a) 90° Li-O-TM interaction and (b) 180° Li-O-TM interaction.

The relative magnitudes of the electron relaxation time, $T_{1e}s$, and the electronnuclear interaction contribute to the effective resolution of paramagnetic ions in NMR spectroscopy. The electron-nuclear interaction can be quantified by a hyperfine coupling constant A/h (in Hz). For the case where $T_{1e}s$ is so great that $1/T_{1e}$ (s-1) is on the same time-scale as A/h then significant line broadening will occur.²⁹ Furthermore, as the number of unpaired electrons increases across paramagnetic samples the spinning sideband manifolds of MAS NMR spectra tend to increase (Figure 1-10).³¹


Figure 1-10. ⁷Li MAS spectra at 25 kHz showing the effect of paramagnetism on the spinning side-band manifold of the olivine type cathodes. ³¹

MAS results in significant heating of the sample (by as much as 80°C in some of the very fast MAS probes),²⁵ and the shifts of the resonances of paramagnetic species can be extremely temperature dependent. This is important to consider for paramagnetic cathode materials. Sample temperature calibration can be achieved by determining the temperature of a standard sample (e.g. Sm₂Sn₂O₇), in which the shift dependence on temperature is known, at different spinning speeds.

Relaxation

When a sample is subject to an external magnetic field the macroscopic nuclear magnetization of the sample gradually grows due to the preference for nuclear spins to be driven towards a low magnetic energy.³² This same phenomenon is responsible for the relaxation of nuclear spins following a pulse. The spin-lattice relaxation time constant T₁ is the exponential time constant for the build-up or relaxation of longitudinal

magnetization. The build up of magnetization after turning on an external magnetic field is described in the following equation and depicted in Figure 1-11.



Figure 1-11. The build-up of longitudinal spin magnetization, after the magnetic field is turned on.³²

The relaxation time constant T_1 depends on the nuclear isotope and its chemical environment. The value of T_1 is typically in the range of milliseconds to seconds.³² The T_1 values for ^{6,7}Li nuclei in paramagnetic cathodes are very small – in the millisecond range.

2.0 Pyrophosphates

Note: This chapter comes from the work titled: <u>Correlation of Electrochemical</u> <u>Performance with Lithium Environments and Cation Dynamics in Li₂($Mn_{1-y}Fe_y$)P₂O₇ Using <u>⁶Li Solid-State NMR</u> published in The Journal of Physical Chemistry C.³³ Only work completed and written by the writer of this thesis is included.</u>

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2.1 Introduction

The pyrophosphate materials Li₂MP₂O₇, where M = Fe, Mn, are interesting prospects as cathodes for lithium ion batteries because they demonstrate high operating voltages and they house two charge carrying lithium ions per transition metal center, giving rise to high theoretical capacities.^{20,34–37} Despite the promise that these materials show, their experimental electrochemical behaviour has not approached their theoretical capacity. Of the pyrophosphate series Li₂Mn_{1-y}Fe_yP₂O₇ (y = 0, 0.2, 0.5, 0.8 and 1), the pure iron analog Li₂FeP₂O₇ shows the best electrochemical behaviour and the pure manganese analog shows very poor to almost no electrochemical activity.²⁰ The electrochemistry of Li₂FeP₂O₇ will be discussed in the following chapter.

It is important to try to understand why Li₂MnP₂O₇ demonstrates such poor electrochemistry. NMR spectroscopy offers the ability to probe the mobile lithium ions in these materials in order to gather dynamic information about the ions. Of the cathodes in this series, Li₂MnP₂O₇ gives the highest resolution Magic Angle Spinning (MAS) ⁶Li NMR spectrum, where all four of its Li sites are partially resolved and assigned. As iron content is increased across the series the lithium resonances broaden such that the peaks become mostly unresolvable. The above published work presents the exchange rates between lithium ions in Li₂MnP₂O₇, determined using 1D ⁶Li selective inversion NMR experiments. The abysmal exchange rates between the lithium atoms give reason for the poor electrochemical performance of Li₂MnP₂O₇. This chapter will focus on ⁶Li NMR spectroscopy of the pristine materials of the series Li₂Mn_{1-y}Fe_yP₂O₇.

2.2 Experimental

Sample Preparation

6-Li enriched Li₂Mn_{1-y}Fe_yP₂O₇ samples of varying composition (y = 0, 0.2, 0.5, 0.8, 1) were prepared by the "wet" method described by Zhou et al.²⁰ Stoichiometric amounts of ⁶Li(CH₃CO₂), Fe(CH₃CO₂)₂, Mn(CH₃CO₂)₂, and NH₄H₂PO₄ were stirred in aqueous solution (0.02 M Li) and heated until dry. The sample was placed in an evacuated drying oven at 90 °C for 12 hours. Using a tube furnace with a constant flow of 5% H₂/N₂ at 5 psi, the sample was heated to 600 °C for 30 hours. The sample was subsequently reground and heated to 600 °C for 12 hours.

⁶LiFeP₂O₇ was prepared by the previously reported high temperature synthesis as described by Padhi et al.¹⁵ Stoichiometric amounts of Fe₂O₃, NH₄H₂PO₄, and ⁶Li₂CO₃ were ground and heated at 200 to 300 °C. The sample was then reground and heated in a tube furnace to 850 °C for 24 hours.

Solid-State NMR

All ⁶Li MAS NMR spectra were acquired at a Larmor frequency of 44.1 MHz on a Bruker AV-300 spectrometer using 1.8 mm diameter rotors in a double-resonance probe. A Hahn-echo pulse sequence with a 90° pulse of 3.5 μ s and a recycle delay of 200 ms was used to acquire the ⁶Li MAS spectra.

2.3 Results and Discussion

Li₂MnP₂O₇ was first synthesized in 2008 by Adam et al.³⁴ where the 3D pyrophosphate framework reportedly consisted of MnO₅ and MnO₆ polyhedra interconnected through P₂O₇ groups, generating a tunnel-like structure that houses the four crystallographically unique Li ions, with Li1 and Li2 sharing one tunnel and Li3 and Li4 occupying another (Figure 2-1 (a)). The powder x-ray diffraction pattern of ⁶Li₂MnP₂O₇, shown in Figure 2-1 (b), agrees with that of ⁷Li₂MnP₂O₇ reported by Adam et al.,³⁴ confirming the successful preparation of the isotopically enriched pyrophosphates via the 'wet method' described by Zhou et al.²⁰ Although the structure is well known by diffraction, detailed information about local environments and dynamics of particular atoms is lacking. Herein solid-state NMR is used to probe local environments in the series of Li₂Mn_{1-v}Fe_vP₂O₇ materials.



Figure 2-1. (a) Unit cell of monoclinic $Li_2MnP_2O_7$ along the a-axis. MnO₅ trigonal bipyramids and MnO₆ octahedra (purple) are connected to PO₄ tetrahedra (gray). Li1, Li2, Li3 and Li4 sit in tunnels formed by the MnO₅, MnO₆ and PO₄ units. (**b)** Powder x-ray diffraction pattern of ⁶Li₂MnP₂O₇, matching that of ⁷Li₂MnP₂O₇ published by Adam et al.³⁴

Characterization of Mixed Metal Pyrophosphates

The ⁶Li MAS NMR spectrum of Li₂MnP₂O₇ is shown in Figure 2-2, where the four Li resonances corresponding to the distinct crystallographic positions in Li₂MnP₂O₇ are partially resolved. The four resonances (at 44, 32, 7 and 2.5 ppm) have been assigned to their respective crystallographic positions based on the Goodenough-Kanamori rules, as previously employed for the assignment of Li resonances in other paramagnetic compounds.²⁵ The transfer of electron spin density from the half-filled t_{2g} orbital of

paramagnetic manganese (II) to the empty Li 2s orbital via a delocalization mechanism causes a shift in the Li resonance where the efficiency of this transfer is maximized when the Li-O-Mn orbitals overlap at angles close to 90 or 180° .²⁹ While monoclinic Li₂MnP₂O₇ contains no Li-O-Mn angles close to 180° , there are angles close to 90° , where this 90° geometric arrangement is expected to give rise to an increase in isotropic shift.¹⁵ Therefore Li3, having two Li-O-Mn angles approaching 90° (89.53 and 94.85°) and the shortest Li-Mn distances (3.01 Å), is assigned to the highest frequency site at 44 ppm and labeled site D in the ⁶Li NMR spectrum. In contrast Li2, having no Li-O-Mn bond angles close to 90° , corresponds to the lowest frequency resonance at 2.5 ppm (denoted site A). The Li-O-Mn contacts for each lithium site are depicted in Figure 2-3, with the relevant bond angles, bond lengths, and peak assignments for the four crystallographic Li sites outlined in Table 2-1.



Figure 2-2. ⁶Li MAS (25kHz) spectrum of Li₂MnP₂O₇ at 298 K and the deconvoluted spectrum indicating the four partially resolved Li resonances corresponding to the four unique crystallographic sites in the structure.



Figure 2-3. Local environments for the four Li sites in $Li_2MnP_2O_7$, showing Li-O bonds and Li-O-Mn contacts. Li1 (a) and Li4 (d) show distorted square pyramidal geometry, Li2 (b) shows nearly tetrahedral geometry and Li3 (c) shows distorted tetrahedral geometry. Only Li-O-Mn contacts with Li-Mn distances less than 3.92 Å are shown.

Li site	Li-O-Mn angle	Distance to Mn (Å)	Li-O distance (Å)
	(deg)		
Li1 _p	99.37 (Li1-06-Mn2)	3.171	1.982
Б	88.20 (Li1-013-Mn2)	3.171	2.327
	94.23 (Li1-013-Mn1)	3.352	2.327
	96.10 (Li1-014-Mn1)	3.352	2.351
	110.74 (Li1-03-Mn1)	3.463	2.092
Li2 _A	105.67 (Li2-014-Mn1)	3.309	1.999
Li3 _D	89.53 (Li3-012-Mn2)	3.010	1.950
D	94.85 (Li3-08-Mn2)	3.010	1.966
	111.64 (Li3-01-Mn1)	3.697	2.288
Li4 _c	100.37 (Li4-04-Mn2)	3.175	1.969
	90.86 (Li4-08-Mn2)	3.175	2.333
	116.77 (Li4-01-Mn1)	3.548	1.985
	119.26 (Li4-012-Mn2)	3.915	2.229

Table 2-1. Summary of Crystallographic Data for $Li_2MnP_2O_7$. Li-O-Mn contacts with Li-Mn distances less than 3.92 Å are shown.

A deconvolution of the peaks in the ⁶Li MAS spectrum of Li₂MnP₂O₇ enables the determination of relative site occupancies. Integration over the entire spinning sideband manifold reveals an equal population of the two sites in each of the two tunnels, although the integrated intensities of Li3 and Li4 are 84% that of Li1 and Li2 (Table 2-2).

Site	Integral over entire spinning sideband manifold	Intensity (normalized to site 2 _A)
3 _D	1.12E+11	0.84
4 _C	1.13E+11	0.84
1 _B	1.37E+11	1.02
2 _A	1.34E+11	1.00

Table 2-2. Peak Intensities of the Four Lithium Resonances in Li₂MnP₂O₇.

The set of 1D ⁶Li MAS NMR spectra of the pyrophosphate series (Li₂Mn_{1-y}Fe_yP₂O₇, $0 \le y \le 1$) are shown in Figure 2-4. Although the four Li sites are partially resolved in the Li₂MnP₂O₇ spectrum, as iron content increases the signal broadens and the resonances overlap removing the site resolution. The measured spin-lattice (T₁) and spin-spin (T₂) nuclear relaxations of the pyrophosphates are given in Table 2-3. The T₁s were found to increase with iron content (3.06 ± 0.43 ms for Li₂MnP₂O₇ and 17.26 ± 0.06 ms for Li₂FeP₂O₇) with the differences in T₂s being negligible. As such, the differences in line width cannot be attributed to a difference in nuclear relaxation properties across samples.



Figure 2-4. ⁶Li MAS NMR spectra of $Li_2Mn_{1-y}Fe_yP_2O_7$ (y=0, 0.2, 0.5, 0.8, 1) with MAS=25 kHz. Full spectra and isotropic peaks are shown in (b) and (a), respectively. The "*" indicates an unidentified impurity in the $Li_2MnP_2O_7$ material.

Table 2-3. The Spin-Lattice (T_1) and Spin-Spin (T_2) Relaxation Times for the Pyrophosphates.

Li ₂ Mn _{1-y} Fe _y P ₂ O ₇	avg. T ₁ (ms)	avg. T ₂ (ms)
y=0	3.06 ± 0.43	1.08 ± 0.15
y=0.2	4.33 ± 0.03	0.69 ± 0.06
y=0.5	4.70 ± 0.05	2.04 ± 0.26
y=0.8	10.97 ± 0.07	2.99 ± 0.48
y=1	17.26 ± 0.06	1.82 ± 0.19

Broadening of the ⁶Li resonance can also be caused by the nuclear spin interaction with the time averaged magnetic moments of the electronic spins at the paramagnetic transition metals. These hyperfine interactions are known to occur either via a throughspace (dipolar) or through-bond (Fermi-contact) mechanism.²⁹ When the magnetic moment of the electronic spins is anisotropic there is an additional dipolar interaction that causes inhomogeneous line broadening. The symmetric electron configuration of $Mn^{2+} (t_{2g}^{3}e_{g}^{2})$ gives rise to an isotropic magnetic moment. In contrast, the asymmetric electron configuration of Fe²⁺ ($t_{2g}^{4}e_{g}^{2}$) gives rise to an anisotropic magnetic moment, thereby causing additional line broadening in the iron (II) containing pyrophosphates. The effect of magnetic moment anisotropy on line broadening is also demonstrated by simply comparing the ⁶Li MAS spectrum of LiFeP₂O₇ to that of Li₂FeP₂O₇ (Figure 2-5). Akin to the Mn²⁺ example, the electronic configuration of Fe³⁺ ($t_{2g}^{3}e_{g}^{2}$) in LiFeP₂O₇ is symmetric, corresponding to an isotropic magnetic moment, and in consequence the NMR spectrum of LiFeP₂O₇ is well resolved.



Figure 2-5. ⁶Li MAS NMR spectra of singly lithiated LiFeP₂O₇ (blue) and doubly lithiated Li₂FeP₂O₇ (black) with MAS=25 kHz. Full spectra and isotropic peaks are shown in (b) and (a), respectively.

2.4 Conclusions

The ⁶Li MAS NMR spectra of the $Li_2Mn_{1-y}Fe_yP_2O_7$ series are presented. All four Li sites in the crystal structure of $Li_2MnP_2O_7$ have been assigned to specific resonances in its spectrum based on Goodenough-Kanamori rules. As the iron content increases across the

series $Li_2Mn_{1-y}Fe_yP_2O_7$ the resonances broaden such that the peaks become unresolvable. However, despite the poor resolution in its NMR spectrum, the pure iron analog $Li_2FeP_2O_7$ shows the best electrochemical performance. It is therefore studied in the next chapter to see how cycling affects its NMR spectrum.

3.0 Cycled Li₂FeP₂O₇

3.1 Introduction

Despite almost twenty years since its advent and the exploration of many alternatives, olivine LiFePO₄ is still one of the most widely used commercial polyanionic cathodes. Pyrophosphate (P_2O7^{4-}) materials of Li₂MP₂O₇ (M = Fe, Mn), which can house two molar equivalents of lithium, have been explored due to their potential for higher gravimetric energy density as compared to LiFePO₄. Although the theoretical capacity of Li₂FeP₂O₇ is 220 mAh/g with the occurrence of a two-electron reaction, its capacity has been limited to the one-electron theoretical value of 110 mAh/g.³⁸ The extraction of the second lithium ion would require the oxidation of Fe³⁺ to Fe⁴⁺, occurring at a potential of approximately 5 V and would thus require the use of an electrolyte with a larger window of stability.²⁰

The pristine structure and electrochemical performance of Li₂FeP₂O₇ have been well-studied,^{20,38} and lithium-diffusion pathways in Li₂FeP₂O₇ have been examined theoretically.³⁹ However, experimental data about how the structure changes as a function of cycling does not exist to date. This type of information is crucial for determining which lithium atoms are most readily extracted and for verifying theoretical predictions about the most favourable lithium-diffusion pathways. In this study, electrochemical samples of Li₂FeP₂O₇ are examined using ⁷Li NMR spectroscopy and a model of lithium extraction is built.

3.2 Experimental

Synthesis

Li₂FeP₂O₇ samples were prepared by the "wet" method described by Zhou et al.²⁰ Stoichiometric amounts of Li(CH₃CO₂), Fe(CH₃CO₂)₂, Mn(CH₃CO₂)₂, and NH₄H₂PO₄ were stirred in aqueous solution (0.02 M Li) and heated until dry. The sample was placed in an evacuated drying oven at 90 °C for 12 hours. Using a tube furnace with a constant flow of 5% H₂/N₂ at 5 psi, the sample was heated to 600 °C for 30 hours. The sample was subsequently reground and heated to 600 °C for 12 hours. After cooling, the final sample was ground and used for NMR and electrochemical measurements.

In an effort to improve upon the electrochemical performance, Li₂FeP₂O₇ was also synthesized via a method described by Nishimura et al.³⁸ Stoichiometric amounts of Li₂CO₃, FeC₂O₄·2H₂O, and (NH₄)₂HPO₄ were ground together for 30 minutes and then thoroughly mixed by planetary ball-milling for 3 hours in acetone. The obtained slurry was evaporated under vacuum and then calcined at 300 °C for 6 hours under argon flow, reground for 30 minutes and calcined again at 600 °C for 12 hours under argon flow. One 500 mg sample was ground with laboratory grade sugar (5% by weight) and heated at 650 °C for 12 hours in an effort to increase the conductivity of the cathode material.

Electrochemical Measurements

The cathode for pyrophosphate coin cells consists of active material (AM), carbon black CB and polyvinylidene fluoride (PVDF) in a 75:15:10 weight % ratio. Active material and CB were ground together for 30 minutes and dried, then a solution of 2% PVDF in Nmethyl-2-pyrrolidene (NMP) was added and the resultant slurry was stirred for 2-3 hours. The slurry was cast onto aluminum foil and the NMP was evaporated in an evacuated drying oven at 110 °C for 12 hours. Discs, 1.27 cm in diameter, were punched and coin cells were assembled in an argon atmosphere glove box. The anode is lithium metal and the electrolyte is LiPF₆ in ethylene carbonate/dimethyl carbonate.

Coin cells were cycled with Arbin battery testing equipment and MITS Pro software using a galvanostatic cycling with potential limitation experiment. They were cycled between 2-4.5 V at a C/50 rate (i.e. one full charge in 50 hours). They were then disassembled in an argon atmosphere glove box at different charging and discharging potentials. The cathode material was washed with acetonitrile, dried under vacuum and packed in 1.3 mm diameter rotors.

Solid-state NMR

All ⁷Li magic-angle spinning MAS NMR spectra were acquired under a 4.7 T applied magnetic field using a Bruker DRX console. Spectra were collected using 1.3 mm rotors at a 60 kHz sample-spinning rate using a Bruker high speed MAS probe. A Hahn-echo pulse sequence was used with 1 µs 90° pulses and 50 ms recycle delays.

Structural Characterization using PXRD

Powder X-ray diffraction measurements were acquired on a PANalytical diffractometer with Cu K α radiation. Data was collected from diffraction angles of 10°-60° with 4786 steps at 45s/step.

3.3 Results and Discussion

Figure 3-1 shows the crystal structure of Li₂FeP₂O₇, which is essentially isostructural with Li₂MnP₂O₇, crystallizing in the same space group, P2₁/c. However, in Li₂FeP₂O₇ there is significant static disordering between the Li and Fe sites due to the similar sizes of radii of the Fe²⁺(0.78 Å) and Li⁺(0.74 Å) ions. Thus the Li1 and Fe2 sites are crystallographically identical, with a Li1/Fe2 ratio of approximately 1:2 and likewise for the Li2 and Fe3 sites, with a Li2/Fe3 ratio of approximately 2:1. The [P₂O₇]⁴⁻ anions are corner-sharing dimers of PO₄ tetrahedra. Iron atoms reside in FeO₆ octahedra and FeO₅ distorted trigonal-bipyramids, as three unique sites.



Figure 3-1. Crystal structure of $Li_2FeP_2O_7$ depicted using Vesta along the b-axis. FeO₅ trigonal bipyramids and FeO₆ octahedra (brown) are connected to PO₄ tetrahedra (gray). Li2, Li3, Li4 and Li5 sit in 2D planes formed by the FeO₅, FeO₆ and PO₄ units.

Lithium atoms occupy five crystallographic sites and reside in two-dimensional planes formed by corner and edge-sharing Fe/O and P/O polyhedral. Through simulations, Clark et al. have shown that the lowest energy lithium-diffusion pathways exist parallel to the *b*- and *c*-axes with energy barriers of 0.40 eV.³⁹ As can be seen in Figure 3-1, two lithium channels exist in the *bc*-plane, one housing Li4 (blue) and Li2 (green) and the other housing Li3 (red) and Li5 (orange). Table 3-1 gives cross-reference to the lithium atom labels between this work and Clark et al. The energy barrier for migration parallel to the *a*-axis was calculated to be 0.73 eV, which suggests that migration between the two lithium channels is significantly lower than migration within the *bc*-plane. This is due to the larger Li-Li distances and hindrance from Fe/O and P/O polyhedral. Although Clark et al. showed the long-range Li⁺ migration involving Li5 and Li3 sites, they did not show migration involving Li2 and Li4. We suppose that Li⁺ migration occurs in both lithium channels, and, as will be shown later, NMR data of cycled cathodes shows that Li4 is the most readily extracted lithium atom.

Table 3-1. Cross-reference for lithium labels

Clark et al. ³⁹ Li labels	1	2	3	4	5
My labels for Li atoms	5	4	3	1	2

In order to make assignments of lithium resonances in the ⁷Li NMR spectrum of Li₂FeP₂O₇ it is necessary to analyze the local environment of each lithium site. In the spectrum of the Mn-analogue, Li₂MnP₂O₇, the four lithium resonances corresponding to the four crystallographic sites in Li₂MnP₂O₇ are resolved. However, in the spectrum of

 $Li_2FeP_2O_7$ the five crystallographic lithium sites are not resolved. Despite this, tentative peak assignments can be made to this spectrum based on Goodenough-Kanamori rules, as previously employed for the assignment of Li resonances in other paramagnetic compounds (and shown for Li₂MnP₂O₇ above).²⁵

Figure 3-2 shows the local environments of Li2, Li3, Li4 and Li5 with Li-O bonds and Li-O-Fe contacts. The transfer of electron spin density from the half-filled t_{2g} orbitals of paramagnetic iron (II) to the empty Li 2s orbital via a delocalization mechanism causes a shift in the Li resonance where the efficiency of this transfer is maximized when the Li-O-Fe orbitals overlap at angles close to 90° or 180°.²⁹ While Li₂FeP₂O₇ contains no Li-O-Fe angles close to 180°, there are angles close to 90°, where this 90° geometric arrangement is expected to give rise to an increase in isotropic shift.¹⁵ Table 3-2 shows the Li-O-Fe contacts, Li-Fe distances and Li-O distances for four lithium sites. From this data it is clear that Li4, with only one Li-O-Fe contact at an angle of 104° would have the lowest chemical shift of any of the lithium sites. Thus we can confidently assign the two partially resolved peaks in the pristine spectrum (Figure 3-3). The blue resonance at -55 ppm corresponds to the Li4 site and the remaining lithium sites give rise to the broad unresolved resonance at 27 ppm.



Figure 3-2. Local environments for Li2, Li3, Li4 and Li5 sites in $Li_2FeP_2O_7$, showing Li-O bonds and Li-O-Fe contacts. Li3 (a) shows distorted square pyramidal geometry, Li5 (b), Li4 (c) ad Li2 (d) show distorted tetrahedral geometry. Only Li-O-Fe contacts with Li-Fe distances less than 3.9 Å are shown.

Table 3-2. Summary of	crystallographic data	for Li ₂ FeP ₂ O ₇ . Li-O-Fe	contacts with Li-Fe
distances less than 3.9	Å are shown.		

Li Site	Li-O-Fe angle (deg)	Distance to Fe (Å)	Li-O distance (Å)
Li2 (green)	97.78 (Li2-O10-Fe2)	3.209	2.115
	112.13 (Li2-O1-Fe2)	3.444	2.034
	100.86 (Li2-O9-Fe1)	3.292	2.113
	95.22 (Li2-O2-Fe1)	3.292	2.251
	91.17 (Li2-O2-Fe2)	3.209	2.251
Li3 (red)	118.03 (Li3-O5-Fe2)	3.455	1.898
	90.12 (Li3-O8-Fe1)	3.150	2.237
	118.33 (Li3-O11-Fe1)	3.814	2.227
	100.93 (Li3-O12-Fe1)	3.150	1.968

Li4 (blue)	104.03 (Li4-O10-Fe2)	3.262	1.944
Li5 (orange)	88.73 (Li5-O11-Fe1)	2.846	1.836
	88.93 (Li5-O8-Fe1)	2.846	1.938
	114.43 (Li5-O5-Fe2)	3.824	2.417



Figure 3-3. (a) ⁷Li MAS NMR spectrum of pristine Li₂FeP₂O₇ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz. The deconvolution shows two main resonances shown in blue and purple. The blue resonance is assigned to Li4 in the crystal structure and the purple resonance is assigned to the remaining Li sites (Li1, Li2, Li3 and Li5).

Figure 3-3 shows the ⁷Li MAS NMR spectrum of pristine Li₂FeP₂O₇. The integrated intensity of the entire spinning sideband manifold of the blue peak at -55 ppm (isotropic) is 24% that of the integrated intensity of the entire spinning sideband manifold of the whole spectrum. This is consistent with the assignment of this peak to the Li4 crystallographic site because this site corresponds to one fourth of the lithium in the crystal structure.

Figure 3-4 shows the NMR spectra of cycled cathodes of Li₂FeP₂O₇ as well as a galvanostatic cycling curve associated with Li₂FeP₂O₇. The green 3.75 V, orange 4.1 V, and blue 2 V spectra follow the cycling curve shown in this figure. However, the 4.6 V red spectrum corresponds to a cycling curve with higher capacity (99 mAh/g as opposed to 68 mAh/g). The effect of the method of synthesis and different ways of carbon-coating on the cell performance will be discussed below. It is clear from both the full MAS spectra as well as the zoom-in on the isotropic region that as the cell is charged the overall signal intensity decreases in the associated spectra. And as the cell is subsequently discharged the signal intensity increases and full recovery of the signal is obtained at full discharge. The blue 2 V spectrum is the same as the black pristine spectrum. This result demonstrates the reversibility of intercalation and stability of this structure. Furthermore, the decrease in signal intensity relative to the intensity of the pristine (i.e. assembled but not cycled) material is approximately equal to the ratio of capacity, shown by galvanostatic cycling, to the overall theoretical capacity of $Li_2FeP_2O_7$, which is 220 mAh/g. For example, the overall integrated intensity of the red 4.6 V spectrum is approximately 60% that of the pristine spectrum, which means that there is a 40% intensity loss in this fully charged spectrum. Accordingly, this cathode exhibited a capacity of 99 mAh/g, which is 45% of the theoretical capacity in $Li_2FeP_2O_7$. Let's take a closer look at what is happening in the spectra of the cycled materials by examining their deconvolutions.



Figure 3-4. (a) ⁷Li MAS NMR spectra of cycled $Li_2FeP_2O_7$ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz. (b) The different states of charge for each spectrum are indicated by colored stars in the galvanostatic cycling curve on the right. The red 4.6 V spectrum is associated with another galvanostatic cycling curve which exhibits higher capacity than the one shown. (c) Zoom in on the isotropic region of the MAS spectra.

Figure 3-5 shows the deconvolutions of the isotropic region of the NMR spectra of cycled cathodes. What is most evident from these spectra is that the blue peak at -55 ppm corresponding to Li4 is completely depleted by full charge. As the intensity of this peak decreases with charge the chemical shift of the peak does not change. This data suggests that the Li4 site is completely gone by full charge, and so Li4 is the most easily extracted/mobile lithium atom within the crystal structure. This is the extent to which can be ascertained in building a model of extraction using this data. Thus the model of extraction shows the complete depletion of Li4 from the structure. Whether the

remaining unaccounted ~20% capacity comes from only one lithium site or a mixture of the other four lithium sites is not certain.

In addition to the depletion of the peak at -55 ppm there are two other trends seen in these spectra. The peak corresponding to Li1, Li2, Li3 and Li5 at 27 ppm shifts to 52 ppm and decreases in width and height, while a new peak is formed at 125 ppm. This new peak increases in intensity with charge. The chemical shift of lithium that remains in the structure upon charging is increased due to the change in oxidation state of iron. Lithium extraction is accompanied by oxidation of d⁶ Fe²⁺ to d⁵ Fe³⁺, as depicted in Figure 3-5 (c). The change in the number of unpaired electrons in the d-orbitals of iron affect the paramagnetic character of iron and thus the chemical shift of neighbouring lithium. Let's shift gears and examine possible diffusion pathways in Li₂FeP₂O₇ to understand why Li4 is preferentially extracted.



Figure 3-5. (a) Deconvoluted ⁷Li MAS NMR spectra of cycled $Li_2FeP_2O_7$ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz. Experimental spectra are shown in black. (b) A model of lithium extraction based on the spectra. (c) The change in oxidation state of Fe upon charging.

Figure 3-6 shows possible diffusion pathways between lithium ions in the two twodimensional channels where lithium atoms reside. The VALMAP program, developed by Gonzalez-Platas et al.,⁴⁰ uses unit cell parameters and atomic coordinates to calculate two-dimensional contour maps of bond valence density within a unit cell. This program deploys the empirical parameters established by Brown et al.^{41,42} The valence of an atom, *i*, is equal to the sum of all bond valences, s_{ij} , for that particular atom, such that: $V_i = \sum s_{ij}$. An individual bond valence, *s*, is given by: $s = (d/d_0)^{-N}$ or $s = \exp[(d_0 - d)/B]$; where d is the bond length and N, B, and d₀ are experimentally determined constants that depend on the nature of the atoms that form the bond. Furthermore, the value of N is a function of electronegativity. Thus high bond valence is correlated with shorter bond lengths and higher valences of the atom of interest.



Figure 3-6. Two-dimensional contour maps of bond valence using the VALMAP program and corresponding Vesta structures showing possible pathways for diffusion between lithium ions. For each valence map the density contour level increment is 0.453. (a) The Li3-Li5 distance is 2.96 Å. (b) The Li3-Li5 distance is 3.19 Å. (c) The Li2-Li4 distance is 3.22 Å. (d) the Li4-Li4 distance is 2.70 Å.

For each valence map in Figure 3-6 there exists one colour scale in which a given color correlates to a given degree of bond valence density. Light blue and turquoise

regions correlate to regions of low bond valence density and are most amenable to ion diffusion, while dark blue, red, orange, and yellow regions correlate to regions of high bond valence density and impede ion diffusion. Accordingly, oxygen atoms impede ion diffusion and their locations in the crystal structure define the window frames for Li ion diffusion. The windows separating Li2-Li4 (Figure 3-6 c) and Li4-Li4 (d) are visibly larger than those separating Li3-Li5 (a and b). Furthermore, the smallest distance between two lithium atoms is 2.70 Å for Li4-Li4. This suggests that Li4 is most amenable to diffusion and explains why the resonance at -55 ppm in the NMR spectra of cycled Li₂FeP₂O₇ is completed depleted by full charge.

3.4 Conclusions

In summary, Li₂FeP₂O₇ exhibits a maximum capacity of 99 mAh/g upon charging to 4.6 V, which is approximately 45% of its theoretical capacity. This capacity is attributed to complete depletion of the Li4 site and partial depletion of lithium in the remaining sites. The Li4 site is assigned to the peak at -55 ppm in the NMR spectra of pristine and charged samples of Li₂FeP₂O₇. This assignment is based on the local environments of each of the lithium atoms; specifically, the type and number of Li-O-Fe interactions, where paramagnetic electron spin density on iron is transferred to lithium through Li-O-Fe interactions. The angle of these interactions determines the efficiency of electron spin density transfer and contributes to the lithium chemical shift. Upon electrochemical charging, the peak at -55 ppm is depleted steadily until there is no intensity here at full charge (4.6 V). The appearance of a new peak at 125 ppm and the shift in the original peak from 27 to 52 ppm is the result of the oxidation of d⁶ Fe²⁺ to d⁵ Fe³⁺, where the increase in the number of unpaired electrons on iron increases its paramagnetic character and thus the chemical shift of interacting lithium atoms. The preferential extraction of lithium from site Li4 can be explained by the small Li4-Li4 distance (2.70 Å) and the large window separating Li4-Li4, as demonstrated by the bond valence density maps using the Valmap program.

3.5 Supplementary Information on Li₂FeP₂O₇: The Effect of the Method of Synthesis on Electrochemical Performance

The method of synthesis of Li₂FeP₂O₇, whether that reported by Nishimura et al.³⁸ or Zhou et al.²⁰, affects the electrochemical performance of the coin cell, as demonstrated in Figure 3-7. The powder X-ray diffraction patterns of each product indicate that Li₂FeP₂O₇ was formed, as verified by comparing to literature diffraction patterns of Li₂FeP₂O₇, in both cases. When synthesizing Li₂FeP₂O₇ using the method described by Zhou et al. the resulting cathode exhibits extremely small capacity (~10 % of that of the Nishimura method) which is due to large over-potential of the coin cell. The large over-potential arises from poor electric and ionic conductivity, which is a known characteristic of the pyrophosphate materials.²⁰ As already established, the poor electric and ionic conductivity of polyanionic materials can be compensated for by carbon coating and nanosizing.²⁰ The reason for the difference in performance between the two methods of

synthesis attempted in this lab is likely due to differences in particle size. The Nishimura method involves more grinding and ball-milling than the other, which likely generates smaller particle sizes.



Figure 3-7. Four cycles of $Li_2FeP_2O_7$ synthesized via the method described by Nishimura et al.³⁸ (blue), and 3 cycles of $Li_2FeP_2O_7$ synthesized via the method described by Zhou et al.²⁰ (red). The capacity in the latter is approximately one tenth of the former. Cycled at a C/50 rate.

Figure 3-8 shows the powder X-ray diffraction patterns of Li₂FeP₂O₇ synthesized via the two aforementioned methods. Both powder patterns match the reference pattern of Li₂FeP₂O₇, suggesting that the desired product was indeed synthesized in both cases. However, there is a peak at 27 ° that is unique to the powder pattern of Li₂FeP₂O₇ synthesized via the 'Zhou' method, which means that this product is not pure. This may contribute to the poor electrochemical performance exhibited by this cathode.



Figure 3-8. Powder X-ray diffraction patterns of $Li_2FeP_2O_7$ synthesized via the method described by Nishimura et al.³⁸ (blue) and via the method described by Zhou et al.²⁰ (red). Also plotted here is a literature reference pattern of $Li_2FeP_2O_7$ synthesized by Clark et al.³⁹

4.0 Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ – NMC

Note: This chapter comes from the work titled: <u>Chemical and structural evolution of</u> <u>stoichiometric layered lithium transition metal oxide cathode upon cycling</u>. This manuscript was submitted to *Physical Chemistry Chemical Physics* on July 28th 2016. Only work completed and written by the writer of this thesis is included. The following authors contributed to the manuscript: Hanshuo Liu, Matthieu Bugnet, Matteo Z. Tessaro, Kristopher J. Harris, Meng Jiang, Gillian R. Goward, and Gianluigi A. Botton.

4.1 Introduction

Since its discovery in 2003, LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ NMC has been characterized extensively both structurally and electrochemically.⁴³ NMC shares the same cubic close packed (R3m) layered structure (Figure 4-1) as its precedent, LCO,⁴⁴ and its capacity exceeds that of LCO (140 mAh/g).⁴⁵ The oxidation states of the metal cations of the pristine material are Ni²⁺, Mn⁴⁺ and Co³⁺. In the study mentioned above, Electron Energy Loss Spectroscopy (EELS) analysis shows that the charge compensation at transition metal sites during delithiation is mainly achieved by oxidation of Ni²⁺ \rightarrow Ni⁴⁺, whereas Mn⁴⁺ and Co³⁺ remain essentially unchanged. Thus 65% of the lithium can be extracted without a change in unit cell volume, giving rise to the 175 mAh/g reversible capacity between 2.5-4.5 V, as demonstrated by the galvanostatic cycling curve in Figure 4-2.

Although the pristine material has been studied by ssNMR, there are no published NMR studies of the cycled material. The electrochemical reaction of transition metals in NMC during the charge-discharge process was analyzed in detail using ⁷Li magic-angle spinning (MAS) NMR. ⁷Li projection magic-angle-turning phase-alternating spinning-sideband, pj-MATPASS, NMR allows for the analysis of the evolution of Li resonances in the transition metal and Li layers, which can be related back to reversible and irreversible structural changes in bulk NMC.



Figure 4-1. Crystal structure of cubic close packed $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$. Oxygen atoms are shown in red, lithium atoms are shown in green, and the transition metals are shown purple, silver and blue.



Figure 4-2. Galvanostatic cycling curve; twelve cycles of NMC; 175 mAh/g reversible capacity. Potential limits are 2.5 V and 4.5 V. Cycled at a C/20 rate.

4.2 Experimental

Electrochemical Measurements

The positive electrode consisted of NMC, carbon black (CB) and polyvinylidene fluoride (PVDF) in an 80:10:10 weight % ratio. NMC and CB were ground together for 30 minutes and dried, then a solution of 3% PVDF (by weight) in N-methyl-2-pyrrolidene (NMP) was added and the resultant slurry was stirred for 2-3 hours. The slurry was cast onto aluminum foil and the NMP was evaporated in an evacuated drying oven at 110 °C for 12 hours. Discs, 1.27 cm in diameter, were punched and coin cells were assembled in an argon atmosphere glove box. The average mass of NMC in each cell was 8 mg. The anode used was lithium metal and the electrolyte was LiPF₆ in ethylene carbonate/dimethyl carbonate.

Coin cells were cycled with Arbin battery testing equipment and MITS Pro software. Cells were cycled galvanostatically between 2.5-4.6 V at rates of C/10 and were held potentiostatically at various voltages until the measured current was less than 5 μ A (i.e. the rate was approximately C/200).

NMR Spectroscopy

All ⁶Li and ⁷Li magic-angle spinning MAS NMR spectra were acquired under a 4.7 T applied magnetic field using a Bruker DRX console. The sample isotopically enriched with ⁶Li was prepared from ⁶LiCO₃, as described previously.⁴⁶ Spectra are referenced to 1 M LiCl_(aq) at 0 ppm. The ⁶Li Hahn-echo NMR spectrum was collected with 46 kHz sample spinning in a specially built probe supporting 1.8 mm rotors, and employed 1.7 µs 90° pulses and 0.5 s recycle delays. All ⁷Li NMR spectra were collected using 1.3 mm rotors at a 60 kHz sample-spinning rate using a Bruker high speed MAS probe. ⁷Li Hahn-echo spectra were collected using 1.1 µs 90° pulses and 50 ms recycle delays. ⁷Li spectra containing only isotropic shifts were generated using the projection magic-angle-turning phase-alternating spinning-sideband, pj-MATPASS, method of separating sidebands into different slices of a 2D spectrum, which were then aligned and summed to yield the presented spectra. ⁷Li pj-MATPASS spectra were collected using slightly more conservative rf power and recycle delay settings (1.5 us $\pi/2$ pulses and 100 ms delays) than the Hahn-echo spectra.

4.3 Results and Discussion

Lithium NMR spectroscopy was used to study NMC at various states of charge (SOCs), since the spectrum is uniquely sensitive to the electronic state of the paramagnetic metals surrounding each lithium ion. The spectra are somewhat complicated to acquire and analyze, so the pristine material is discussed first. Figure 4-3 shows a stack plot of ⁶Li and ⁷Li NMR spectra of pristine NMC. Clearly, sufficient ⁶Li NMR

signal intensity requires isotopic labeling, particularly for the small peak at ~1300 ppm, and this labeling is quite costly for charge-discharge studies which may involve ⁶Li labeled lithium metal or salt. ⁷Li NMR spectroscopy, however, yields high signal intensity from the electrode of a single coin cell, and requires just minutes rather than the *multiple days* required for ⁶Li at natural abundance. It should be noted that overlap of spinning sidebands with isotropic peaks obscures the information content of the ⁷Li spectra, again, particularly in the region near the small peak at ~1300 ppm. ⁷Li MATPASS NMR spectroscopy solves this final issue entirely,²³ and is therefore used here to study NMC as a function of electrochemical cycling.



Figure 4-3. Lithium NMR spectra of pristine NMC using four different methods of collection. The bottom two ⁶Li NMR spectra were collected under 46 kHz MAS; the much higher S/N spectrum of a ⁶Li-enriched sample (in black) is compared to that of a natural abundance sample (in blue). The top two ⁷Li NMR spectra were collected from a natural isotopic abundance sample under 60 kHz MAS; the Hahn-echo spectrum (in green) is compared to that generated using MATPASS (in red), and the dotted line highlights the undesirable overlap of the * sideband with the TM-layer Li sites. These sidebands are suppressed in the red spectrum. Spinning sidebands are indicated with stars. The inset

shows oxygen-mediated interactions between Li and the transition metal ions in the NMC structure.

The inset of Figure 4-3 shows the 1st and 2nd coordination sphere lithium-oxygentransition metal (Li-O-TM) bonding interactions relative to a single lithium atom. There are three 90° and three 180° Li-O-TM bonding interactions above and below each lithium atom, leading to a myriad of possible lithium environments. These possible local environments give rise to different chemical shifts, depending on the combination of transition metals in the coordination spheres of the lithium ions. Table 4-1 lists the contribution of each transition metal to the overall chemical shift, based on the combination of its oxidation state, and its orientation relative to the lithium center. Specifically, lithium in the lithium layer gives rise to the broad peak centered at 500 ppm, though it should be noted that this is a sum of a variety of coordination environments based on the twelve possible metal sites, and three possible transition metals that can occupy those sites. The exchange of Ni²⁺ and Li⁺ results in the presence of Li within the transition metal layer (1300 ppm peak).⁴⁶ Lithium in the transition metal layer is known to be surrounded by either 6 or 5 Mn atoms, which cause the large chemical shift observed for these particular ions.^{29,30}

Table 4-1. Contribution of each transition metal TM ion to the overall ⁷Li chemical shift of NMC type materials.^{29,30}

TM ion	1 st Coordination Shell	2 nd Coordination Shell
	(ppm)	(ppm)
Mn ⁴⁺	255	-52
Ni ²⁺	-25	120
Co ³⁺	0	0
Although the ⁷Li lineshape of the LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ formulation is too broad to assign specific local environments, studies of stoichiometries containing fewer paramagnetic ions have shown line shapes consistent with local ordering. In fact, several authors have proposed that Coulomb-driven local ordering of Mn⁴⁺-Ni²⁺ exists in the transition metal layers, using NMR spectroscopy and EPR spectroscopy^{46–50} and pairdistribution function data.⁴⁷ Below, we will show evidence of such preferential clustering by studying the ⁷Li NMR spectra of the delithiated NMC for the first time.

Figure 4-4 (a) shows MATPASS NMR spectra of NMC on the first cycle, with their corresponding cut-off voltages. Upon charging NMC, Li ions are extracted from both the lithium layers (NMR peaks centered at 500 ppm) and the transition metal layers (~1300 ppm), and by 4.4 V there are no Li ions in the transition metal layer. Li ions remain in the lithium layer at the top of charge (4.6 V) as indicated by the two peaks at 360 and 100 ppm. The observation of two clearly resolved peaks definitively indicates the presence of local ordering in the transition metal layer. The ordering in the charged sample must also have existed in the pristine NMC starting material, as it is highly unlikely that the transition metal ions reorganize themselves substantially during a single charging process.

The charging process produces a constant shift to lower frequency and narrowing of the ⁷Li NMR peaks. While broadening effects coupled with the extremely large number

of local sites prevents a complete peak assignment, this trend is still easily understood. A general description of the broad lithium-layer peak is that the more Mn⁴⁺ and Ni²⁺ present in the Li coordination sphere, the higher the chemical shift of that site. Given that the charging process is Ni²⁺→Ni⁴⁺, as demonstrated by EELS data (see full paper, reference at top of chapter), the removed lithium atoms are those near nickel, i.e., those that resonate at the high-frequency edge of the Li-layer ⁷Li NMR peak. Furthermore, the fact that diamagnetic Ni⁴⁺ does not induce any frequency shift in neighboring Li atoms, in contrast to the large shifts caused by paramagnetic Ni²⁺, leads to a reduced NMR frequency for the remaining Li sites (those not yet removed for charge balance). Crucially, the NMR spectra demonstrate that the sites from which the Li ions are removed are those near Mn atoms, because otherwise NMR peaks from the charged samples would still have high-frequency components from their multiple Mn neighbors. The fact that only low-frequency peaks are observed demonstrates clearly that Mn⁴⁺ and Ni²⁺ are clustered together. We also note that the improved resolution at high states of charge results from the fact that diamagnetic Ni⁴⁺ does not contribute line-broadening like that induced by paramagnetic Ni²⁺. While it is intriguing that the ⁷Li resonance splits into two resolved regions, it is not possible to assign these to specific environments, due to the host of possible transitionmetal distributions. Nevertheless, we can use the arguments above to describe the relatively narrow 100 ppm peak to by Li⁺ surrounded by mostly diamagnetic ions. In contrast, the peak at 360 ppm is broader, and has a higher chemical shift, and is therefore attributed to lithium sites that contain paramagnetic ions in their coordination sphere.

We note that the transverse relaxation rates for the two ⁷Li peaks observed in the 4.6 V sample are not substantially different, both are ca. 100 μ s, as might be expected given that chemical shifts are a localized phenomenon, while relaxation mechanisms can act over longer distances.

When the cell is subsequently discharged to 2.5 V, (Figure 4-4 b) its ⁷Li NMR spectrum matches nearly exactly with that of pristine NMC, which demonstrates that the Li extraction/insertion is reversible. The re-inserted Li ions are clearly in environments that are nearly unchanged from their locations in the starting material, in both the lithium layer and the transition-metal layer. As noted above, conclusions based on the small peak associated with the latter environment are only available via the MATPASS technique that allows its observation. The reversible nature of Li extraction/insertion in NMC is also demonstrated by comparing NMR spectra of NMC at 4.6 V after the first and tenth cycles. As shown in Figure 4-4 (c), the spectra of the aforementioned cathodes have the same line-shape and chemical shifts. This suggests that there is no change in local ordering of the transition metal layer in the bulk sample after multiple cycles.



Figure 4-4. (a) Galvanostatic cycling curve of NMC on the first cycle, where the colored boxes indicate the SOC at which the cathodes were extracted from coin cells and analyzed by NMR. (b) ⁷Li MATPASS NMR spectra of NMC cathode at different SOCs on the first cycle. (c) ⁷Li 60 kHz Hahn Echo MAS NMR spectra of NMC cathode stopped at 4.6 V at the first and the tenth cycle.

4.4 Conclusion

Analysis of ⁷Li NMR spectra reflect a change of paramagnetic Ni²⁺ toward diamagnetic Ni⁴⁺ accompanying delithiation. ⁷Li NMR study of NMC at high voltage resolves distinct environments, definitively proving local ordering of Mn⁴⁺ and Ni²⁺ in the transition-metal layer. The relithiated spectrum of 2.5 V NMC is almost identical to that of pristine NMC, which demonstrates the reversible nature of lithium extraction/insertion in bulk NMC. The structure, including the local Mn⁴⁺/Ni²⁺ ordering, is stable, as reflected

by unchanged ⁷Li spectra collected at 4.6 V after the first and tenth electrochemical cycles. We note that the ⁷Li pj-MATPASS method does not require isotopic labeling and is about two orders of magnitude faster than ⁶Li NMR spectroscopy, demonstrating that NMR studies are possible for an even wider range of cathode materials when using this method.

5.0 L_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂

5.1 Introduction

The original layered transition metal oxide cathode LiCoO₂ and Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂ (NMC) remain two of the most widely used cathodes in LIBs for portable electronic devices. However, with the ever-growing incentive for a shift to electric vehicles in the automotive market, there is a need for low-cobalt and cobalt-free layered oxides due to the high cost of cobalt. Cathodes of Li-Mn-Ni oxide composition show promise as alternatives to cobalt-containing layered oxides. This is in part what motivates the present study on the Li-Mn-Ni series of Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂. This series also offers the chance to systematically study the effect of increasing the degree of lithiation on the electrochemical behavior of the LIB.

Lithium-rich oxides, in which excess lithium is present in transition metal sites, are of particular interest to battery scientists and automotive companies because they exhibit high specific capacity after a first 'activation' charge above 4.6 V. The first lithium-rich oxide material, Li[Ni_xLi_(1/3-2x/3)Mn_(2/3-x/3)]O₂, was reported by Lu et al. in 2002.⁵¹ Since then there has been much debate about the mechanisms which give rise to the extra capacity. At the time of this discovery it was expected that lithium can be removed from the cathode only until the transition metals (i.e. Ni and Mn) reach oxidation states of 4+, but this study showed that lithium could be removed beyond the capacity limit of transition metal oxidation. The surprising boost to capacity was accounted for by an irreversible loss of oxygen during the first charge to 4.8 V.⁵¹ It is now well-established that oxygen loss does occur in these materials.^{52,53} However, lithium-rich oxides also exhibit extra *reversible* capacity beyond the expected limit of transition metal oxidation, which means that irreversible oxygen loss is not the only mechanism responsible for this phenomenon.

Koga et al. suggest that both oxygen loss and reversible oxygen oxidation account for the extra capacity demonstrated by lithium-rich oxides.⁵⁴ They conclude, through their powder X-ray diffraction work on electrochemical samples of Li_{1.20}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂, that irreversible structural reorganization occurs, where two phases are formed on the high voltage plateau and the surface and bulk react differently. The two phases are formed because there is oxygen loss at the surface and subsequent densification of the host structure. As strong evidence for the reversible oxygen redox process, McCalla et al. used transmission electron microscopy and neutron diffraction on Li₂IrO₃, as a model lithium-rich oxide, to show that the O-O dimer distance changes with cycling.¹⁴ Thus, as well as the irreversible oxygen loss, it is established that a reversible oxygen redox process occurs, but more work needs to be done to fully elucidate the mechanisms giving rise to the extra capacity in lithium-rich oxides.

Linking the exploration of both Co-free and lithium-rich oxides, Li et al. published an extensive study on the synthesis and electrochemical performance of the Li-Mn-Ni oxide system with many variations on the ratio of manganese to nickel in the transition metal layer as well as different degrees of lithiation.¹³ The aim of their study was to understand the effect of transition metal composition and lithium content on the electrochemical performance. The current study utilizes NMR spectroscopy to investigate one particular series of the Li-Mn-Ni oxide system, Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂, with the aim of exploring how the evolution of the structure of lithium-rich oxides compares with that of non-lithium-rich oxides.

5.2 Experimental

Synthesis

Please refer to the study by Li et al. for a full description of the synthesis of this series, $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$.¹³ The metal hydroxide precursor $Ni_yMn_{1-y}(OH)_2$ (y = 0.5) was prepared via coprecipitation in a continuously stirred tank reactor. With a 10.0 M NaOH (aq) solution used as the source of base for the reaction, the reaction progressed with the addition of 2.0 M NiSO₄:MnSO₄ in a 1:1 ratio at 0.5 mL/min and 5.0 M NH₃ (aq) at 0.14 mL/min. The NH₃ (aq) solution was used for metal ion coordination to facilitate spherical and dense particle growth during the reaction. The reaction took place for 20 h and the hydroxide precursor was subsequently rinsed and dried.

The precursor was then mechanically ground with a stoichiometric equivalent of Li_2CO_3 . The powder mixtures were sintered in a box furnace at 900 °C for 10 h, with a heating rate of 10 °C/min and a cooling rate of 20 °C/min. Finally, the Li-Mn-Ni-O products were mechanically ground and passed through a 75 µm sieve. All products were characterized by elemental analysis and powder X-ray diffraction.

Electrochemical Measurements

The positive electrode consisted of Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ or Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ as active material (AM), carbon black (CB) and polyvinylidene fluoride (PVDF) in an 80:10:10 weight % ratio. AM and CB were ground together for 30 minutes and dried, then a solution of 3% PVDF (by weight) in N-methyl-2-pyrrolidene (NMP) was added and the resultant slurry was stirred for 2-3 hours. The slurry was cast onto aluminum foil and the NMP was evaporated in an evacuated drying oven at 110 °C for 12 hours. Discs, 1.27 cm in diameter, were punched and coin cells were assembled in an argon atmosphere glove box. The average mass of AM in each cell was about 10 mg. The anode used was lithium metal and the electrolyte was LiPF₆ in ethylene carbonate/dimethyl carbonate.

Coin cells were cycled with Arbin battery testing equipment and MITS Pro software. Cells were cycled galvanostatically between 2.5-4.8 V and 2.5-4.4 V at rates of C/80 and were held potentiostatically at various voltages until the measured current was less than 5 μ A (i.e. the rate was approximately C/200).

NMR Spectroscopy

All ⁷Li NMR spectra were collected using 1.3 mm rotors at a 60 kHz samplespinning rate using a Bruker high speed MAS probe, and under a 4.7 T applied magnetic field using a Bruker DRX console. Spectra are referenced to 1 M LiCl _(aq) at 0 ppm. ⁷Li spectra containing only isotropic shifts were generated using the projection magic-angleturning phase-alternating spinning-sideband, pj-MATPASS,⁵⁵ method of separating sidebands into different slices of a 2D spectrum. ⁷Li pj-MATPASS spectra were collected using 1.5 μ s $\pi/2$ pulses and 100 ms recycle delays.

5.3 Results and Discussion

Electrochemical Results

Figure 5-1 shows the galvanostatic cycling curves and NMR spectra of samples along the composition series $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ (0.00 $\leq x \leq$ 0.20). The cells were first tested between 2.5 – 4.4 V for four cycles, then charged to 4.8 V for one cycle and followed by cycling between 2.5 – 4.6 V. Cycling between 2.5 – 4.4 V captures the reversible nickel redox process only (i.e. Ni²⁻³⁺/Ni⁴⁺), whereas cycling to 4.8 V involves an additional redox process which begins around 4.5 V. As the content of lithium is increased along this composition series two clear trends in the electrochemical cycling are observed: 1) the reversible capacity due to the nickel redox process between 2.5 – 4.4 V decreases and 2) the irreversible capacity due to the second redox event increases. The highest reversible capacity when cycling between 2.5 – 4.4 V is exhibited by $Li_{1.04}Ni_{0.48}Mn_{0.48}O_2$ and the highest total irreversible capacity is exhibited by $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$.



Figure 5-1. Samples along the composition series $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ (0.00 $\le x \le 0.20$). The voltage curves for the aforementioned samples from the paper by Li et al.¹³ The cells were first tested between 2.5 – 4.4 V for four cycles, then charged to 4.8 V for one cycle and followed by cycling between 2.5 – 4.6 V.

These observed trends are well accounted for. The decrease in reversible redox capacity between 2.5 - 4.4 V with increasing lithium content is due to the increase in oxidation state of nickel in the pristine materials with increasing lithium content. In order to achieve charge balance with increasing lithium content the oxidation state of nickel must increase. As a result, the average oxidation state of nickel in LiNi_{0.5}Mn_{0.5}O₂ is +2, whereas in Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ the average oxidation state of nickel is +3. Theoretically, the Ni²⁺/Ni⁴⁺ redox process in LiNi_{0.5}Mn_{0.5}O₂ involves the transfer of two electrons, whereas the Ni³⁺/Ni⁴⁺ redox process in Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ involves the transfer of only one electron.

The extra capacity exhibited by lithium-rich cathodes is of great interest to Li-ionbattery researchers due to both the promise of higher capacity cathodes and the uncertainty surrounding the understanding of the second redox process. Thus electrochemical samples of Li_{1.2}Ni_{0.4}Mn_{0.4}O₂, which shows the highest capacity due to this second redox process amongst this series of cathodes, are examined using NMR spectroscopy. However, prior to examining the spectra of cycled cathodes of lithium-rich Li_{1.2}Ni_{0.4}Mn_{0.4}O₂, it is important to discuss the nature of ⁷Li spectra of paramagnetic cathode materials and to become familiar with the properties of the spectra of the pristine series.

NMR Results and Discussion

Lithium NMR spectroscopy is sensitive to the interactions between paramagnetic transition metals and lithium nuclei. Unique combinations of surrounding transition metals give rise to unique chemical shifts in a spectrum. Consequently, NMR gives detailed structural information about transition metal arrangements around lithium nuclei and relative populations of those lithium environments. However, the multitude of different chemical environments and the magnitude of paramagnetic chemical shifts in these layered oxide materials gives rise to very broad spectrum with large spectral widths. State-of-the-art MAS and a clever pulse sequence are therefore required to collect useful spectra.

It can be seen in Figure 5-2 (a) (blue spectrum) that spinning sidebands in a simple solid-state ⁷Li 1D MAS Hahn-echo experiment overlap with isotropic peaks, obscuring the information contained in a spectrum. This obstruction is most notable in the region of

~1100 – 1500 ppm of these layered oxide materials. To eliminate such overlap, ⁷Li MATPASS NMR spectroscopy eliminates spinning sidebands (Figure 5-2 (a) – black spectrum),⁵⁵ and so the full isotropic region can be observed. It is therefore used herein to study pristine and cycled cathode samples.



Figure 5-2. ⁷Li spectra of Li_{1.2}Mn_{0.4}Ni_{0.4}O₂ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz. (a) The blue spectrum on the left is a 1D Hahn-echo experiment where spinning sidebands (blue stars) are located at the spinning speed away from the isotropic peaks (black stars). The black spectrum is a projection-MATPASS spectrum, in which spinning sidebands are completely eliminated. (b) The spectrum on the right is a deconvolution of the MATPASS spectrum, in which three types of Li environments are shown: Li in the transition metal layer (blue), which would otherwise be overlapped by spinning sidebands; Li in the Li-layer (green); and diamagnetic Li (red). The inset shows a single Li environment in a generic layered transition metal oxide cathode.

Figure 5-3 shows the ⁷Li MATPASS NMR spectra of pristine samples from the

aforementioned series. We will now discuss the assignment of peaks within these spectra. As seen in the spectra of Figure 5-2 (b) and Figure 5-3, there are three main types of lithium environments: diamagnetic lithium from starting material at 0 ppm and, in electrochemical samples, electrolyte also at 0 ppm; lithium in the lithium layer of cathodes in the approximate range of 100 – 1100 ppm; and lithium in the transition metal layer in the approximate range of 1100 – 1500 ppm. The chemical shift of each lithium environment is the result of a sum of all lithium-oxygen-transition metal (Li-O-TM) bonding interactions within the first and second coordination sphere, where each transition metal contributes a specific chemical shift depending on its orientation relative to lithium (see Table 5-1). The inset of Figure 5-2 shows the environment of a lithium atom in the lithium layer, where there are three 90° and three 180° Li-O-TM interactions above and below each lithium atom, leading to a multitude of possible lithium environments. When lithium is in the transition metal layer, however, there are six 90° Li-O-TM interactions due to the hexagon of transition metals surrounding each lithium in this layer. Let's now take a look at some specific lithium environments.



Figure 5-3. Samples along the composition series $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ (0.00 $\le x \le 0.20$). ⁷Li MATPASS spectra of pristine samples with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz.

TM ion	1 st Coordination Shell	2 nd Coordination Shell
	(ppm)	(ppm)
Mn^{4+}	255	-52
Ni ²⁺	-25	120
Co ³⁺	0	0

Table 5-1. Contribution of each transition metal TM ion to the overall ⁷Li chemical shift of NMC type materials.^{29,30}

The easiest resonance to assign in these spectra to a specific environment is lithium in the transition metal layer surrounded by six manganese (i.e. six 90° Li-O-Mn bonding interactions), which correlates with the 'honeycomb' structure of Li₂MnO₃ and gives a chemical shift of ~1415 ppm.⁵⁶ A comparison of the NMR spectra of Li₂MnO₃ and LiNi_{0.5}Mn_{0.5}O₂ is shown in Figure 5-4. The next highest chemical shift of ~1235 ppm corresponds to lithium in the transition metal layer surrounded by five manganese and one nickel. It is clear from Figure 5-3 that the intensity of this peak changes across the series.



Figure 5-4. ⁷Li MATPASS spectra of LiNi_{0.5}Mn_{0.5}O₂ and Li₂MnO₃ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz, showing that local 'honeycomb' ordering exists in the Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂ series.

As lithium content (x) is increased across the series $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$, the most notable trend that occurs in the spectra of Figure 5-3 is an increase in intensity in the peak at ~1235 ppm, which corresponds to lithium in the transition metal layer surrounded by five manganese and one nickel. Also the peak at ~530 ppm increases in intensity, which is lithium in the lithium layer. In the parent structure, $LiNi_{0.5}Mn_{0.5}O_2$, the predominant peaks are at ~1415 ppm and ~700 ppm, which are lithium in the transition metal layer and lithium in the lithium layer, respectively, and both correspond to the honeycomb structure, as demonstrated in Figure 5-4. At the other extreme (x = 0.2) of the series, in the spectrum of Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ there are four predominant peaks at 1415 ppm, 1235 ppm, 700 ppm, and 530 ppm. The simultaneous increase in intensity of the peaks at 1235 ppm and 530 ppm suggests that these lithium environments are correlated analogously to the peaks at 1415 and 700 ppm; such that the peak at 1415 ppm corresponds to lithium in the transition metal layer surrounded by five manganese and one nickel and the peak at 700 ppm is lithium in the lithium layer above/below this environment. It is beyond the scope of this paper to provide full assignment and full deconvolution of these NMR spectra and it is also important to note that all of these peaks correspond to a distribution of lithium environments. Our tentative assignment is enough to allow us to gather information about how the cathode changes as a function of charge. Next we will take a look at NMR spectra of cycled Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ samples.

NMR of Cycled Cathodes

Figure 5-5 shows the ⁷Li MATPASS NMR spectra of charged samples of Li_{1.2}Ni_{0.4}Mn_{0.4}O₂. As the sample is charged there is a decrease in intensity in both regions of the spectra: lithium in the lithium layer and lithium in the transition metal layer. Until about 4.4 V, which is approaching the voltage limit for the complete oxidation of Ni³⁺ to Ni⁴⁺, the depopulation of every lithium resonance is non-selective and there is still some remaining signal intensity from lithium in the transition metal layer. However, subsequent charging to higher voltages leads to the complete depletion of lithium in the lithium layer, and there is only one peak, centered around 450 ppm, remaining in the 4.8 V spectrum. It is crucial to see how the spectrum of Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ in its fully lithiated state is affected by charging based on the first redox process and the second redox process. For this information we will look at the spectra of discharged species after being charged to 4.4 V and after being charged to 4.8 V.



Figure 5-5. ⁷Li MATPASS NMR spectra of charged Li_{1.2}Mn_{0.4}Ni_{0.4}O₂ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz. The different states of charge for each spectrum are indicated by colored stars in the galvanostatic cycling curve on the right.

Figure 5-6 shows the spectra of 2.5 V samples of $Li_{1.2}Ni_{0.5}Mn_{0.5}O_2$ after being charged to 4.4 V for one cycle and for two cycles. In comparing these spectra to the spectrum of the pristine sample it is clear that there is no change to the position of the peaks and negligible change to the intensity of the peaks. This suggests that the structure of the cathode is not affected by reversible cycling between 2.5 - 4.4 V, which, as mentioned above, is due to the redox process of Ni³⁺/Ni⁴⁺/Ni³⁺. In contrast, the spectra of samples that have been cycled between 2.5 - 4.8 V (in Figure 5-7), show depletion of lithium in the lithium layer and transition metal layer and this depletion grows from the first cycle to the second cycle. Although there is depletion in signal intensity, the peak positions remain relatively constant as compared to the pristine spectrum. This suggests that the initial structure is kept where lithium is re-inserted. However, the partial repopulation of these peaks suggests that there are permanent structural changes to the cathode, and in such areas lithium is not able to re-intercalate.



Figure 5-6. ⁷Li MATPASS NMR spectra of discharged Li_{1.2}Mn_{0.4}Ni_{0.4}O₂ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz. The different states of charge for each spectrum are indicated by colored stars in the galvanostatic cycling curve on the right.



Figure 5-7. ⁷Li MATPASS spectra of discharged Li_{1.2}Mn_{0.4}Ni_{0.4}O₂ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz. The different states of charge for each spectrum are indicated by colored stars in the galvanostatic cycling curve on the right.

The non-lithium-rich cathode, Li_{1.04}Mn_{0.48}Ni_{0.48}, is now examined in order to compare the above work on the lithium-rich sample of Li_{1.2}Mn_{0.4}Ni_{0.4}O₂ to a sample which does not exhibit an oxygen related redox process. The published electrochemical result of Li_{1.04}Mn_{0.48}Ni_{0.48}O₂ from Li et al. shows almost complete reversible capacity (see the yellow curve shown in Figure 5-8) even up to 4.8 V charging, and more importantly does not exhibit the oxygen-loss region during charge. Based on these published results it is expected that there would be no or very little difference in the NMR spectrum of a pristine sample of Li_{1.04}Mn_{0.48}Ni_{0.48}O₂ and the NMR spectrum of a sample that has been charged to 4.8 V and subsequently discharged to 2.5 V. However, as can be seen in the spectra of Figure 5-8, this predicted result does not occur.

Figure 5-8 shows the spectra of pristine $Li_{1.04}Mn_{0.48}Ni_{0.48}O_2$ (black), charged to 4.8 V (red), and discharged to 2.5 V from 4.8 V (blue). Clearly the lithium signal intensity is not fully recovered in the discharged spectrum, as would be expected based on the cycling of $Li_{1.04}Mn_{0.48}Ni_{0.48}O_2$ shown by Li et al., suggesting that an irreversible structural change did occur. Surprisingly, in the charge curve of $Li_{1.04}Mn_{0.48}Ni_{0.48}O_2$ there is about 60% excess irreversible capacity as compared to the literature cycling curve. There is a second redox event occurring within the 4.4 - 4.8 V region like in the lithium-rich material, which is accounting for the irreversible capacity loss after the first cycle and also the irreversible structural change seen in the NMR spectra. The shape of the cycling curve up to 4.4 V looks very similar in the two galvanostatic curves, but the second redox event is unique to the work presented here.



Figure 5-8. ⁷Li MATPASS spectra of charged and discharged Li_{1.04}Mn_{0.48}Ni_{0.48}O₂ with a spinning speed of 60 kHz and a Larmor frequency of 77.66 MHz. The different states of charge for each spectrum are indicated by colored stars in the galvanostatic cycling curve

of $Li_{1.04}Mn_{0.48}Ni_{0.48}O_2$ on the bottom right. The already published galvanostatic cycling from Li et al. is shown on the same x-scale above in yellow.¹³

Whether this extra 60 mAh/g capacity is due to an oxygen redox event or not can only be speculated for the time being. It is not unreasonable to suggest that this extra capacity is due to oxygen-loss, considering the voltage range at which this plateau exists and that the theoretical capacity of Li_{1.04}Mn_{0.48}Ni_{0.48}O₂ is 297 mAh/g based on the available lithium in the structure. However, further efforts need to be taken to replicate the cycling shown by Li et al. to see whether, when the cycling behaves as expected, there are indeed no structural changes to layered oxides that do not exhibit the oxygen-loss region during charging.

5.4 Conclusions

The cobalt-free Li-Ni-Mn oxide series, Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂, which was previously extensively studied electrochemically has been investigated using solid-state NMR spectroscopy. The MATPASS pulse sequence eliminates spinning sidebands in solid-state ⁷Li MAS spectra. This allows for the full isotropic region of the spectra to be observed, whereas previously the transition metal layer would be overlapped by spinning sidebands in ⁷Li NMR spectra of layered oxide materials. As seen in the NMR spectra of the pristine materials, the total amount of lithium in the transition metal layer and the lithium layer increases with increasing lithium content. There are four main resonances in the pristine spectra: at 1415 ppm, 1235 ppm, 700 ppm, and 530 ppm. These resonances have been

assigned to specific lithium environments in the transition metal layer and lithium layer. The intensity of the peaks at 1235 and 530 ppm increase as lithium content is increased across the series.

Cycling beyond the oxygen-loss region of lithium-rich oxides gives rise to irreversible structural changes as seen in the spectrum of Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ that has been discharged to 2.5 V after being charged to 4.8 V. Oxygen-loss changes structure. The NMR spectra of pristine Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ and that of the discharged 2.5 V from 4.4 V are the same, which means that cycling within the potential range due solely to nickel redox (2.5-4.4 V) has no effect on the structure. It is predicted that an oxide material that does not exhibit the oxygen-loss plateau region upon charging to higher voltages, like Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ in this series, would not give rise changes in its NMR spectra upon cycling to high voltages (4.8 V). Unexpectedly, the cycling of Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ exhibits 60 mAh/g of extra unexpected capacity above 4.5 V, which may be due to oxygen loss. This gives rise to the difference in spectra between the pristine material and that of Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ discharged to 2.5 V after being charged to 4.8 V. Further efforts need to be taken to obtain cycling like that reported in the literature.

6.0 Conclusions and Future Work

Fast MAS and pj-MATPASS has facilitated the use of ⁷Li NMR in place of ⁶Li, drastically increasing the signal to noise of the obtained spectra of layered oxide and polyanionic cathode materials and reducing the experiment time. This has enabled the systematic *ex-situ* study of electrochemical samples of cathode materials for LIBs.

NMC

⁷Li pj-MATPASS NMR gives the full isotropic region of NMC without spinning sidebands. ⁷Li NMR spectra of cycled NMC reflect a change of paramagnetic Ni²⁺ toward diamagnetic Ni⁴⁺ accompanying delithiation. Spectra of NMC at high voltage shows distinct environments, proving local ordering of Mn⁴⁺ and Ni²⁺ in the transition-metal layer. The relithiated spectrum of 2.5 V NMC is almost identical to that of pristine NMC, which demonstrates the reversible nature of lithium extraction/insertion in bulk NMC. The structure, including the local Mn⁴⁺/Ni²⁺ ordering, is stable, as reflected by unchanged ⁷Li spectra collected at 4.6 V after the first and tenth electrochemical cycles.

In some of our more recent work, the full spectrum of pristine NMC has been assigned using Monte Carlo simulations.⁵⁷ In the simulated spectrum there are many environments that overlap to give rise to the broad peak, spanning ~1000 ppm, in the experimental spectrum. This work can be extended to spectra of cycled samples. In order to more fully understand the process of lithium extraction from NMC it would be very beneficial to know what the structure is as a function of cycling. Preliminary work has

been done to incorporate a model of lithium extraction into these Monte Carlo simulations. This involved effectively changing the oxidation of Ni²⁺ to Ni⁴⁺ by removing any shift contribution from nickel and seeing how the simulated spectrum changed. Future work involves building a more complete model of lithium extraction, involving not only nickel oxidation but also localized lithium removal. Comparing simulated spectra to already obtained experimental spectra of cycled cathodes acts as a positive feedback loop, whereby the model of extraction can be verified by how well the simulated spectrum matches the experimental spectrum.

$Li_{1+x}(Ni_{0.5}Mn_{0.5})O_2$

The Li-Ni-Mn oxide series, Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O₂, has been investigated using the pj-MATPASS NMR technique. The spectra of the pristine materials show that the total amount of lithium in the transition metal layer and the lithium layer increases with increasing lithium content. Groups of resolved resonances in the pristine spectra have been assigned to lithium environments in the transition metal layer and lithium layer.

Cycling beyond the oxygen-loss region of lithium-rich oxides gives rise to irreversible structural changes as seen in the spectrum of Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ that has been discharged to 2.5 V after being charged to 4.8 V. Oxygen-loss changes structure. The NMR spectra of pristine Li_{1.2}Ni_{0.4}Mn_{0.4}O₂ and that of the discharged 2.5 V from 4.4 V are the same, which means that cycling within the potential range due solely to nickel redox (2.5-4.4 V) has no effect on the structure.

It is predicted that an oxide material that does not exhibit the oxygen-loss plateau region upon charging to higher voltages, like Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ in this series, would not give rise to changes in its NMR spectra upon cycling to high voltages (4.8 V). Unexpectedly, the cycling of Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ exhibits 60 mAh/g of extra unexpected capacity above 4.5 V, which may be due to oxygen loss. This gives rise to the difference in spectra between the pristine material and that of Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ discharged to 2.5 V after being charged to 4.8 V.

Future work in this project first involves working towards obtaining electrochemical cycling of Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ that matches cycling seen by Jing Li et al.,¹³ without the 60 mAh/g of extra capacity. In order to improve cycling performance in coin cells, cathode sheets should be calendered using high pressure to improve contact between the cathode and current collector (aluminum foil). The incentive for calendering is to reduce the observed over-potential often seen in coin cells cycled at high currents in this lab. Cycling at slow rates diminishes this over-potential but increases experiment time. As another option, using industrial style pouch cells would certainly lead to better and more consistent cycling and would provide larger amounts of sample to be analyzed. As electrochemical cycling is improved and the capacity of Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ matches that seen in the literature without, what appears to be, the second, oxygen-loss, redox process occurring then NMR spectra of cycled samples of Li_{1.04}Ni_{0.48}Mn_{0.48}O₂ should be collected.

As with the NMC sample, in the spectra of this series of materials, groups of resonances have been assigned to different types of lithium environments and the most prominent peaks in the spectra have been assigned to specific resonances. However, despite these efforts to make assignments to the spectra, the full spectra cannot be assigned without simulating the structure and analyzing the simulated spectrum's corresponding spectrum. Work on building a 3D model, incorporating both the lithium and transition metal layers into the structure of these layered oxides is being done, starting with the parent LiNi_{0.5}Mn_{0.5}O₂ material. Future work involves improving this 3D model so that the full spectra of this series of materials, and more broadly speaking all layered oxide materials, can be assigned to specific environments. This can also be extended to electrochemical samples in order to help build a model of extraction in Lirich cathodes. This work could prove to be invaluable to understanding the oxygen-loss and reversible oxygen redox processes seen in Li-rich layered oxides.

Pyrophosphates

⁶Li MAS (25 kHz) NMR spectroscopy has been implemented on the pristine pyrophosphate series $Li_2Mn_{1-y}Fe_yP_2O_7$ and, with the implementation of a probe housing 1.3 mmm rotors, ⁷Li MAS (60 kHz) NMR has been implemented on cycled samples of $Li_2FeP_2O_7$. All four Li sites in the crystal structure of $Li_2MnP_2O_7$ have been assigned to specific resonances in its spectrum based on Goodenough-Kanamori rules. As the iron content increases across the series $Li_2Mn_{1-y}Fe_yP_2O_7$ the resonances broaden such that the

peaks become unresolvable. The pure iron analog Li₂FeP₂O₇ shows the best electrochemical performance.

 $Li_2FeP_2O_7$ exhibits a maximum capacity of 99 mAh/g upon charging to 4.6 V, which is approximately 45% of its theoretical capacity. This capacity is attributed to complete depletion of the Li4 site and partial depletion of lithium in the remaining sites. The Li4 site is assigned to the peak at -55 ppm in the NMR spectra of pristine and charged samples of Li₂FeP₂O₇. This assignment is based on the local environments of each of the lithium atoms; specifically, the type and number of Li-O-Fe interactions, where paramagnetic electron spin density on iron is transferred to lithium through Li-O-Fe interactions. The angle of these interactions determines the efficiency of electron spin density transfer and contributes to the lithium chemical shift. Upon electrochemical charging, the peak at -55ppm is depleted steadily until there is no intensity here at full charge (4.6 V). The appearance of a new peak at 125 ppm and the shift in the original peak from 27 to 52 ppm is the result of the oxidation of d⁶ Fe²⁺ to d⁵ Fe³⁺, where the increase in the number of unpaired electrons on iron increases its paramagnetic character and thus the chemical shift of interacting lithium atoms. The preferential extraction of lithium from site Li4 can be explained by the small Li4-Li4 distance (2.70 Å) and the large window separating Li4-Li4, as demonstrated by the bond valence density maps using the Valmap program.

Future work with Li₂FeP₂O₇ involves simulating its NMR spectrum in order to make more confident assignment of the partially resolved peak at -55 ppm. This work would

require further training and expertise from a different research group that specializes in DFT calculations. The 3D framework and non-ideal Li-O-TM bond angles of these pyrophosphates is much more complicated than the 2D sheets in layered oxide materials, so simulations will be more involved.

The bond valence density maps of lithium environments in Li₂FeP₂O₇ presented here give more of a qualitative picture of lithium diffusion windows. Another possibility for future work involves more stringently assessing the diffusion pathways of the different lithium sites by extracting quantitative information from the Valmap program. For instance, the size of the diffusion windows for each lithium atom can be obtained.

Lastly, in order to improve upon the existing performance of the $Li_2FeP_2O_7$ cathode it is necessary to explore alternative electrolytes that are stable at high voltages. The Fe^{3+}/Fe^{4+} redox process occurs around 5 V,²⁰ so electrolytes stable above 5 V will allow for the extraction of all of the lithium from $Li_2FeP_2O_7$, which would drastically improve the electrochemical performance of $Li_2FeP_2O_7$.

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