NMR STUDIES OF CATHODE MATERIALS FOR LITHIUM ION BATTERIES
MULTINUCLEAR NMR STUDIES OF ION MOBILITY PATHWAYS IN CATHODE MATERIALS FOR LITHIUM ION BATTERIES

BY

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ABSTRACT

This thesis investigates the structure and ion mobility properties within the phosphate and fluorophosphate family of cathode materials for Li ion batteries using solid-state NMR. Developments in lithium ion battery technology are now directed towards automotive applications meaning that many of the cost and safety issues associated with current lithium ion battery technology need to be addressed. Within the current systems the high cost is largely attributed to the use of LiCoO₂ as the positive electrode. Many new and inexpensive Li intercalation materials have been put forward as alternatives to LiCoO₂, however the details concerning the structural and ion-transport properties of these new phases are not well defined. ⁶,⁷Li, ³¹P, and ¹⁹F NMR measurements are an ideal tool to study these properties, as ⁶,⁷Li is able to probe the local environment and dynamics of the mobile ion while ³¹P and ¹⁹F monitor changes in the host framework. Materials selected for study in this thesis include olivine LiFePO₄, monoclinic Li₃M₂(PO₄)₃ (M = V, Fe), the tavorite-based Li₂VPO₄F and Li₂VOPO₄, and the novel layered Li₅V(PO₄)₂F₂. The fluorophosphates have been introduced as higher voltage cathode materials for lithium batteries, however our ⁶,⁷Li 1D selective inversion and 2D EXSY measurements reveal timescales of ion hopping that are relatively slow when compared to those measured in the phosphates. This indicates that the improved power output from the voltage gains may be lost to slow charge/discharge rates.
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This manuscript is dedicated to my parents, Reid and Thea.
Table of Contents

ABSTRACT ................................................................................... iii
Acknowledgements ....................................................................... iv
Table of Contents ......................................................................... v
List of Tables ................................................................................. ix
List of Figures ................................................................................ xi
List of Abbreviations and Symbols ................................................... xix

Chapter 1: Introduction to Cathode Materials for Li Ion Batteries........ 1
1.1 Thesis Layout ........................................................................... 1
1.2 Motivation for Using Li ion Batteries ......................................... 2
1.3 Description of a Li Ion Battery .................................................. 4
1.4 Layered LiCoO₃ and Spinel LiMn₂O₄ ............................................ 7
1.5 Materials Studied in this Thesis ................................................ 9
  1.5.1 LiFePO₄ ........................................................................... 12
  1.5.2 Monoclinic Li₃M₂(PO₄)₃ (M = V, Fe) .................................. 14
  1.5.3 Li₃VPO₄F (1 ≤ x ≤ 2) ........................................................ 17
  1.5.4 LiₓVOPO₄ (1 ≤ x ≤ 2) ........................................................ 20
  1.5.5 Li₃V(PO₄)₂F₂ ................................................................. 21
1.6 Summary .................................................................................. 23
1.7 References ................................................................................ 25

Chapter 2: Introduction to Solid-State NMR .................................... 31
2.1 Introduction .............................................................................. 31
2.2 Spin Properties of Nuclei in an Applied Magnetic Field .............. 31
  2.2.1 Definition of Nuclear Spin and Magnetic Moment ................. 31
  2.2.2 Zeeman Splitting in an Applied Magnetic Field ..................... 32
  2.1.1 Precession and Larmor Frequency ...................................... 34
  2.2.3 The RF Pulse .................................................................. 35
2.3 Spin Properties of Unpaired Electrons in an Applied Magnetic Field 36
2.4 NMR of Solid-state Paramagnetic Materials ............................. 38
  2.4.1 Chemical Shielding and Anisotropy .................................. 39
  2.4.2 Dipolar coupling ................................................................ 43
  2.4.3 Quadrupole Coupling ....................................................... 47
2.5 Isotropic Shifts in Paramagnetic Materials ................................ 48
  2.5.1 The Contact Shift: Defining the Fermi-Contact Term, A_F ........ 49
  2.5.2 The Pseudo-Contact Shift: Defining A_D and A_L .................. 52
Chapter 3: Introduction to Solid-State NMR Techniques Used in This Thesis...59
3.1 Introduction .................................................................59
3.2 REDOR Measurements ..................................................60
  3.2.1 Introduction & Motivation ...........................................60
  3.2.2 6Li{19F} and 6Li{31P} REDOR Experiments ......................60
  3.2.3 Simulations Using SIMPSON .......................................63
  3.2.4 REDOR Measurements of Paramagnetic Materials .............63
  3.2.5 REDOR for Studying Ion Dynamics ................................64
3.3 6,7Li MAS Two Dimensional Exchange Spectroscopy ...............65
  3.3.1 Introduction & Motivation ...........................................65
  3.3.2 2D NMR Measurements .............................................65
  3.3.3 2D NMR to Study Chemical Exchange ............................66
  3.3.4 Quantification of Ion-Hopping Timescales using 2D EXSY .....69
3.4 6,7Li One-Dimensional Selective Inversion Measurements ..........70
  3.4.1 Introduction & Motivation ...........................................70
  3.4.2 One-Dimensional Selective Inversion Experiments .............71
  3.4.3 CIFIT ......................................................................74
  3.4.4 Experimental Methods For Selective Inversion ..................76
    3.4.4.1 6Li 1D EXSY .......................................................77
    3.4.4.2 Selective Inversion Using Shaped Pulse ......................78
3.5 Summary .....................................................................79
3.6 References ....................................................................81

Chapter 4: Solid-State NMR Studies of the Olivine Family of Phosphate Cathode Materials .........................................................84
4.1 Introduction .....................................................................84
4.2 Experimental.................................................................85
  4.2.1 Sample Preparation .....................................................85
  4.2.2 Solid-State NMR ..........................................................86
4.3 Results and Discussion .....................................................88
  4.3.1 7Li and 31P MAS NMR of LiMnPO4 and LiFePO4. ..............88
  4.3.2 Studying Li Dynamics in the Olivine Phases .....................91
  4.3.3 Phase Transformation in Li_4FePO_4 (x = 0.5) ....................97
    4.3.3.1 XRD of 0.5LiFePO_4:0.5FePO_4 .............................98
    4.3.3.2 31P MAS NMR of 0.5LiFePO_4:0.5FePO_4 .................99
    4.3.3.3 In-Situ 31P NMR Study of the Thermally Driven Solid Solution in Li_10.5FePO_4 .........................102
  4.3.4 7Li MAS NMR Investigation of Phase Boundary Regions in Nanoparticles 106
Chapter 5: Quantification of Li Ion Mobility in $\alpha$–Li$_3$Fe$_2$(PO$_4$)$_3$ using Variable Temperature $^6$Li 2D EXSY Measurements

5.1 Introduction .................................................................................................................. 119
5.2 Experimental ................................................................................................................. 121
5.2.1 Sample Preparation ................................................................................................. 121
5.2.2 Solid-State NMR .................................................................................................... 122
5.2.3 Electrochemical Measurements ............................................................................. 122
5.2.4 Bond Valence Density Maps .................................................................................. 123
5.3 Results and Discussion ............................................................................................... 124
5.3.1 $^6$Li 2D EXSY Study of Li$_3$Fe$_2$(PO$_4$)$_3$ ............................................................. 124
5.3.1.1 $^6$Li MAS NMR and Site Assignment of Li$_3$Fe$_2$(PO$_4$)$_3$ ............................ 125
5.3.1.2 $^6$Li 2D EXSY Over a Variable Temperature Range ......................................... 127
5.3.1.3 Correlating $E_a$ to Structural Constraints in Li$_3$Fe$_2$(PO$_4$)$_3$ ....................... 133
5.3.2 $^6$Li MAS Study of Electrochemically Cycled Li$_3$V$_2$(PO$_4$)$_3$ ....................... 137
5.4 Summary and Outlook ............................................................................................... 141
5.5 References .................................................................................................................. 143

Chapter 6: Structural Features and Li Ion Hopping Timescales in Li$_3$VPO$_4$F from $^6$Li MAS Measurements

6.1 Introduction .................................................................................................................. 146
6.2 Experimental ................................................................................................................. 149
6.2.1 Sample Preparation ................................................................................................. 149
6.2.2 Solid State NMR .................................................................................................... 149
6.2.3 1D EXSY Data Analysis ......................................................................................... 151
6.2.4 Bond Valence Density Maps .................................................................................. 152
6.3 Results and Discussion ............................................................................................... 153
6.3.1 $^6$Li MAS NMR of Li$_x$VPO$_4$F (1 $\leq$ x $\leq$ 2) ......................................................... 153
6.3.2 $^6$Li 2D EXSY Measurements of Li$_2$VPO$_4$F ......................................................... 156
6.3.3 Site Assignment of Li$_2$VPO$_4$F ............................................................................. 157
6.3.3.1 Site Assignment Based on the Fermi-Contact Interaction ................................ 157
6.3.3.2 Site Assignment in Li$_2$VPO$_4$F from $^6$Li{$^19$F} REDOR NMR ....................... 159
6.3.3.3 Site Assignment Using $^7$Li Sideband Manifolds of 0.5LiVPO$_4$F:0.5Li$_2$VPO$_4$F ......................................................................................................................... 160
6.3.4 Quantification of Ion Dynamics in Li$_2$VPO$_4$F Using $^6$Li 1D EXSY ............... 162
6.3.5 Correlating the Timescales of Exchange to Structural Constraints ................... 167
6.4 Conclusions ................................................................................................................ 170
6.5 References .................................................................................................................. 172

Chapter 7: Expansion of $^6$Li 1D Selective Inversion Methods to Multi-Spin Systems

7.1 Introduction .................................................................................................................. 174
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1.1</td>
<td>Selective Inversion Using 1D EXSY</td>
<td>175</td>
</tr>
<tr>
<td>7.1.2</td>
<td>Selective Inversion Using Shaped Pulses</td>
<td>176</td>
</tr>
<tr>
<td>7.2</td>
<td>Experimental</td>
<td>177</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Sample Preparation</td>
<td>177</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Solid State NMR</td>
<td>177</td>
</tr>
<tr>
<td>7.2.3</td>
<td>1D EXSY</td>
<td>177</td>
</tr>
<tr>
<td>7.2.4</td>
<td>Shaped Pulse Experiments</td>
<td>178</td>
</tr>
<tr>
<td>7.2.5</td>
<td>Nonselective Inversion Recovery</td>
<td>178</td>
</tr>
<tr>
<td>7.2.6</td>
<td>Data Analysis</td>
<td>178</td>
</tr>
<tr>
<td>7.3</td>
<td>Results and Discussion</td>
<td>179</td>
</tr>
<tr>
<td>7.4</td>
<td>Conclusions</td>
<td>188</td>
</tr>
<tr>
<td>7.5</td>
<td>References</td>
<td>190</td>
</tr>
<tr>
<td>Chapter 8: Quantification of Li Ion Hopping Timescales in Li₅V(PO₄)₂F₂</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>192</td>
</tr>
<tr>
<td>8.2</td>
<td>Experimental</td>
<td>193</td>
</tr>
<tr>
<td>8.2.1</td>
<td>Sample Preparation</td>
<td>193</td>
</tr>
<tr>
<td>8.2.2</td>
<td>Bond Valence Density Maps</td>
<td>193</td>
</tr>
<tr>
<td>8.2.3</td>
<td>Solid State NMR</td>
<td>193</td>
</tr>
<tr>
<td>8.2.4</td>
<td>Data Analysis</td>
<td>194</td>
</tr>
<tr>
<td>8.3</td>
<td>Results and Discussion</td>
<td>196</td>
</tr>
<tr>
<td>8.3.1</td>
<td>Timescales of Ion Hopping Determined from ⁶Li SI Experiments</td>
<td>203</td>
</tr>
<tr>
<td>8.3.1.1</td>
<td>⁶Li Selective Inversion Results for Inversion of Li₁A</td>
<td>204</td>
</tr>
<tr>
<td>8.3.1.2</td>
<td>⁶Li Selective Inversion Results for Inversion of Li₄C</td>
<td>208</td>
</tr>
<tr>
<td>8.3.1.3</td>
<td>CIFIT Results for Unresolved Exchange Pairs</td>
<td>214</td>
</tr>
<tr>
<td>8.3.2</td>
<td>Comparison to Materials Studied in this Thesis and Other Works</td>
<td>219</td>
</tr>
<tr>
<td>8.4</td>
<td>Conclusions</td>
<td>224</td>
</tr>
<tr>
<td>8.5</td>
<td>References</td>
<td>225</td>
</tr>
<tr>
<td>Chapter 9: Summary and Outlook</td>
<td>227</td>
<td></td>
</tr>
<tr>
<td>9.1</td>
<td>Summary</td>
<td>227</td>
</tr>
<tr>
<td>9.2</td>
<td>References</td>
<td>236</td>
</tr>
</tbody>
</table>
List of Tables

Table 1.1– Summary of electrochemical performance of cathode materials investigated in this thesis. ...................................................................................................................11

Table 2.1 – Nuclear spins measured in this thesis with their corresponding spin number (I) and gyromagnetic ratio. Also included is the gyromagnetic ratio of a free electron (e). ..................................................................................................................32

Table 2.2 – Summary of magnetic field strengths used in this thesis and the corresponding Larmor frequencies of $^{6,7}$Li, $^{19}$F, and $^{31}$P nuclei. ...........................................35

Table 2.3 – Summary of homonuclear, heteronuclear, and nuclear-electron dipolar coupling constants in LiFePO$_4$ .............................................................................................................................44

Table 2.4 – Summary of spin quadrupole moments for quadrupolar nuclei measured in this thesis. ..............................................................................................................47

Table 4.1 - Summary of changes to transmitter frequency due to migration of the $^{31}$P resonance as temperature is increased. ......................................................95

Table 4.2 – Summary of M-O-P orbital overlap angles in LiFePO$_4$, $^{35}$FePO$_4$, $^{35}$ and LiMnPO$_4$. .....................................................................................................................102

Table 4.3 - Summary of deconvolution parameters for the $^7$Li MAS NMR spectrum of biphasic Li$_{10.5}$FePO$_4$ (Figure 4.10) .................................................................................108

Table 5.1 – Summary of crystallographic data for Li$_3$Fe$_2$(PO$_4$)$_3$ with assignment to the A, B, and C, resonance provided. .........................................................127

Table 5.2 – Summary of exchange rates determined from $^6$Li 2D EXSY measurements over a variable temperature range for Li$_3$Fe$_2$(PO$_4$)$_3$. ........................................130

Table 5.3 - Summary of activation energy values for the three Li-Li exchange pairs as well as the calculated Li-O bottlenecks of diffusion for Li$_3$V$_2$(PO$_4$)$_3$. ........133

Table 5.4 - Summary of activation energy values for the three Li-Li exchange pairs as well as the calculated Li-O bottlenecks of diffusion for Li$_3$Fe$_2$(PO$_4$)$_3$. ..............133

Table 6.1 - Summary of $^7$Li spin-lattice relaxation times (T$_1$) for LiVPO$_4$F and Li$_2$VPO$_4$F at 4.7 T ........................................................................................................................155

Table 6.2 – Summary of $^6$Li spin-lattice relaxation times (T$_1$) for Li$_{1.5}$VPO$_4$F and Li$_2$VPO$_4$ at 4.7 T ...............................................................................................................156

Table 6.3 - Summary of Li-X-V bond angles for the Li1 and Li2 environments in Li$_2$VPO$_4$F. .........................................................................................................................158
Table 6.4 - Summary of bond distances for the Li environments in Li$_2$VPO$_4$F. ..........160

Table 6.5 - Summary of CSA parameters for individual sites of Li$_{1.5}$VPO$_4$F ..........162

Table 6.6 – Summary of CIFIT results for $^6$Li 1D EXSY measurements of Li$_2$VPO$_4$F.164

Table 6.7 - Summary of face-shared Li1-Li2 pathways in Li$_2$VPO$_4$F with the corresponding bottlenecks for diffusion and internuclear distances. .......................169

Table 7.1 – Summary of Li-hopping rates in Li$_2$VPO$_4$F as determined from the SP and 1D EXSY inversion methods. .........................................................183

Table 7.2 – Summary of exchange rates determined from $^6$Li SP measurements of Li$_2$VOPO$_4$. Each rate of ion exchange was determined twice from separate inversion of each resonance involved in the ion exchange process. Example: $\bar{AB}$ indicates the results from inversion of A, whereas $A\bar{B}$ is from inversion of B......186

Table 7.3 - Summary of activation energies for Li ion hopping from the variable temperature $^6$Li SP studies of Li$_2$VOPO$_4$.................................................................188

Table 8.1 – Summary of the five exchange pairs/pathways in Li$_5$V(PO$_4$)$_2$F$_2$ identified previously in the Goward group using $^6$Li 2D EXSY measurements.1 ..........198

Table 8.2 – Summary of all possible exchange pairs/pathways in Li$_5$V(PO$_4$)$_2$F$_2$. Pairs where ion exchange has been observed are presented in italicized typeface. ....200

Table 8.3 – Summary of CIFIT results over a variable temperature range of $^6$Li SI measurements where Li$1_A$ was the site chosen for inversion. The forward rate coefficients ($k_{12}$) are reported from CIFIT while the backward coefficients ($k_{51}$) are predicted from the site-populations.................................................................207

Table 8.4 – Summary of exchange rates and activation energies of Li ion hopping as determined from $^6$Li selective inversion studies of Li$_5$V(PO$_4$)$_2$F$_2$. .........................214

Table 8.5 – Summary of fits for $k_{45}$ and $k_{46}$ rates at 348 K when the values of $k_{36}$, $k_{35}$ and $k_{56}$, are held at non-zero values. .................................................................215

Table 8.6 – Summary of Li ion hopping rates, energy barriers, internuclear distances, bottleneck area, bond sum valence (BSV) values and bond sum value distribution ($\Delta$BSV) for ion hopping pairs in a series of Li intercalation compounds. .................220
List of Figures

Figure 1.1 – Plot of the volumetric and gravimetric energy densities of different battery systems. ...

Figure 1.2 - Schematic of a Li ion battery having LiCoO₂ as the positive electrode and graphite (grey sheets) as the negative electrode. The LiCoO₂ structure has layers of CoO₆ octahedra (blue) interleaved with layers of Li ions (red spheres) ...

Figure 1.3 – Open-circuit diagram of an aqueous electrolyte from Goodenough et al. \( \Phi_A \) and \( \Phi_C \) are the work function for the anode and cathode, respectively. \( V_{OC} \) is the open circuit voltage as defined by the redox potentials of the anode \( (\mu_A) \) and cathode \( (\mu_C) \) ...

Figure 1.4 – Structure of cubic spinel LiMn₂O₄. Yellow octahedra are the MnO₆ sites with the tetrahedral Li environments showing a navy blue sites ...

Figure 1.5 - Structure of olivine LiFePO₄ with space group Pnma. FeO₆ are shown as blue octahedral with yellow tetrahedra representing the corner-shared PO₄³⁻ units. Li ions are shown as red spheres occupying tunnels along the b-axis are shown as red-spheres ...

Figure 1.6 – Structure of Li₃M₂(PO₄)₃ where M = V or Fe. The MO₆ octahedra shown as grey square with PO₄³⁻ shown as yellow tetrahedra. The Li ions occupying the interstitial spaces as shown as pink, orange, and red spheres ...

Figure 1.7 - Structures of a) LiVPO₄F and b) Li₂VPO₄F. VO₄F₂ octahedra are shown in grey with red oxygen atoms and green fluorine atoms sitting at the vertices. Tetrahedral PO₄³⁻ groups shown as yellow with Li-atoms shown as orange and lilac spheres ...

Figure 1.8 – Structure of LiVOPO₄. Grey polyhedra represent the VO₆ octahedral environments and yellow tetrahedra indicate PO₃⁻ units. Lithium environments are shown as orange and lilac spheres ...

Figure 1.9 – Structure of Li₂V(PO₄)₂F₂. Vanadium centered octahedra (grey) corner share with PO₄ tetrahedra to create 2D layers sandwiching Li ions (coloured spheres) ...

Figure 2.1 - Schematic showing the relative population of the energy levels of a spin ½ nucleus. A Boltzmann distribution governs the \( \alpha \) and \( \beta \) populations (small spheres) ...

Figure 2.2 – \(^{7}\text{Li}\) MAS spectra of LiMgPO₄ (bottom), LiFePO₄ (middle), and LiMnPO₄ (top) with a spinning speed of 25 kHz. The materials are isostructural with one
another, differing only in the metal center. LiMgPO\(_4\) is a diamagnetic analogue of the paramagnetic LiFePO\(_4\) and LiMnPO\(_4\). Asterisks denote spinning sidebands.

**Figure 2.3** – Schematic (reproduced from Ref.\(^{10,11}\) detailing two mechanisms for electron spin density transfer. a) Shows delocalization of unpaired electron spin density from the M \(t_{2g}\) to the empty Li 2s orbital either directly or via the O 2p orbital. This leads to spin density being of the same sign as that on the M center. b) Shows the 90° orbital overlap where the unpaired electron spin density in the \(e_g\) orbital (shown with hatching) polarizes the spin in the \(t_{2g}\) orbital leading to density transfer to the empty Li 2s orbital of opposite sign to that of the M center. The 180° geometry involves the polarization of the \(e_g\) spins by the \(t_{2g}\) orbitals, also leading to a transfer of spin density to the Li 2s nucleus of opposite sign to that of the metal center.

**Figure 3.1** – Illustration styled after a figure from Gullion et al.\(^5\) showing the influence of the \(^{31}\)P local field on the \(^6\)Li spin. Application of a \(\pi\)-pulse on the \(^{31}\)P spin changes the direction of the local field at the \(^6\)Li spin, causing an attenuation of the \(^6\)Li magnetization aligned along the z-direction.

**Figure 3.2** – Example of a \(^6\)Li\(_{\{^{31}\}P}\) REDOR experiment.

**Figure 3.3** – Schematic showing the partitioning of the time axis in a 2D NMR experiment.

**Figure 3.4** – Pulse sequence for a 2D EXSY experiment. 90° pulses are shown as black rectangles.

**Figure 3.5** – Schematic of a 2D EXSY spectrum for a 3-site material, A, B, and C. Diagonal peaks of the A, B, and C signals stored during \(F_1\) are shown as red, yellow, and blue circles. Crosspeaks evolving from A-C and B-C exchange are shown as green and purple circles on either side of the diagonal region.

**Figure 3.6** – Example of data collected using \(^6\)Li SI experiments over a variable mixing time range. Inversion of Peak A (highlight in green) returns to equilibrium due to the combined effects of inherent \(T_1\) as well as exchange with Peak B (highlighted in purple). This results in a characteristic “transient” curve for Peak B (left). Error bars on the integration values are within the size of the data points.

**Figure 3.7** – Schematic showing the basic principle of a selective inversion experiment. The selective inversion period creates the initial conditions where one of the environments known to undergo ion-exchange is selectively inverted. This is followed by the mixing period where the return to equilibrium of the inverted peak is measured as a function of time. Detection of the signal at different mixing times gives rise to a buildup curve of the inverted site and transient curve(s) for non-inverted spin(s).

**Figure 3.8** – Schematic showing the pulse sequence for a 1D EXSY experiment.
Figure 3.9 – Schematic showing the pulse sequence for selective inversion where a shaped pulse is employed to selectively invert an on-resonance pulse. ..................79

Figure 4.1 - $^7$Li MAS NMR (25 kHz) of isostructural LiMnPO$_4$ (top) and LiFePO$_4$ (bottom). Asterisks denote spinning sidebands. This figure illustrates the changes to the Li environment when the redox center changes from a $t_{2g}^4e_g^2$ (LiFePO$_4$) to a $t_{2g}^3e_g^2$ (LiMnPO$_4$) .................................................................89

Figure 4.2 – $^{31}$P MAS spectra of LiFePO$_4$ (top) and LiMnPO$_4$ bottom, with MAS speed of 25 kHz. Isotropic shifts values are given for each phase with sidebands denoted with asterisks. .............................................................................91

Figure 4.3 – Changes to the $^{31}$P MAS resonance of LiFePO$_4$ as a function of temperature. .......................................................................................................................94

Figure 4.4 – $^6$Li$_{({^{31}}P)}$ REDOR curve of LiFePO$_4$ over a variable temperature range. The static simulated curve from SIMPSON is also shown as the data points connected by a line. .................................................................................................95

Figure 4.5 - Powder X-ray diffraction pattern of biphasic Li$_{0.5}$FePO$_4$ prepared from chemical oxidation of LiFePO$_4$. Selected reflections of LiFePO$_4$ (triphylite, T) and FePO$_4$ (heterosite, H) are indexed. Inset: SEM micrograph of the Li$_{0.5}$FePO$_4$ material which consists of uniform sub-micron sized particles, with a narrow particle size distribution.................................................................99

Figure 4.6 - $^{31}$P MAS NMR of FePO$_4$ (top), LiFePO$_4$ (middle) and biphasic 0.5LiFePO$_4$:0.5FePO$_4$ (bottom) all at room temperature. Isotropic shifts for FePO$_4$, LiFePO$_4$ found at 5800 and 3800 ppm respectively. Asterisks denote spinning sidebands. ......................................................................................101

Figure 4.7 – Schematic showing the P environment as coordinated via oxygen to the metal centers (either Mn or Fe) in the olivine phases of LiMnPO$_4$, LiFePO$_4$ and FePO$_4$.................................................................102

Figure 4.8 – $^{31}$P static solid-state NMR spectra under variable temperature conditions. Frequency stepped sub-spectra (grey) added to yield total spectrum (black). ..........104

Figure 4.9 – Static $^{31}$P sub-spectra of Li$_{0.5}$FePO$_4$ at 250 °C measured before and after the solid solution phase was reached. The two-phase features observed before the solid solution was formed do not reappear in the cooled sample on a timescale of 24 hr following heat treatment..............................................................................105

Figure 4.10 – a) $^7$Li MAS NMR spectra of LiFePO$_4$ (top, MAS = 40 kHz) and biphasic Li$_{0.5}$FePO$_4$ (0.5LiFePO$_4$:0.5FePO$_4$) (bottom, MAS = 40 kHz). Asterisks denote spinning sidebands. b) Deconvolution of biphasic Li$_{0.5}$FePO$_4$ with MAS = 40 kHz. Fitted spectrum (grey) sits on top of experimental spectrum (black). Deconvoluted peaks shown in black......................................................107
Figure 4.11 – Schematic detailing the local Li environment with respect to Fe transition metal center proximity. **Left.** Oxidation of Fe centers that have orbital overlap close to 90° leading to Li environments with high paramagnetic shift. **Right.** Oxidation of Li environments with orbital overlap of 110-122° leading to a smaller impact on paramagnetic shift but similar impact on lineshape and breadth of CSA.

Figure 4.12 – Schematic detailing the new Li environment generated if a Fe atom was found along the Li diffusion channel. The Fe\textsubscript{defect}-O-Li orbital overlap angles are very close to 90° resulting in a further increase of the paramagnetic shift value.

Figure 4.13 - \(^{7}\text{Li}\) MAS NMR (40 kHz) of micro-diameter LiFePO\(_4\) before (top) and after (bottom) electrochemically cycling to a composition of Li\(_{0.43}\)FePO\(_4\). Asterisks denote spinning sidebands. Inset is SEM image of pristine particles.

Figure 5.1 - Unit cell of monoclinic Li\(_3\)Fe\(_2\)(PO\(_4\))\(_3\) along the a-axis. FeO\(_6\) octahedra (blue) are connected to PO\(_4^{3-}\) tetrahedra (yellow) at oxygen vertices. Li1 (orange), Li2 (pink) and Li3 (green) sit in channels formed by the PO\(_4\) and FeO\(_6\) units.

Figure 5.2 - \(^{6}\text{Li}\) MAS NMR spectrum of Li\(_3\)Fe\(_2\)(PO\(_4\))\(_3\) with MAS = 25 kHz. Asterisk denotes peak belonging to impure phase.

Figure 5.3 – \(^{6}\text{Li}\) 2D EXSY spectrum at MAS = 25 kHz, T = 311 K, with a) \(\tau_{\text{mix}} = 0.5\) ms and b) \(\tau_{\text{mix}} = 3.0\) ms

Figure 5.4 – Normalized cross peak volume as a function of mixing time for exchange pair AB (□), BC (●), and AC (△) for Li\(_3\)Fe\(_2\)(PO\(_4\))\(_3\). Clockwise from top left acquisition temperatures for each data set are 283 K, 292 K, 302 K, and 311 K. Due to \(T_1\) limitations, plateaus, for lower temperature data sets were not achieved.

Figure 5.5 – Arrhenius analysis for determination of activation energies for Li-Li hopping between exchange pairs AB (top), AC (middle), and BC (bottom). For the AB exchange pair (top), the large error bar of the lowest temperature data point (283K) obscures the fit significantly. The analysis was therefore performed with the 283 K data point set to the uppermost limit of the error bar to yield a better linear fit (open squares with dashed linear fit (top)).

Figure 5.6 – Bond valence maps (right column) for the Li1-Li2 (top), Li1-Li3 (middle), and Li2-Li3 (bottom) exchange pathways. The maps shown were defined by the plane of the vertices of the faces of the Li-polyhedra orientated towards each other for exchange, with a 1.5 Å radius and contour increment of 0.485. A schematic showing how these panes were defined is shown in the right column for the Li1-Li2 (top), Li1-Li3 (middle), and Li2-Li3 (bottom) exchange pathways. On each map the coordinates of shared atoms and midpoints are given with lines radiating from shared atoms to midpoints of unshared atoms.
Figure 5.7 - Schematic showing the geometries of the shared polyhedra of the Li ion sites undergoing ion exchange in Li$_3$Fe$_2$(PO$_4$)$_3$, Li1-Li2 left, Li1-Li3 middle and Li2-Li3 left. ................................................................. 136

Figure 5.8 – Right: GITT experiments of the two coin cells combined for NMR measurements. Cells were each cycled to x ~ 2.2. Left: $^6$Li MAS spectra of the as-prepared Li$_3$V(PO$_4$)$_3$ (bottom) and the cycled material. .................................................. 139

Figure 5.9 – $^6$Li MAS spectra under variable conditions of as-prepared Li$_3$V$_2$(PO$_4$)$_3$, an uncycled cast of Li$_3$V$_2$(PO$_4$)$_3$ with carbon black and PVDF (middle) and a sample cycled to x = 2.2 giving 0.73Li$_3$V$_2$(PO$_4$)$_3$:V$_2$(PO$_4$)$_3$ .................................................. 140

Figure 6.1 – $^7$Li MAS (40 kHz, 330 K) spectra of Li$_x$VPO$_4$F at various stages of lithiation resulting in single site LiVPO$_4$F (bottom), two-phase 0.5LiVPO$_4$F:0.5Li$_2$VPO$_4$F (middle), and single-phase Li$_2$VPO$_4$F (top)................. 153

Figure 6.2 – Deconvolution of $^7$Li MAS isotropic resonance of LiVPO$_4$F (MAS 40 kHz, 330 K). The Li1:Li2 sites integrate in a ratio of 0.2(±0.1):0.8(±0.1) ......................... 154

Figure 6.3 – Schematic showing the split site in LiVPO$_4$F which both Rietveld refinement and NMR showed to be a Li1:Li2 0.18:0.82 occupancy .................. 154

Figure 6.4 - $^6$Li 2D EXSY spectrum over a variable temperature range shows evidence of thermally activated chemical exchange in the Li$_2$VPO$_4$F phase. On left a) T = 303 K (MAS = 25 kHz) and b) T = 330 K (MAS = 40 kHz). For both experiments, $\tau_{mix}$ = 15 ms ................................................................. 157

Figure 6.5 – $^6$Li$_{\{^{19}F\}}$ REDOR buildup curves for resonances A (triangles) and B (circles). MAS = 35 kHz ................................................................. 159

Figure 6.6 – Deconvolution of sideband manifold for $^7$Li MAS spectrum of 0.5LiVPO$_4$F:0.5Li$_2$VPO$_4$F. Experimental spectrum shown on left. Sideband manifolds for each of the crystallographic Li sites (as modeled in DMfit) on right from top to bottom—Parent LiVPO$_4$F, A site, and B site. Asterisks denote spinning sidebands. ......................................................................................... 161

Figure 6.7 – Results of the $^6$Li 1D EXSY experiments over a variable temperature range. Clockwise from the top left, 331 K, 337 K, 343 K and 350 K. The points represent measured values and the lines are the best fit to the data from the CIFIT program. The depth of the transient well increases with increasing temperature .......... 163

Figure 6.8 – Results of the $^6$Li 1D EXSY experiments over a variable temperature range. Plots are separated into the inverted A spin (left) and non-inverted B spin (right). Data points represent measured values and the lines are the best fit to the data from the CIFIT program ........................................ 164
Figure 6.9 – Results of selective 1D $^6$Li EXSY (left) and nonselective inversion (NSI) recovery (right) experiments of the A resonance over the same temperature range. The x-axis is minimized to the time region where chemical exchange is expected to dominate the buildup curves. The 1D EXSY results show an increase in buildup intensity as the temperature is raised. The NSI recovery shows only a slight variation with temperature.

Figure 6.10 – Arrhenius plot of ion exchange rates as a function of temperature for Li1-Li2 ion exchange in Li$_2$VPO$_4$F.

Figure 6.11 - Schematic of the simplified unit cell highlighting the two face-shared Li1-Li2 (orange-lilac) diffusion pathways. Each has a bottleneck area (shaded triangle) created by 1 F atom (green) and 2 O atoms (red). Depending on the population of the half occupancy Li1 and Li2 environments, the $\alpha$-bottleneck (red triangle) is present as either $\alpha_1$ (Li1a-Li2a) or $\alpha_2$ (Li1a-Li2b). Similarly, the $\beta$-bottleneck (blue triangle) exists as either $\beta_1$ (Li1b-Li2b) or $\beta_2$ (Li1b-Li2a). The coordination environments and pathways lend themselves to 3D ion transport.

Figure 6.12 – Bond valence maps of the planes defining the shared face of the $\alpha_2$ (left) and $\beta_2$ (right) pathways. Atoms that define the space are marked with an X.

Figure 7.1 – $^6$Li MAS (25 kHz) spectra of Li$_2$VPO$_4$F (top) and Li$_2$VOPO$_4$ (bottom). Labeling of sites A, B, and C, indicate spins involved in ion hopping processes. The resonances at zero ppm arise from diamagnetic impurities from the lithiation process.

Figure 7.2 - 2D EXSY spectra of Li$_2$VPO$_4$F (left, $^6$Li MAS 40 kHz, $\tau_{\text{mix}}$ = 15 ms) and Li$_2$VOPO$_4$ (right, $^7$Li MAS 40 kHz, $\tau_{\text{mix}}$ = 6 ms). A 2-site, 1-exchange process system is shown in Li$_2$VPO$_4$F as crosspeaks between the A and B Li ion crystallographic positions are present. Similarly, a 3-site, 3-exchange process system in Li$_2$VOPO$_4$, is proven with observation of A–B, A–C, and B–C, crosspeaks.

Figure 7.3 – Selective inversion results of the 2-site, 1-exchange material, Li$_2$VPO$_4$F, at 360 K. Left: Comparison of NSI recovery, 1D EXSY, and SP experiments of the inverted A resonance. Right: 1D EXSY and SP results of the non-inverted B resonance.

Figure 7.4 – $^6$Li SP results over a variable temperature range (304 K – 327 K) of the 3-site, 3-exchange material, Li$_2$VOPO$_4$. Top row shows results from the inversion of A with A, B, and C magnetization curves plotted from left to right. The middle row contains results from the inversion of B where the B, A, and C, magnetization curves are plotted from left to right. Results from the inversion of C are shown in the bottom row where from left to right the C, A, and B magnetization curves are given.
Figure 7.5 - Eyring plots where the slope of the natural log of the averaged ion hopping rate over temperature plotted against inverse temperature gives the energy barrier for the A-B, (top), A-C (middle), and B-C (bottom) exchange processes. ............... 187

Figure 8.1 – Structure of Li$_5$V(PO$_4$)$_2$F$_2$, which crystallizes in the monoclinic space group, P2$_1$/c. Corner shared vanadium octahedra (grey) and phosphate tetrahedra create a two-dimensional sheet that sandwiches layers of lithium ions (coloured spheres). Li$_1$ (pink) and Li$_2$ (blue) sit on the 2$b$ and 2$d$ Wyckoff positions, respectively, each with occupancy of 0.5. The remaining lithium environments, Li$_3$ (purple), Li$_4$ (red), Li$_5$ (orange), and Li$_6$ (green), all sit on the 4$e$ Wyckoff position with full occupancy. ................................................................... 196

Figure 8.2 – Top: $^6$Li MAS NMR spectrum of Li$_5$V(PO$_4$)$_2$F$_2$ at MAS frequency of 25 kHz and temperature of 312 K. Deconvolution of the isotropic region is shown as the bottom spectrum. The experimental spectrum (black) was deconvoluted into the known six crystallographic sites (green). The difference map (blue) between the experimental (back) and modeled spectrum (red) is shown at the bottom of the spectrum. ........................................................................................................ 197

Figure 8.3 – $^6$Li 2D EXSY spectrum of Li$_5$V(PO$_4$)$_2$F$_2$ collected at the NICPB. MAS = 40 K, T = 349 K, and $\tau_{\text{mix}}$ = 2 ms. ................................................................. 199

Figure 8.4 – Bond valence maps of ion exchange pathways in Li$_5$V(PO$_4$)$_2$F$_2$ for the ion hopping pairs that have either face-shared (left) or pseudo-face-shared (right) Li polyhedral geometries. ................................................................. 202

Figure 8.5 – Results of the $^6$Li 1D selective inversion of Li$_1$ (resonance A) over a variable temperature range (312 K – 348 K as indicated on legend on each plot). Clockwise from the top left, magnetization curves of Li$_1$, Li$_2$, Li$_3$, Li$_4$, Li$_5$ and Li$_6$. The points represent measured values and the lines are the best fit to the data from the CIFIT program. For the non-inverted resonances, the depth of the transient well increases with increasing temperature, as expected for the ion exchange process. ........................................................................................................ 205

Figure 8.6 – $^6$Li SI spectra showing the inversion of Li$_1$ at different mixing times and temperatures. Left: inversion of Li$_1$ at 312 K. Right: Inversion of Li$_1$ at 348 K. The red spectra are at a mixing time of 100 ms, where complete relaxation of the inverted peak is accomplished. The black spectra are at mixing times of 5 $\mu$s where maximum inversion is observed. ........................................................................................................ 206

Figure 8.7 – Eyring plot of the natural log of the Li$_1$-Li$_5$ ion hopping rate (k) over temperature plotted against 1000/T ................................................................. 208

Figure 8.8 – Results of the $^6$Li 1D selective inversion of Li$_4$ over a variable temperature range. Clockwise from the top left, magnetization curves of Li$_1$, Li$_2$, Li$_3$, Li$_4$, Li$_5$, Li$_6$. The points represent measured values and the lines are the best fit to
the data from the CIFIT program. For the non-inverted resonances, the depth of the transient well increases with increasing temperature, as expected for ion exchange processes.

**Figure 8.9** – $^6$Li SI spectra showing the inversion of Li$_4$C at different mixing times and temperatures. The red spectra are at a mixing time of 100 ms, where complete relaxation of the inverted peak is accomplished. The black spectra are at mixing times of 5 µs where maximum inversion is observed. Left: inversion of Li$_4$C at 312 K Right: Inversion of Li$_4$C at 348 K.

**Figure 8.10** – Eyring plots of the natural log of the Li$_4$C-Li$_6$D (top) and Li$_4$C-Li$_5$F (bottom) ion hopping rates (k) over temperature against 1000/T.

**Figure 8.11** - Fit of Li$_6$D (left) and Li$_5$F (right) transient wells at 348 K as the values of $k_{36}$, $k_{35}$ and $k_{56}$ are varied in the fitting regimes of LD1, LD2, LD3, LD4, and LD5. Parameters for each fit are summarized in Table 8.5.

**Figure 8.12** - Fit of Li$_6$D (left) and Li$_5$F (right) transient wells at 348 K as the values of $k_{36}$, $k_{35}$ and $k_{56}$ are varied in the fitting regimes of LD1, LD6, LD7, and LD8. Parameters for each fit are summarized in Table 8.5.

**Figure 8.13** – Fit of Li$_6$D (left) and Li$_5$F (right) transient wells at 348 K as the values of $k_{36}$, $k_{35}$ and $k_{56}$ are varied in the fitting regimes of LD1, LD9, LD10, LD11, and LD12. Parameters for each fit are summarized in Table 8.5.

**Figure 8.14** - Left: Plot of the fit values of $k_{45}$ and $k_{46}$ at 348 K against the held values of $k_{35}$, $k_{36}$ and $k_{56}$ (from fitting regimes LD1, LD5, LD9-12). Right: Fit of Li$_4$C over all fitting regimes (LD1-LD12). Parameters for each fit are summarized in Table 8.5.

**Figure 8.15** – Comparison of bond valence density maps of the Li1-Li2 α-pathway in Li$_2$VPO$_4$F (left) and the Li$_1$A-Li$_5$F exchange pathway in Li$_5$V(PO$_4$)$_2$F$_2$. Each map shown has a viewing radius of 2 Å and contour increment of 0.485.

**Figure 8.16** – Bond valence density maps of the Li1-Li2 (left) and Li1-Li3 (right) exchange pathways in Li$_3$VF$_6$. Contour increment is 0.485 with a 2 Å radius shown.
List of Abbreviations and Symbols

SSNMR  Solid State Nuclear Magnetic Resonance
MAS    Magic Angle Spinning
VT     Variable Temperature
REDOR  Rotational-Echo, Double-Resonance
EXSY   Exchange Spectroscopy
SI     Selective Inversion
NSI    Nonselective Inversion
SEDOR  Spin-echo, double-resonance
GHG    Greenhouse Gas
EV     Electric Vehicle
HEV    Hybrid Electric Vehicle
Ni-MH  Nickel Metal Hydride
\(\mu_a\) Redox potential of the anode
\(\mu_c\) Redox potential of the cathode
\( E_g \) Band gap

\( V_{OC} \) Open circuit voltage

\( V \) Volt

\( Z \) Atomic number

\( I \) Spin quantum number

\( \mu_N \) Nuclear magnetic moment

\( \mu_e \) Electron magnetic moment

\( \gamma_N \) Nuclear gyromagnetic ratio

\( \gamma_e \) Electron gyromagnetic ratio

\( h \) Reduced Planck constant

\( B_0 \) Applied magnetic field strength

\( \omega_0 \) Larmor frequency

\( \tau_r \) Rotor period

\( \hat{H} \) Hamiltonian

\( \langle S_z \rangle \) Unpaired electron spin density
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{ij}$</td>
<td>Dipolar coupling constant</td>
</tr>
<tr>
<td>CSA</td>
<td>Chemical Shift Anisotropy</td>
</tr>
<tr>
<td>$C_q$</td>
<td>Quadrupole coupling</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Chemical shielding</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>ppm</td>
<td>Part per million</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width at Half-Maximum</td>
</tr>
<tr>
<td>$A_H$</td>
<td>Hyperfine coupling constant</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Spin-lattice relaxation rate</td>
</tr>
<tr>
<td>$T_2$</td>
<td>Spin-spin relaxation rate</td>
</tr>
<tr>
<td>BVS</td>
<td>Bond Valence Sum</td>
</tr>
<tr>
<td>$k$</td>
<td>Ion hopping rate</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$K$</td>
<td>Equilibrium constant</td>
</tr>
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</table>
Chapter 1: Introduction to Cathode Materials for Li Ion Batteries

1.1 Thesis Layout

This thesis details the use of Solid-State Nuclear Magnetic Resonance (SSNMR) techniques to investigate the structural features and lithium ion mobility pathways in a series of phosphate and fluorophosphate lithium intercalation materials used as positive electrodes in lithium ion batteries. Chapter 1 provides the project motivation with a description of current lithium ion battery technology and a summary of the structural and electrochemical properties of cathode materials selected for investigation in subsequent chapters. Chapter 2 outlines the properties of nuclear and electron spin with a description of the unique spectral features expected from SSNMR measurements. Also included is a description of Magic Angle Spinning (MAS) techniques and how it is used to minimize unwanted spectral features. Chapter 3 is a summary of specific SSNMR experiments used to unravel the structural and ion mobility properties of the materials summarized in Chapter 1. Chapter 4 details the use of variable temperature (VT) and $^{6}\text{Li}^{(3)\text{P}}$ rotational-echo, double resonance (REDOR) measurements to evaluate ion and electron mobility in $\text{Li}_x\text{FePO}_4$ ($0 \leq x \leq 1$). Chapter 5 demonstrates the use of $^{6}\text{Li}$ two-dimensional MAS exchange spectroscopy (2D MAS EXSY) to study Li ion hopping pathways in monoclinic $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and also characterizes the electrochemical extraction of a single lithium in $\text{Li}_3\text{V(PO}_4)_3$ using $^{6}\text{Li}$ MAS NMR. Chapter 6 introduces the use of $^{6}\text{Li}$ 1D selective-inversion (SI) measurements as a more efficient means of studying ion dynamics in the two-site system, $\text{Li}_2\text{VPO}_4\text{F}$. Also included is a detailed structural
characterization of Li$_x$VPO$_4$F with $x=1.0$, 1.5, and 2.0, using $^6$Li-${}^{19}$F REDOR measurements as well as analysis of the sideband manifolds observed in $^7$Li MAS spectra of the mixed phase 0.5LiVPO$_4$F:0.5Li$_2$VPO$_4$F. Chapter 7 expands $^6$Li 1D SI experiments to a three-site material, Li$_2$VOPO$_4$, where the reproducibility of the inversion method is tested. Chapter 8 is a further expansion of $^6$Li 1D SI methods, where the many possible ion exchange pathways in Li$_5$V(PO$_4$)$_2$F$_2$ are discussed in terms of their structural bottlenecks, ion internuclear distances, as well as bond sum valence values. The final chapter provides a summary and proposes future work for research in this field.

1.2 Motivation for Using Li ion Batteries

Investigation into alternative energy storage and conversion systems is an important step towards not only reducing greenhouse gas (GHG) emissions but also minimizing the dependence of global economies on fossil fuels sourced from unstable regions. One area that has large potential for use of alternative energy conversion and storage systems is the transportation sector. Within Canada, the ground transportation sector (excluding freight transport) constitutes 9.6 % of total energy consumption.$^1$ Of that energy, 87% is sourced from refined fossil fuels with gasoline (54.5 %) and diesel (32.5 %) being the most heavily consumed.$^1$ Moreover, use of these energy sources is accompanied by substantial GHG emissions where 11.8% of total emissions in Canada are from gasoline and diesel fueled passenger vehicles.$^2$ Advancing automotive technology towards zero-emissions through modification and/or replacement of the combustion engine, can have a
significant impact on minimizing the economic and environmental hazards of fossil fuel consumption and combustion.

Electric and hybrid electric vehicles (EV and HEV, respectively) have an electric motor that either fully replaces or is paired with, a traditional combustion engine. To maximize the efficiency of EV and HEV motors, use of lightweight lithium ion battery systems is desired. **Figure 1.1** (from Tarascon et al.)\(^3\) illustrates the higher volumetric and gravimetric energy density of Li ion batteries as compared to more traditional car batteries including lead-acid and nickel metal hydride (Ni-MH) systems.

![Figure 1.1](image-url)  
**Figure 1.1** – Plot of the volumetric and gravimetric energy densities of different battery systems.\(^3\)
The high energy density of these battery systems has resulted in their widespread application towards small electronic devices (laptops, mobile phones, etc.). To apply this technology towards larger scale applications such as HEV and EV’s, many of the cost and safety issues of the current systems need to be addressed.

The remainder of this chapter outlines the current state of Li ion battery technology and highlights the chemical components that are targeted for improvement.

1.3 Description of a Li Ion Battery

A schematic of a Li ion battery is shown in Figure 1.2. Rechargeable lithium ion batteries involve a reversible insertion/extraction of lithium ions (the guest species) from a host matrix. This Li guest/host species is referred to as an intercalation compound and possesses a redox active metal center where the movement of the Li ions is accompanied by a flow of electrons through the external circuit. In the systems discussed throughout this thesis, the positive electrode material is the redox active Li intercalation compound while the negative electrode is comprised of a conductive layered material such as graphite.
Figure 1.2 - Schematic of a Li ion battery having LiCoO$_2$ as the positive electrode and graphite (grey sheets) as the negative electrode. The LiCoO$_2$ structure has layers of CoO$_6$ octahedra (blue) interleaved with layers of Li ions (red spheres)

The performance of an electrode material is described by its gravimetric and/or volumetric energy capacity. Both values are a measure of the number of electrons transferred through a circuit either per gram of electrode material (mAh g$^{-1}$) or per unit volume (mAh cm$^{-3}$), respectively. The gravimetric capacity is more often reported, as it is easier to measure in electrochemical experiments. The *theoretical gravimetric capacity* is calculated based on the number of charge transporters (in this case, the Li ions) that are intercalated into a unit mass of a given material. This makes the Li:anode and Li:cathode stoichiometry at the fully intercalated potential important. The *specific gravimetric capacity* is the measured number of charge transporters found at the fully charged or discharged potential. Under experimental conditions, irreversible capacity loss is often found and attributed to the reaction of the intercalated Li ions with the electrodes and/or the electrolyte.
The Li ions are shuttled from the anode to the cathode via the electronically insulating electrolyte, which is typically comprised of a Li salt dissolved in an organic solvent. The choice of electrolyte can impose limitations on the choice of electrode material, as the redox potentials of the anode ($\mu_A$) and/or cathode ($\mu_C$) must lie within the band gap ($E_g$) of the electrolyte (Figure 1.3, adapted from Goodenough et al.\textsuperscript{5}). The most commonly used electrolyte, LiPF$_6$ has a decomposition voltage of 4.9 V at room temperature, limiting many electrode redox potentials to below this level.\textsuperscript{6}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{Open-circuit diagram of an aqueous electrolyte from Goodenough et al.\textsuperscript{5} $\Phi_A$ and $\Phi_C$ are the work function for the anode and cathode, respectively. $V_{OC}$ is the open circuit voltage as defined by the redox potentials of the anode ($\mu_A$) and cathode ($\mu_C$).}
\end{figure}

The cycling rate capabilities are also an important parameter for describing the performance of an electrochemical cell. This is a measure of the time needed for the cell
to charge or discharge. For example, a charge rate of C/100, indicates that a total of 100 hours is needed for a complete charge cycle. Fast charge/discharge rates are not only needed for high-power output, but also for fast recharging such that the battery can be used again in a reasonable amount of time.

The battery shown in Figure 1.2 represents the most commonly used Li ion battery, with LiCoO$_2$ as the positive electrode and graphite as the negative electrode. Many of the cost, safety, and performance issues associated with this design need to be addressed in order to apply Li ion battery technology towards larger scale applications such as HEVs and EVs.$^{5,7}$ While most chemical components have been targeted for improvement, the high cost of the LiCoO$_2$ has singled it out as the economic crutch of the battery system. In addition to this, much structural instability is present in this material leading to poor electrochemical performance. Details of this are outlined in Section 1.4.

1.4 Layered LiCoO$_2$ and Spinel LiMn$_2$O$_4$

It was first observed in 1976 that Li could be reversibly intercalated between layers of TiS$_2$ in a paper by Whittingham et al.$^8$ Here, Li was reversibly intercalated in a solid solution phase with TiS$_2$ and LiTiS$_2$ end members. This occurred in a potential range of 2.5 V to 1.5 V against Li metal. It was later reported that higher cell potentials were obtained using metal oxides leading to commercialization of two major materials; layered LiCoO$_2$ and cubic spinel LiMn$_2$O$_4$. $^{9,10}$
The LiMO$_2$ ($M = \text{Co, Ni, Mn}$) family of compounds crystallize in a layered $R\overline{3}m$ structure.\textsuperscript{9} The Li$^+$ and M$^{3+}$ ions sit in alternating (111) sheets within the rocksalt structure. This allows for two-dimensional movement of the lithium ions in and out of the structure (\textbf{Figure 1.2}). Despite its predominance in portable electronic devices, this material exhibits many shortcomings and its application to larger scale applications has been stalled. Aside from high cost, a significant limitation of LiCoO$_2$ is that only half of the 280 mAh g$^{-1}$ theoretical capacity is reached, as the material becomes unstable and the structure degrades when Li is deintercalated below this level.\textsuperscript{11-13} This drawback coupled with slow charge-discharge rates, high cost, and environmental toxicity prevent LiCoO$_2$ from being used in larger scale applications such as batteries needed for hybrid electric vehicles (HEV).\textsuperscript{14}

This led to an interest in the low-cost cubic spinel phase of LiMn$_2$O$_4$ (space group $Fd\bar{3}m$).\textsuperscript{10,15} The edge shared MnO$_6$ octahedra create tetrahedral holes in which Li ions reside in the 8a crystallographic site (\textbf{Figure 1.4}). This is a mixed valent compound where the Mn ions in the +3 and +4 oxidation are equally populated with an average oxidation state of +3.5 observed due to the delocalization of the $e_g$ electrons in the semi-conducting framework. Lithium extraction in Li$_x$Mn$_2$O$_4$ occurs at 4 V opposite Li metal where the cubic structure is retained over the $0 < x < 1$ range.\textsuperscript{15-18} For insertion of a second Li ion at a voltage of 2.96 V for $1 < x < 2$, the cubic structure irreversibly adopts a tetragonal Li$_2$Mn$_2$O$_4$ phase ($F4/\overline{d}dm$) due to Jahn-Teller distortion around the Mn$^{3+}$ centers.\textsuperscript{10,19} The 4 V cycling range is also not immune to this phase transformation as
fast cycling rates can lead to over lithiation at the surface of the LiMn$_2$O$_4$ cubic phase leading to formation of the tetragonal phase.$^{20}$

Overall, the poor electrochemical performance of the two most popular metal oxide phases has prompted investigation into entirely new Li intercalation phases, where structural fatigue leading to capacity fading is not as severe. This thesis will investigate the structure and electrochemical properties of newer, inexpensive cathode materials, using multinuclear solid-state nuclear magnetic resonance experiments.

Figure 1.4 – Structure of cubic spinel LiMn$_2$O$_4$. Yellow octahedra are the MnO$_6$ sites with the tetrahedral Li environments shows a navy blue sites.

1.5 Materials Studied in this Thesis

For the positive electrode material, many new intercalation compounds have been introduced based on phosphates, and more recently fluorophosphates.$^{21,22}$ These newer cathodes show impressive cycling capabilities and are typically environmentally benign and economically accessible. The systems are built up of tetrahedral PO$_4^{3-}$ and octahedral
MO₆ of MO₄F₂ groups where M = Ti, V, Mn, Fe, Co. The PO₄³⁻ groups create an inductive effect where the strongly covalent P-O bond results in greater ionic character of the Li-O bonds, opening up large interstitial space in which the Li ions can reversibly be (de)intercalated. The inductive effect also results in higher redox potentials of many important redox couples as compared to the potentials found in oxide lattices. This includes Fe²⁺/Fe³⁺ and V²⁺/V³⁺, redox couples, which are two very low-cost transition metal centers. The phosphate groups also offer significant structural support such that a fully deintercalated phase is isostructural with its fully lithiated phase, which is key to retaining the full capacity and long lifetime of the material.

With these new materials however, in order to better understand cycling failure and/or successes, the behaviour of the mobile ion must be understood. While powder X-ray diffraction, as well as a variety of other spectroscopic techniques can provide useful information about structural changes to the lattice during chemical/electrochemical cycling, very few techniques can directly monitor the mobile ion. Solid-state nuclear magnetic resonance (NMR) is one of these few techniques, where ⁶,⁷Li NMR is able to monitor the mobile guest species while ³¹P and ¹⁹F can monitor changes to the host-framework. Further to this, ⁶,⁷Li NMR is sensitive to local site dynamics that take place on the NMR timescale. This includes site-specific rattling and site-to-site Li ion hopping. Determination of these timescales is then correlated to structural constraints within the host framework, offering insight into what factors govern fast ion mobility within a given lattice.
The remainder of this chapter provides a summary of the bulk structure and electrochemical performance of the phosphate and fluorophosphate cathode materials that will be investigated in this thesis. This includes olivine Li$_x$FePO$_4$ (0 ≤ x ≤ 1), monoclinic Li$_3$V$_2$(PO$_4$)$_3$ and Li$_3$Fe$_2$(PO$_4$)$_3$, tavorite based Li$_x$VPO$_4$F and Li$_x$VOPO$_4$ (1 ≤ x ≤ 2), and layered Li$_5$V(PO$_4$)$_2$F$_2$. Many of these materials show impressive theoretical and specific capacities with improved reversibility over LiCoO$_2$ and LiMn$_2$O$_4$ (Table 1.1). Chapter 3 outlines the solid-state NMR techniques used to study the ionic and structural properties of these electrochemically promising materials.

**Table 1.1**– Summary of electrochemical performance of cathode materials investigated in this thesis.

<table>
<thead>
<tr>
<th>Cathode Material</th>
<th>Highest Redox Potential (V)</th>
<th>Available Range (Δx)</th>
<th>Reversible Range (Δx)</th>
<th>Theoretical capacity (mAh g$^{-1}$)</th>
<th>Specific capacity (mAh g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>4.0</td>
<td>1.0</td>
<td>0.5</td>
<td>280</td>
<td>140</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>3.8</td>
<td>2.0</td>
<td>1.0</td>
<td>148</td>
<td>120</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>3.5</td>
<td>1.0</td>
<td>0.95</td>
<td>170</td>
<td>162</td>
</tr>
<tr>
<td>LiMnPO$_4$</td>
<td>4.1</td>
<td>1.0</td>
<td>0.88</td>
<td>171</td>
<td>150</td>
</tr>
<tr>
<td>Li$_3$Fe$_2$(PO$_4$)$_3$</td>
<td>2.8</td>
<td>2.0</td>
<td>2.0</td>
<td>128</td>
<td>116</td>
</tr>
<tr>
<td>Li$_3$V$_2$(PO$_4$)$_3$</td>
<td>3.5</td>
<td>3.0</td>
<td>2.8</td>
<td>197</td>
<td>185</td>
</tr>
<tr>
<td>Li$_2$VPO$_4$F</td>
<td>4.1</td>
<td>2.0</td>
<td>1.8</td>
<td>300</td>
<td>270</td>
</tr>
<tr>
<td>Li$_2$VOPO$_4$</td>
<td>3.5</td>
<td>2.0</td>
<td>1.5</td>
<td>305</td>
<td>229</td>
</tr>
<tr>
<td>Li$_3$V(PO$_4$)$_2$F$_2$</td>
<td>4.2</td>
<td>2.0</td>
<td>1.0</td>
<td>170</td>
<td>165</td>
</tr>
</tbody>
</table>
1.5.1 LiFePO$_4$

Olivine LiFePO$_4$ has been the most extensively studied cathode material proposed as an alternative to LiCoO$_2$. Structural and electrochemical details of this material were first published in 1997 by Padhi and associates.\textsuperscript{21} It was shown that the environmentally benign, inexpensive, cathode material, had a reversible capacity of 162 mAh g$^{-1}$ (theoretical 170 mAh g$^{-1}$) with a Fe$^{2+}$/Fe$^{3+}$ redox potential of 3.5 V. The high degree of reversibility was attributed to structure retention of the fully delithiated heterosite phase, FePO$_4$ which experiences a reversible 7\% decrease in cell volume upon Li removal. LiFePO$_4$ crystallizes in the $Pnma$ space group where lithium ions occupy the M(1) octahedral sites forming a linear chain of ions that run parallel to the $b$-axis.\textsuperscript{37} The Fe atoms sit on the M(2) sites with the octahedra forming a “zig-zag” plane of corner-shared environments supported by PO$_4$ tetrahedra. The Li ions are not able to diffuse through the FeO$_6$-PO$_4$ planes and are thus confined to one-dimensional mobility through a “tunnel” created by the Li ion octahedra (\textbf{Figure 1.5}).\textsuperscript{38-40} Moreover, the two-phase (de)lithiation observed in the electrochemical cycling forms a phase interface that impedes Li ion diffusion and consequently restricts this material to slow cycling rates.\textsuperscript{21,39,41-46} This resulted in LiFePO$_4$ being proposed as a material for low-power battery applications.

Despite this, the high electrochemical and thermal stability of LiFePO$_4$ as compared to LiCoO$_2$ and LiMn$_2$O$_4$ lead to extensive efforts to advance the performance of this material for high-power batteries needed for the automotive industry. Well over 1500 publications have emerged, detailing chemical and/or physical manipulation of the
material in order to achieve faster cycling rates. Some more noteworthy results include coating of the particles in a conductive layer such as graphite and reducing the particle size to nanometric dimensions. \(^{27,47-49}\) Both of these strategies lead to better contact between particles and resulted in high capacity retention at faster cycling rates (70% capacity retention at 5C). Another attractive feature of LiFePO\(_4\) is the high temperature solid-state synthesis has been replaced by more environmentally benign hydrothermal methods.\(^{50}\) Initial reports showed M(1) and M(2) site mixing where Fe atoms were found within the Li ion tunnels leading to diminished electrochemical performance. It was later shown that site mixing was limited when heating temperatures were set higher than 175 °C with 190-195 °C being the more commonly reported synthesis temperatures.\(^{51-53}\) Moreover, it has been shown that nano-morphologies were easily obtained and controlled using this hydrothermal method.\(^{53}\) Chapter 4 of this thesis will focus on better understanding the two-phase reaction as well as characterization of Li ions at the phase interface in hydrothermally prepared Li\(_x\)FePO\(_4\) \((x \leq 1)\) using solid-state \(^6^7\)Li and \(^{31}\)P NMR experiments. The samples studied were prepared both in the Goward research group and by collaborators at the University of Waterloo.
Figure 1.5 - Structure of olivine LiFePO$_4$ with space group Pnma. FeO$_6$ are shown as blue octahedral with yellow tetrahedra representing the corner-shared PO$_4^{3-}$ units. Li ions are shown as red spheres occupying tunnels along the b-axis are shown as red-spheres.

1.5.2 Monoclinic Li$_3$M$_2$(PO$_4$)$_3$ (M = V, Fe)

To overcome the limits of 1D conduction in LiFePO$_4$, many phases of phosphate and fluorophosphate Li intercalation compounds with frameworks having a higher degree of dimensionality and larger theoretical capacities have been introduced. Included in this analysis are the Li$_3$M$_2$(PO$_4$)$_3$ (M = V, Fe) phases$^{29,54}$ Both Li$_3$V$_2$(PO$_4$)$_3$ and Li$_3$Fe$_2$(PO$_4$)$_2$ crystallize in either a monoclinic $\alpha$-Li$_3$M$_2$(PO$_4$)$_3$ or a rhombohedral NASICON $\beta$-Li$_3$M$_2$(PO$_4$)$_3$ framework. For the V-analogue, $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ is the more thermodynamically stable and therefore preferred phase.$^{55}$ For Li$_3$Fe$_2$(PO$_4$) both the $\alpha$ and $\beta$ phases show promising electrochemical performance. In this thesis, only the $\alpha$-
phase of both materials is discussed in order to easily compare the ion mobility results obtained from SSNMR experiments.

The $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ phase has a three-dimensional framework created by the VO$_6$-octahedra sharing all six of its oxygen vertices with the PO$_4^{3-}$ tetrahedral units. Similarly, each PO$_4$ unit has a corner shared VO$_6$ found at each of its oxygen vertices. Three crystallographically unique Li sites occupy the spaces between the MO$_6$ and PO$_4$ units. Li1 occupies the tetrahedral position and Li2 and Li3 both occupy distorted trigonal bipyramidal sites. The lithium polyhedra corner share with one another forming chains of Li ions along the $a$-axis (Figure 1.6).

Figure 1.6 – Structure of Li$_3$M$_2$(PO$_4$)$_3$ where M = V or Fe. The MO$_6$ octahedra shown as grey square with PO$_4^{3-}$ shown as yellow tetrahedra. The Li ions occupying the interstitial spaces as shown as pink, orange, and red spheres.
For Li$_3$V$_2$(PO$_4$)$_3$, all three lithium environments can be reversibly extracted approaching the theoretical capacity of 197 mAh/g.$^{31,32,56,57}$ The extraction of the first lithium takes place over two voltage plateaus of 3.61 V and 3.69 V. The second and third Li ions are extracted at voltages of 4.07 V and 4.6 V, respectively, with the latter voltage corresponding to the V$^{4+}$/V$^{5+}$ redox couple. Reinsertion occurs with solid solution formation accompanied by a small amount of hysteresis.$^{32}$ Previous NMR studies have reported the timescales of both Li ion hopping as well as local Li-site rattling using advanced NMR methods.$^{23,24}$ Local lithium environments were also characterized upon extraction of materials electrochemically cycled to points between voltage plateaus. In this thesis, Chapter 6 evaluates the local lithium environment of materials prepared in the Goward group that are cycled and extracted at the first voltage plateau of the discharge curve.

For $\alpha$-Li$_3$Fe$_2$(PO$_4$)$_3$, the Fe$^{3+}$/Fe$^{4+}$ redox potential falls outside of the voltage window created by most lithium battery electrolytes (upper limit is ~ 5 V). Therefore reversible insertion of 1.8 Li has been reported for Li$_{3+x}$Fe$_2$(PO$_4$)$_3$ with two separate voltage plateaus of 2.85 V (for $0 \leq x \leq 1$) and 2.70 V (for $1 \leq x \leq 1.8$). The observed discharge capacity of 115-116 mAh/g for this insertion process comes close to the theoretical value of 128 mAh g$^{-1}$.$^{29,30}$ Again kinetic limitations are reported, similar to that observed in LiFePO$_4$. However the primary source of slow kinetics in this case is the slow electron and/or lithium transport found within each phase rather than due to slow phase-front migration.$^{58}$
In this thesis, the timescales of ion mobility in Li$_3$Fe$_2$(PO$_4$)$_3$ were determined using solid-state $^6$Li MAS NMR techniques and correlations of ion hopping rates made to structural constraints within the lattice. The materials studied were prepared using a high temperature solid-state reaction in the Goward research group. Results are compared to timescales of ion mobility in Li$_3$V$_2$(PO$_4$)$_3$ determined from MAS NMR studies.$^{24}$

1.5.3 Li$_x$VPO$_4$F (1 ≤ $x$ ≤ 2)

Lithium ion fluorophosphates represent a new generation of cathode materials for Li ion batteries. The addition of the electronegative fluorine atoms to the metal octahedra enhances the inductive effect resulting in higher redox potentials of the transition metal centers. Li$_2$Ni(PO$_4$)F was the first fluorophosphate material reported for electrochemical applications. Its synthesis was first reported in 1999 where an ordered mixed anionic framework of chains of NiO$_4$F$_2$ octahedra are joined by PO$_4^{3-}$ tetrahedra.$^{59}$ No electrochemical studies of this material were reported, nor for the isostructural Li$_2$CoPO$_4$F as the redox potentials were too high (> 5 V) for most liquid electrolytes.$^{60}$ More accessible redox potentials are found in tavorite-based LiMPO$_4$F fluorophosphate compounds where M is either Fe or V. LiVPO$_4$F which has a V$^{4+}$/V$^{5+}$ redox potential of 4.1 V and theoretical capacity of 155 mAh/g, for the extraction of one Li, is a material proposed for high-power electrochemical applications.$^{22}$ This compound is isostructural with the naturally occurring minerals, tavorite LiFePO$_4$OH and amblygonite LiAlPO$_4$F, which all crystallize in a triclinic space group.$^{22,61-63}$ These materials also have a 3D
framework, created by corner sharing units of PO₄ tetrahedra and VO₄F₂ octahedra (Figure 1.7a). Li-disorder is present over two crystallographic positions as shown from electrochemical results and also through NMR measurements of the isostructural, LiAlPO₄F. It was later shown that LiVPO₄F could also intercalate Li at a potential of about 1.8 V yielding a higher capacity, Li₂VPO₄F cathode material for battery applications. This reduced phase crystallizes in a monoclinic phase (space group C2/c) as recently reported by our collaborators at the University of Waterloo. Although a different space group is found for the reduced phase, the structures of LiVPO₄F and Li₂VPO₄F are closely related, where the PO₄ and VO₄F₂ continue their corner-sharing network, retaining the 3D framework. The Li ions now occupy two distinct crystallographic positions where Li₁ takes on a position very similar to the disordered Li position of the parent LiVPO₄F while Li₂ is a completely new environment resulting from the electrochemical/chemical insertion (Figure 1.7b).
Figure 1.7 - Structures of a) LiVPO$_4$F and b) Li$_2$VPO$_4$F. VO$_4$F$_2$ octahedra are shown in grey with red oxygen atoms and green fluorine atoms sitting at the vertices. Tetrahedral PO$_4^{3-}$ groups shown as yellow with Li-atoms shown as orange and lilac spheres.

Chapter 6 of this thesis details the structural characterization of Li$_x$VPO$_4$F (x = 1, 1.5, or 2) using multinuclear MAS NMR techniques in samples prepared by collaborators at the University of Waterloo. Also presented is a study of the timescales of ion mobility and
energy barriers in the reduced phase, Li$_2$VPO$_4$F using one and two-dimensional $^6$Li exchange spectroscopy.

**1.5.4 Li$_x$VOPO$_4$ (1 ≤ x ≤ 2)**

Oxyphosphates are another class of compounds being considered for high-power battery applications. The synthesis of ε-VOPO$_4$ was first reported by Lim et al. in 1996 from the heating of hydrothermally prepared VPO$_4$·H$_2$O in O$_2$. The resulting ε-VOPO$_4$ has a monoclinic unit cell (space group $P2_1/n$) able to intercalate one Li in a two-phase process at 3.8 V with a specific capacity of 128 mAh/g (theoretical capacity is 159 mAh/g). This new phase has the same structure as triclinic α-LiVOPO$_4$ (space group $P1$) as reported from the high-temperature synthesis by Lavrov et al. Chains of corner sharing VO$_6$ octahedra are connected in three-dimensions by (PO$_4$)$_3^-$ tetrahedra (Figure 1.8). Two crystallographically distinct Li ions sit in the interstitial spaces opposite the phosphate groups. Intercalation of the second Li was shown to occur at a $V^{3+}/V^{4+}$ redox potential of ~ 2.5 V.
Figure 1.8 – Structure of LiVOPO$_4$. Grey polyhedra represent the VO$_6$ octahedral environments and yellow tetrahedra indicate PO$_3^{3-}$ units. Lithium environments are shown as orange and lilac spheres.

Chapter 7 of this thesis offers the first solid-state $^6$,$^7$Li NMR study of Li$_x$VOPO$_4$ ($x = 1, 1.5, \text{ or } 2$) samples prepared by collaborators at the University of Waterloo. The timescales of ion mobility in Li$_2$VOPO$_4$ were determined using one and two-dimensional $^6$,$^7$Li NMR techniques and reveal faster ion dynamics than its Li$_2$VPO$_4$F cousin.

1.5.5 Li$_5$V(PO$_4$)$_2$F$_2$

A newer fluorophosphate material, layered Li$_5$V(PO$_4$)$_2$F$_2$, is generated from the dimensional reduction of $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ with LiF.$^{36}$ The term “dimensional reduction” is in reference to the structure being lowered from the 3D framework to a 2D layered framework.$^{68}$ Li$_5$V(PO$_4$)$_2$F$_2$ crystallizes in monoclinic $P2_1/c$ symmetry with two dimensional sheets of VO$_4$F$_2$-PO$_4$ interleaved with layers of Li ions. Six
crystallographically distinct Li environments are found in this compound, many of which have distorted octahedral coordination. The exception is Li3 and Li5 which are only five coordinate. Li1, Li2, and Li5 comprise the layer of Li ions found between the metal-fluorophosphate sheets, while Li3, Li4, and Li6 occupy interstitial spaces within the metal sheets (Figure 1.9). The high theoretical capacity of 170 mAh/g for this layered phase is accompanied by the possibility of spanning the entire $V^{3+}/V^{4+}/V^{5+}$ redox couple by removal of two Li. A specific capacity of 85 mAh/g was observed for the extraction of one Li with an average voltage plateau of 4.15 V. A second voltage plateau of 4.65 V was reported in microcrystalline phases of $\text{Li}_5\text{V(PO}_4\text{)}_2\text{F}_2/\text{carbon composites}$ raising the specific capacity to 165 mAh/g. $\text{69}$ This second electrochemical process is not reversible due in large part to the structural instability of the $\text{Li}_3\text{V(PO}_4\text{)}_2\text{F}_2$ framework where $\text{V}^{5+}$ is not stable in octahedral coordination. $\text{70}$

![Figure 1.9 – Structure of $\text{Li}_5\text{V(PO}_4\text{)}_2\text{F}_2$. Vanadium centered octahedra (grey) corner share with $\text{PO}_4$ tetrahedra to create 2D layers sandwiching Li ions (coloured spheres)](image_url)
Previous solid-state $^{6,7}$Li NMR studies of this material in the Goward research group resolved all six crystallographic Li ion positions in Li$_5$V(PO$_4$)$_2$F$_2$ and showed ion exchange taking place between many of the environments.$^{69}$ A study of Li$_4$V(PO$_4$)$_2$F$_2$ showed qualitatively that the ion dynamics increased considerably upon removal of one unit of Li.$^{70}$ Chapter 8 of this thesis quantifies the timescale of ion hopping within the fully lithiated phase (prepared by collaborators at the University of Waterloo) using one-dimensional solid-state NMR techniques. Here the large number of possible exchange pairs with different geometries, reveals the structural properties that better accommodate fast ion mobility.

1.6 Summary

In order to better understand the success and failure mechanisms of many of these new cathode materials for Li ion batteries, greater detail regarding the local lithium structure and mobility pathways is needed. Moreover, determination of the timescales and energy barriers of these mobility processes will help to better understand what structural features can enhance or hinder ion diffusion. Multinuclear solid-state NMR is a tool that is sensitive to the local environments of both the mobile ion and the host framework, giving us a powerful tool for identifying these properties. The following chapters demonstrate how solid-state NMR techniques were applied to characterize formation of phase interface regions in LiFePO$_4$ as well as determine the timescales and energy barriers of ion mobility in the multi-Li site materials, Li$_3$Fe$_2$(PO$_4$)$_3$, Li$_2$VPO$_4$F and
Li$_2$VOPO$_4$, and Li$_5$V(PO$_4$)$_2$F$_2$. Overall, identification of the structural constraints that lead to fast or slow kinetics assists in a more targeted development of cathode materials with enhanced electrochemical performance.
1.7 References


(8) Whittingham, M. S. *Science* 1976, 192, 1126.


Chapter 2: Introduction to Solid-State NMR

2.1 Introduction

Solid-state Nuclear Magnetic Resonance (NMR) is the primary spectroscopic method utilized in this thesis to characterize the structural and ion mobility properties of the cathode materials presented in Chapter 1. The present chapter will detail the properties of nuclear spins in an applied magnetic field and the spectral features that arise from materials in the solid-state. Moreover, due to the unpaired electrons sitting on the transition metal center of the materials studied in this thesis, the properties of electron magnetic resonance and subsequent interaction with the observed nuclear spins are detailed.

2.2 Spin Properties of Nuclei in an Applied Magnetic Field

2.2.1 Definition of Nuclear Spin and Magnetic Moment

The atomic nucleus is comprised of protons and neutrons and defined by three numbers: the atomic number (Z), the mass number, and spin quantum number (I). Nuclear spin is quantified by the spin angular momentum vector (I) which related to the magnetic moment vector (µ) of the nucleus as well as the nuclear gyromagnetic ratio (γN) (Equation 2-1),\(^1\).
\[ \mathbf{\mu} = \gamma_N \hbar \mathbf{I} = g_N \mu_N \mathbf{I} \]  
Equation 2-1

where \( \gamma_N \) is also expressed by the nuclear g factor \( (g_N) \) and the nuclear magneton \( (\mu_N) \).

The values for \( I \) and \( \gamma_N \) are unique to a given nucleus and allow nuclei to be distinguished from one another spectroscopically. In this thesis, two isotopes of Li, \(^6\text{Li}\) and \(^7\text{Li}\), as well as \(^{19}\text{F}\) and \(^{31}\text{P}\) were measured. The spin numbers and gyromagnetic ratios of these nuclei are summarized in Table 2.1. Also included is the spin number and gyromagnetic ratio of a free electron, whose influence on nuclear spins is introduced in Section 2.3.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Spin number ((I))</th>
<th>Gyromagnetic Ratio ((10^6 \text{ rad s}^{-1} \text{ T}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^6\text{Li})</td>
<td>1</td>
<td>39.37</td>
</tr>
<tr>
<td>(^7\text{Li})</td>
<td>3/2</td>
<td>103.96</td>
</tr>
<tr>
<td>(^{19}\text{F})</td>
<td>1/2</td>
<td>251.81</td>
</tr>
<tr>
<td>(^{31}\text{P})</td>
<td>1/2</td>
<td>108.41</td>
</tr>
<tr>
<td>(e^-)</td>
<td>1/2</td>
<td>-176085.97</td>
</tr>
</tbody>
</table>

**Table 2.1** – Nuclear spins measured in this thesis with their corresponding spin number \((I)\) and gyromagnetic ratio. Also included is the gyromagnetic ratio of a free electron \((e^-)\).

### 2.2.2 Zeeman Splitting in an Applied Magnetic Field

The interaction between an external magnetic field \(B_0\) and the magnetic moments of the spin system or collection of spins results in the Zeeman interaction. For a static magnetic field applied along the z-axis of the laboratory frame, the Zeeman Hamiltonian, \(\hat{H}_z\), is as follows (Equation 2-2):

\[ \hat{H}_z = g_N \mu_N B_0 I_z \]
\[ \hat{H}_Z = -\gamma \hbar \hat{I}_z B_0 \]  

Equation 2-2

For a given nuclear spin there are \(2I+1\) possible energy states each defined by the quantum number \(m\) (where \(m = I, I-1, I-2, \ldots -I\)). The energies for each spin state are degenerate in the absence of an applied magnetic field but lifted to a value \((E_{I,m})\) when \(B_0\) is present. Operating the spin Hamiltonian on the spin wavefunctions (Equation 2-3),

\[ \hat{H} |I,m\rangle = E_{I,m} |I,m\rangle \]  

Equation 2-3

gives,

\[ E_{I,m} = -\gamma \hbar B_0 m \]  

Equation 2-4

For a nucleus with \(I = \frac{1}{2}\), two possible spin states of \(m = +1/2\) and \(m = -1/2\) give rise to the low energy \(+\frac{1}{2}\) state (termed the \(\alpha\) state) and a high-energy \(-\frac{1}{2}\) state (termed the \(\beta\) state) (Figure 2.1).

Figure 2.1 - Schematic showing the relative population of the energy levels of a spin \(\frac{1}{2}\) nucleus. A Boltzmann distribution governs the \(\alpha\) and \(\beta\) populations (small spheres).
In a large sample of spins, the population of spins aligned with and against the applied field ($N_\alpha$ and $N_\beta$, respectively) is governed by a Boltzmann distribution (Equation 2-5),

$$\frac{N_\alpha}{N_\beta} = \exp\left[\frac{-(E_\alpha - E_\beta)}{k_B T}\right]$$

Equation 2-5

where $E_\alpha$ and $E_\beta$ are the respective energies of the $\alpha$ and $\beta$ states, $k_B$ is the Boltzmann constant, and $T$ is the temperature.

2.1.1 Precesssion and Larmor Frequency

The direction of the spin angular momentum is called the spin polarization axis and when placed in a static magnetic field will precess around the applied field. The rate at which the precession occurs is called the Larmor frequency ($\omega_0$) and is governed by the gyromagnetic ratio and the strength of the applied field (Equation 2-6).

$$\omega_0 = \gamma B_0$$

Equation 2-6

For the nuclei studied in this thesis, experiments were carried out at three different applied fields of 4.70 T, 7.05 T and 11.7 T. The Larmor frequencies of $^{6,7}$Li, $^{31}$P, and $^{19}$F nuclei at the respective fields are summarized in Table 2.2.
Table 2.2 – Summary of magnetic field strengths used in this thesis and the corresponding Larmor frequencies of $^6$Li, $^7$Li, $^{19}$F, and $^{31}$P nuclei.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$\omega_0$ at 4.70 T (MHz)</th>
<th>$\omega_0$ at 7.05 T (MHz)</th>
<th>$\omega_0$ at 11.7 T (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6$Li</td>
<td>29.4</td>
<td>44.1</td>
<td>73.6</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>77.3</td>
<td>115.9</td>
<td>193.2</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>188.3</td>
<td>282.4</td>
<td>470.7</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>81.1</td>
<td>121.6</td>
<td>202.6</td>
</tr>
</tbody>
</table>

In NMR communications the strength of the applied magnetic field is often given as the Larmor frequency of protons at that field. For applied fields of 4.70 T, 7.05 T and 11.7 T, the magnet strength is described as 200 MHz, 300 MHz, and 500 MHz, respectively.

2.2.3 The RF Pulse

The basis of the NMR experiment is the movement of the spin polarization axis by applying radiofrequency (RF) pulses tuned to the Larmor frequency. Through these pulses, a second magnetic field, $B_1$, is generated and able to rotate the net magnetization of the chemical sample away from the $z-$axis towards the $xy-$plane of detection. The RF pulse is defined by its flip-angle, $\theta_{rf}$, and phase, $\phi_{rf}$. For example in a single pulse experiment, rotation of the magnetization from the $+z$-axis to the $-y$-axis requires a flip angle of 90° and a phase of 0, (i.e. a $+x$-pulse). This flip-angle is calibrated by setting a RF power (in Watts) and determining the duration, $\tau_{rf}$, of the RF pulse that maximizes the signal placement along the $-y$-axis (Equation 2-7).
\[ \theta_{rf} = \gamma B_1 \tau_{rf} = \omega_1 \tau_{rf} \]  

Equation 2-7

The Hamiltonian to describe the interaction of the nuclear spin with the \( B_1 \) field is similar to the description for the effect from the static field \( (B_0, \text{Equation 2-2}) \). However in this case, the \( B_1 \) field oscillates along the x-axis, leading to inclusion of the flip angle. The result is a Hamiltonian for nuclear spins under the combined influence of the static \( B_0 \) and oscillating \( B_1 \) field (Equation 2-8).

\[ \hat{H} = -\gamma (\hat{I}_z B_0 + \hat{I}_x B_1 \cos(\omega_1 \tau_{rf})) \]  

Equation 2-8

The length of the RF pulse also determines the range of frequencies that may be excited. For 90° flip angles generated from a short duration pulse of 2.5 \( \mu s \) at relatively high power, a large bandwidth of frequencies is excited. Subsequently a longer 90° pulse duration at low power leads to excitation of a smaller, more selective bandwidth. The use of selective pulses is discussed in greater detail in Chapter 3.

### 2.3 Spin Properties of Unpaired Electrons in an Applied Magnetic Field

A unique property of NMR studies of Li-cathode materials is the presence of unpaired electrons sitting on the transition metal center, \( M \). Unpaired electrons are spin \( \frac{1}{2} \) with an electron magnetic moment \( (\mu_e) \). The electron magnetic moment is dependent on the Bohr magneton, \( \mu_B \), the electron spin angular momentum, \( S \), and the free electron value, \( g_e \) (Equation 2-9).
\[
\mu_e = -g_e \mu_B S
\]  \hspace{1cm} \text{Equation 2-9}

The value of \(g_e\) for a free electron is 2.0023. For unpaired electrons sitting in a crystal lattice, the \(g\) value and subsequent magnetic moment is altered due to spin-orbit coupling between the unpaired electrons and their local environment. Therefore a tensor, \(g\), is used to better represent the orientation dependence of the local field of a given electron spin. Isotropic \(g\)-tensors give rise to \(g\) values equal to 2.0023, while anisotropic \(g\)-tensors result in \(g\)-values that deviate from 2.0023.\(^1\)

To describe the total electron spin value for a paramagnetic ion, the number of unpaired electrons is multiplied by the electron spin. An example of this is for octahedral coordination of \(V^{2+}\) where the three unpaired electrons give a total spin number of \(S = 3/2\). In an applied magnetic field, the electron spins will align with or against the field, similar to a nuclear spin. The resulting Hamiltonian for the Zeeman interaction of an electron spin in an applied magnetic field is therefore expanded to include the \(g\)-tensor (Equation 2-10)

\[
\hat{H}_{eZ} = -\mu_e \cdot B_0 = g \cdot \mu_B S \cdot B_0
\]  \hspace{1cm} \text{Equation 2-10}

Because the lifetime of the electronic spins states along or against the applied field (\(T_{1e}\)) is shorter than the nuclear spin state lifetimes, only the time averaged spin density along the \(+z\)-axis is reported and termed, \(\langle S_z \rangle\). This spin density is proportional to the molar
magnetic susceptibility of the transition metal, $\chi_M$, as well as the strength of the applied field (Equation 2-11).

$$\langle S_z \rangle = -\frac{B_0}{\mu_0 g N_0 \mu_B} \chi_M$$  \hspace{1cm} \text{Equation 2-11}$$

Where $\mu_0$ is the permeability and $N_0$ is Avogadro’s number.

Coupling between $\langle S_z \rangle$ and the nuclear spins being measured is possible and gives rise to very distinct spectral features in NMR measurements. These couplings often dominate the NMR spectra as the electron $g$ values are considerably higher than the nuclear $g$ values, as shown in Table 2.1 through comparison of $\gamma_N$ and $\gamma_e$. Correlating the NMR spectral features to the spin states of the paramagnetic metal center was needed for a better understanding the local structure of the nuclei being investigated in this thesis.

### 2.4 NMR of Solid-state Paramagnetic Materials

For the cathode materials studied in this thesis, the most relevant phase of study is the solid phase, as the electrochemical cycling involves the movement of the Li ions in and out of a crystalline host framework. Therefore powders of each material were measured using solid-state NMR techniques where features not normally observed in the solution state were observed. The fast molecular tumbling of solute and solvent molecules averages the orientation dependence of the local fields giving rise to narrow, well-
resolved spectra. In the solid-state, orientation dependent interactions such as chemical shift anisotropy (CSA) (Section 2.4.1), heteronuclear, homonuclear and electron-nuclear dipole coupling ($D_{ij}$) (Section 2.4.2), and quadrupole coupling ($C_q$) (Section 2.4.3) result in broadened spectra, where identification of distinct crystallographic environments is difficult. Application of Magic Angle Spinning (MAS) techniques can average the orientation dependent terms of the aforementioned interactions, resulting in better-resolved spectra. MAS involves the physical rotation of the sample at an angle ($\theta$) relative to the applied magnetic field.$^4$ By setting $\theta$ to 54.74°, the geometry dependent term, ($3\cos^2\theta - 1$), found in the equations describing CSA, $D_{ij}$, and $C_q$ is averaged to zero. The rotation frequency must be greater than the combined magnitudes of these terms otherwise spinning sidebands are observed. These sidebands are peaks that emerge at integer multiples of the MAS frequency on either side of the isotropic peak, and have a manifold as broad as the frequency of the combined CSA, $D_{ij}$, and $C_q$ contributions to the NMR spectrum.

### 2.4.1 Chemical Shielding and Anisotropy

The applied magnetic fields, $B_0$ and $B_1$, induce currents in the electron clouds surrounding the nuclear spins giving rise to local magnetic fields termed $B_{ind}$. The resonance frequencies resulting from these local fields give rise to the observed chemical shift and is what makes NMR a sensitive probe of local structure and dynamics. The chemical shielding tensor, $\sigma$, used to describe the behaviour of the electron clouds gives rise to the chemical shielding Hamiltonian (Equation 2-12).
\[ \hat{H}_{CS} = \gamma I \cdot \mathbf{\sigma} \cdot B_0 \]  
\hspace{1cm} \text{Equation 2-12}

The shielding tensor, has both symmetric and asymmetric components however, only the symmetric component (\( \sigma^i \)) contributes to the appearance of the NMR spectrum (Equation 2-13).

\[
\sigma^i = \begin{pmatrix}
\sigma_{xx} & \frac{1}{2}(\sigma_{xy} + \sigma_{yx}) & \frac{1}{2}(\sigma_{xz} + \sigma_{zx}) \\
\frac{1}{2}(\sigma_{xy} + \sigma_{yx}) & \sigma_{yy} & \frac{1}{2}(\sigma_{yz} + \sigma_{zy}) \\
\frac{1}{2}(\sigma_{xz} + \sigma_{zx}) & \frac{1}{2}(\sigma_{yz} + \sigma_{zy}) & \sigma_{zz}
\end{pmatrix}
\hspace{1cm} \text{Equation 2-13}

The three principal components, \( \sigma_{xx}, \sigma_{yy}, \) and \( \sigma_{zz} \) define the isotropic shielding, value \( \sigma_{iso} \) (Equation 2-14).

\[
\sigma_{iso} = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3}
\hspace{1cm} \text{Equation 2-14}
\]

Where the anisotropy (\( \Delta \)) and asymmetry (\( \eta \)) of the tensor reflect the symmetry of the local nuclear environment. These values are also defined by the principal components (Equation 2-15 and Equation 2-16, respectively).

\[
\Delta = \sigma_{zz} - \sigma_{iso}
\hspace{1cm} \text{Equation 2-15}
The chemical shielding is manifested in the NMR spectrum through the chemical shift, where the observed NMR signal, $\omega_{cs}$, has contributions from the isotropic, anisotropic and asymmetry parameters. (Equation 2-17),

$$
\omega_{cs} = -\omega_0\sigma_{iso} - \frac{1}{2}\omega_0\Delta\left\{3\cos^2\theta - 1 + \eta\sin^2\theta\cos2\phi\right\}
$$

where, $\theta$ and $\phi$ are the polar angles defining the $B_0$ direction relative to the principal axis of the sample. In NMR experiments of solution state samples, the fast molecular tumbling averages the orientation dependence of the chemical shielding tensor, resulting in a single observed frequency. In a NMR spectrum of a powdered solid-state material, the fixed orientation of the nuclear spins for each the individual crystallites results in a distribution of shifts giving a broad powder pattern. By setting $\theta$ to 54.7° and rotating the sample, the $3\cos^2\theta - 1$ term averages the anisotropic portion of $\omega_{cs}$ to zero. The result is narrowed resonances resembling a solution state spectrum. However, the shape of the powder pattern reflects the site symmetry at the nucleus, making determination of $\Delta$ and $\eta$, important tools for understanding subtle structural features of a solid material.

The observed frequency, $\nu$, is found by adding the linear frequencies of the Larmor and $\omega_{cs}$ values and referencing it to an agreed upon chemical standard with
frequency $\nu_{ref}$ (Equation 2-18). The resulting chemical shift ($\delta_{iso}$) is reported in units of ppm and is a field independent value.

$$\delta_{iso} = \frac{\nu - \nu_{ref}}{\nu_{ref}}$$  \hspace{1cm} \text{Equation 2-18}

The chemical shift tensor has elements that are closely related to, but more easily observed than, the chemical shielding tensor elements. The principal values of the chemical shift tensor are labeled as, $\delta_{11}$, $\delta_{22}$, and $\delta_{33}$, where by convention, $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. The isotropic shift ($\delta_{iso}$) calculated from the average of the three principal components. The shift anisotropy ($\Delta$) and the axial symmetry ($\eta$) are determined using Equation 2-19 and Equation 2-20, respectively.

$$\Delta = \delta_{11} - \delta_{iso}$$  \hspace{1cm} \text{Equation 2-19}

$$\eta = \frac{\delta_{xx} - \delta_{yy}}{\Delta}$$  \hspace{1cm} \text{Equation 2-20}

Different terminologies are used to describe the shifts of materials having different electron structures. For diamagnetic compounds a chemical shift is reported whereas for metals and semiconductors a Knight shift is given. For the highly paramagnetic materials studied in this thesis a paramagnetic shift is observed. The influences on the paramagnetic shift are significantly more complex than the chemical
shifts observed in diamagnetic solid-state compounds and will be described in greater
detailed in Section 2.5.

2.4.2 Dipolar coupling

Dipolar coupling is a phenomenon that can occur between both homonuclear and
heteronuclear spin pairs. In paramagnetic systems, this coupling can also take place
between a nuclear spin and the local field created by the unpaired electron density. A
simplified dipolar Hamiltonian \( \hat{H}_{dd} \) is given in Equation 2-21, for a dipolar coupling
between an \( i \) and \( j \) spin. This interaction is dependent on both the gyromagnetic ratio of
the spins as well as the internuclear distance, \( r_{ij} \).

\[
\hat{H}_{dd} = -\left( \frac{\mu_0}{4\pi} \right) \frac{\gamma_i \gamma_j \hbar}{r_{ij}^3} \hat{I}_i \hat{I}_j (3\cos^2 \theta - 1)
\]

Equation 2-21

Similar to the treatment of large CSA’s, by applying MAS techniques the \( (3\cos^2 \theta - 1) \) term
is averaged to zero. However, if the frequency of spinning is not as large as the
frequency of the dipolar coupling constant (Equation 2-22) combined with the
broadening contribution of CSA then spinning sidebands are observed.

\[
D_{ij} = \hbar \left( \frac{\mu_0}{4\pi} \right) \frac{1}{r_{ij}^3} \gamma_i \gamma_j
\]

Equation 2-22

As mentioned previously, the gyromagnetic ratio values of the nuclear spins studied in
this thesis are significantly lower than \( \gamma_e \) for an electron spin \( (\gamma_e = -1.760 \times 10^{11} \text{ rad s}^{-1} \text{T}^{-1}) \)
for the free-electron \( g \)-value) (Table 2.1). This results in the effects of nuclear-electron
coupling having orders of magnitude greater dipolar couplings than homonuclear or heteronuclear couplings. **Table 2.3** summarizes the dipolar coupling constants found in olivine LiFePO$_4$ for a homonuclear Li-Li contact, heteronuclear Li-P contact, and electron-nuclear contact. The value of $r_{ij}$ for the electron-nuclear coupling was taken as the internuclear distance of the crystallographic Li and Fe sites.

**Table 2.3** – Summary of homonuclear, heteronuclear, and nuclear-electron dipolar coupling constants in LiFePO$_4$

<table>
<thead>
<tr>
<th>Type of Coupling</th>
<th>$r_{ij}$ (Å)</th>
<th>$D_{ij}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homonuclear Li-Li</td>
<td>3.003</td>
<td>670.4</td>
</tr>
<tr>
<td>Heteronuclear Li-P</td>
<td>2.659</td>
<td>1005.9</td>
</tr>
<tr>
<td>Nuclear-Electron Li-Fe</td>
<td>3.281</td>
<td>84053.1</td>
</tr>
</tbody>
</table>

It is evident that the nuclear-electron couplings are significantly larger than either the homonuclear and heteronuclear couplings. Moreover, this calculation is treated as an underestimate of the true electron-nuclear coupling value, as LiFePO$_4$ is Fe$^{2+}$ with a high spin $d^6$ electron configuration resulting in time averaged spin density arising from 4 unpaired electrons on the metal center. The value given in **Table 2.3** is given for a single, free electron, only.

A primary consequence of this coupling is that sideband manifolds in the NMR spectra of paramagnetic spin systems are considerably more substantial than their diamagnetic counterparts. This is demonstrated in **Figure 2.2** where the $^7$Li MAS spectrum of olivine LiFePO$_4$, which has Fe$^{2+}$ in an octahedral $d^6$ electron configuration (giving four unpaired electrons), is compared with the MAS spectra of two isostructural compounds with different electron configurations at the M(2) metal center. The first
compound is the diamagnetic analogue, LiMgPO₄. The second, compound LiMnPO₄, has a higher amount of unpaired electron spin density as Mn²⁺ in high spin d⁵ octahedral coordination giving five unpaired electrons. The ⁷Li MAS spectrum of LiMgPO₄ shows the combined influences of homonuclear and heteronuclear dipolar couplings, quadrupolar coupling and CSA. These interactions give rise to two small sidebands of low intensity. In contrast the MAS spectra of LiFePO₄ and LiMnPO₄ both have large sideband manifolds arising from the strong nuclear-electron dipolar couplings as all other parameters, C_q and CSA, would be near equivalent in these isostructural compounds. Moreover, when the manifolds of the LiFePO₄ and LiMnPO₄ are compared, the larger amount of unpaired electron spin density on the Mn²⁺ center is reflected in the larger sideband manifold of the latter. The difference in the Full-Width at Half-Maximum (FWHM) of the isotropic peaks in LiFePO₄ and LiMnPO₄ is explained in Section 2.6.2.
Figure 2.2 – $^7$Li MAS spectra of LiMgPO$_4$ (bottom), LiFePO$_4$ (middle), and LiMnPO$_4$ (top) with a spinning speed of 25 kHz. The materials are isostructural with one another, differing only in the metal center. LiMgPO$_4$ is a diamagnetic analogue of the paramagnetic LiFePO$_4$ and LiMnPO$_4$. Asterisks denote spinning sidebands.

A secondary consequence of nuclear spins having dipolar couplings with the unpaired electron spin density, is that structural and dynamic information relating to the magnitude of heteronuclear and homonuclear dipolar couplings is overshadowed. This leads to the use of double resonance MAS NMR techniques where $^6$Li-$^{31}$P and $^6$Li-$^{19}$F dipolar couplings can be reintroduced and thus probed more directly. Details of these experiments are outlined in greater detail in Chapter 3.
2.4.3 Quadrupole Coupling

Nuclei having spin greater than $\frac{1}{2}$ are termed quadrupolar. For the spins identified in Table 2.1 both $^6$Li and $^7$Li nuclear spins have this property and possess a nuclear electric quadrupole moment which interacts not only with the applied and local magnetic fields, but also with electric field gradients (EFG) present at the nucleus. The quadrupolar Hamiltonian, describing the coupling between a nuclear electric quadrupole moment ($eQ$) and an electric field gradient tensor ($V$) is presented in Equation 2.29,

$$\hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \hat{I} \cdot V \cdot \hat{I}$$

Equation 2-23

where $e$ is the proton charge and $Q$ is the nuclear quadrupole moment. The value of $Q$ is unique for each quadrupolar nuclear spin as summarized for $^6$Li and $^7$Li in Table 2.4.

Table 2.4 – Summary of spin quadrupole moments for quadrupolar nuclei measured in this thesis.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Quadrupole Moment (Q/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6$Li</td>
<td>-8.0 x $10^{24}$</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>-4.0 x $10^{26}$</td>
</tr>
</tbody>
</table>

Quadrupolar coupling ($C_q$) gives rise to distinct spectral features in NMR spectra, allowing for interpretation of local site symmetry around the nucleus. The magnitude of $C_q$ is calculated from Equation 2-24,

$$C_q = \frac{e^2qzQ}{\hbar}$$

Equation 2-24
Where \( e_{zz} \) is the largest principal axis value of the EFG tensor. The relatively low \( eQ \) values of the \(^6\)Li and \(^7\)Li as well as the dominance of the nuclear-electron dipolar coupling in spectra of materials (as demonstrated in Figure 2.2), make the contributions from quadrupolar coupling largely negligible.

### 2.5 Isotropic Shifts in Paramagnetic Materials

The chemical shielding that results from the interaction of the local nuclear field with electron clouds of unpaired electrons is significantly more complex. The observed paramagnetic signal (\( \delta_P \)) in the cathode materials studied in the subsequent chapters is described by Equation 2-25,\(^6,7\)

\[
\delta_P = -\frac{A_H}{\omega_0 h} \langle S_z \rangle
\]

Equation 2-25

where the hyperfine coupling constant (\( A_H \)) is a measure of how much unpaired electron spin density has transferred to the nucleus of interest. The size and sign of \( A_H \) dictates the size and direction of the paramagnetic shift, making it an important parameter for understanding the origin of many spectral features. \( A_H \) is made up of three contributions: the Fermi-contact interaction (\( A_F \)), the dipolar coupling contribution (\( A_D \)), and the spin-orbital contribution (\( A_L \)) (Equation 2-26).

\[
A_H = A_F + A_D + A_L
\]

Equation 2-26

The hyperfine terms are more simply separated into two contributions: the contact and pseudocontact interactions. \( A_F \) constitutes the former term as it results from the through-
bond coupling between the local fields of the nuclear spin and the unpaired electron density. The combined effects of $A_D$ and $A_L$ arise from through-space couplings of the spin and orbital angular momentum terms, respectively, of the unpaired electron spin density to the nuclear spin.

### 2.5.1 The Contact Shift: Defining the Fermi-Contact Term, $A_F$

The Fermi-contact Hamiltonian ($\hat{H}_F$) is shown in Equation 2-27 where the geometry dependence of the interaction between the nuclear spin ($I$) and the $i$th electron spin ($s_i$) is represented by a vector $r_i$.

$$\hat{H}_F = \frac{16\pi\hbar\gamma_N\beta}{3} \sum_i \delta(r_i) s_i \cdot I$$  \hspace{1cm} \text{Equation 2-27}

The geometry dependent mechanism of this coupling has been shown to follow the Goodenough-Kanamori rules for spin-spin super-exchange.\(^8\)\(^9\) In this thesis, the super-exchange is between the unpaired electron spin density on the transition metal atom (M) and the nuclear spin on the Li or P nuclei being measured. These atoms are joined through the p-orbitals of an intervening anion giving a general geometry of the M-O-Li/P and/or M-F-Li/P found in the phosphate and fluorophosphates cathode materials, respectively. The transition metal centers of materials studied in this thesis, all have octahedral coordination, resulting in a split of the d-orbital into a triply degenerate $t_{2g}$ state, ($d_{xy}, d_{yz}, d_{zx}$) and higher energy doubly degenerate $e_g$ state (with orbitals $d_{x^2−y^2}$ and $d_{zx}$). The coupling between the unpaired electron density to the nuclear spin is
maximized when the M-O-Li/P orbital geometries are at either 90° or 180°. Two mechanisms are used to describe the geometry of the super-exchange as outlined in Figure 2.3.\textsuperscript{10,11} The first mechanism involves the \textit{delocalization} of unpaired electron spin density from the transition metal d-orbitals to the nucleus of interest via an intervening O 2p orbital. In the case of a 90° orbital overlap the M t\textsubscript{2g} orbitals are the source of the electron density and transferred to the s-orbital of the Li or P nuclei via an O p\textsubscript{π} orbital. For the 180° orbital overlap, the e\textsubscript{g} orbitals are the electron density source which is transferred via the p\textsubscript{σ} orbital. The overall result for both of these geometries is the transfer of electron spin density to the s-orbital of the nucleus where the sign is unchanged leading to an increase in the paramagnetic shift. The second mechanism involves the \textit{polarization} of unpaired electrons in the bonding t\textsubscript{2g} or e\textsubscript{g} orbitals by other unpaired electrons sitting on M. This results in the transfer of electron spin density with sign opposite to the metal center thus leading to a decrease in the overall paramagnetic shift at the nucleus of interest.
a) Delocalization Mechanism

$90^\circ$

$180^\circ$

b) Polarization Mechanism

$90^\circ$

$180^\circ$

**Figure 2.3** – Schematic (reproduced from Ref.\textsuperscript{10,11} detailing two mechanisms for electron spin density transfer. a) Shows delocalization of unpaired electron spin density from the M $t_{2g}$ to the empty Li 2s orbital either directly or via the O 2p orbital. This leads to spin density being of the same sign as that on the M center. b) Shows the 90° orbital overlap where the unpaired electron spin density in the e\textsubscript{g} orbital (shown with hatching) polarizes the spin in the t\textsubscript{2g} orbital leading to density transfer to the empty Li 2s orbital of opposite sign to that of the M center. The 180° geometry involves the polarization of the e\textsubscript{g} spins by the t\textsubscript{2g} orbitals, also leading to a transfer of spin density to the Li 2s nucleus of opposite sign to that of the metal center.
Delocalization of unpaired electron spin density onto the nucleus being measured is the more prominent mechanism and the additive nature of these effects (Equation 2-27) leads to a paramagnetic shift range that is far greater than its diamagnetic counterpart. The paramagnetic shifts arising from materials studied throughout this thesis will be discussed in the context of these mechanisms, where the crystallographic information will be relied on for justifying the size and direction of the shifts.

It is noted that this is largely a qualitative assessment of the observed shifts arising from the Fermi-contact interaction, where more quantitative interpretations are provided from Density Functional Theory (DFT) calculations. For Li-oxide materials, DFT methods were used to calculate the amount of spin density around the transition metal center with the observed shifts rationalized from the orbital geometry arguments detailed above. More recent DFT calculations have extended these calculations to predict the contact shift by including the geometry dependent terms of $A_{\text{FC}}$. These calculations allow for contributions from metal centers at intermediate orbital overlap angles to be better incorporated into the determination of the Fermi-contact interaction leading to estimated paramagnetic shifts.

2.5.2 The Pseudo-Contact Shift: Defining $A_D$ and $A_L$

The first contribution to the pseudo-contact shift is the dipolar term $A_D$ which has a Hamiltonian that is also dependent on the vector between the nuclear spin and the electron density (Equation 2-28)
\[
\hat{H}_D = -\left(\frac{\mu_0}{4\pi}\right)\gamma_s \gamma_e \sum_i \left\{ \frac{3(r_i \cdot s_i)(r_i \cdot I)}{r_i^5} - \frac{s_i \cdot I}{r_i^3} \right\} \quad \text{Equation 2-28}
\]

This term does not arise from a through-bond interaction as found in \( \Lambda_F \), but relies on the through-space internuclear distance, \( r_i \). The size of the dipolar shift (\( \delta_{\text{dipolar}} \)) is derived to include the principal components of the electron \( g \)-tensor (\( g_{xx}, g_{yy}, \) and \( g_{zz} \)) (Equation 2-29)

\[
\delta_{\text{dipolar}} = \frac{\beta^2 S(S+1)}{18kT r_{eN}^3} \left\{ [2g_{zz}^2 - (g_{xx}^2 + g_{yy}^2)](1 - 3\cos^2 \theta) \right. \\
\left. + 3(g_{yy}^2 - g_{zz}^2)\sin^2 \theta \cos 2\Omega \right\} \quad \text{Equation 2-29}
\]

where \( r_{eN} \) is the distance between the metal center and the nucleus being observed, \( \theta \) is the angle between the \( z \)-axis and \( r_i \), and \( \Omega \) is the angle between the \( x \)-axis and the projection of \( r_i \) onto the \( xy \)-plane. For isotropic \( g \)-tensors, this term vanishes to zero and there is no dipolar contribution to the observed shift.\(^6,13,14\) Qualitative determination of the \( g \)-tensor for materials studied in this thesis, can be made through evaluation of the symmetry at the metal center. For a symmetrical metal environment, an isotropic \( g \)-tensor is presumed and there is little to no dipolar shift present.\(^6\) For asymmetrical metal centers, the contribution from the dipolar shift is considered.

The orbital term, \( \Lambda_L \), represents the interaction between the nuclear magnetic moment and the magnetic field generated by the orbital motion of the electrons. It is
non-zero for states with net orbital angular momentum (where \( l_i \) is the orbital angular momentum of the \( i \)th electron) (Equation 2-30).

\[
\hat{H}_L = 2\hbar \gamma \beta \sum_i l_i \cdot \frac{I}{r_i^3}
\]

Equation 2-30

Overall, the contribution of this value to the overall shift is considerably smaller as the finite NMR signal is primarily governed by the s-orbital of the nuclear spin, which has zero net angular momentum.\(^6\)\(^12\) Therefore, only the Fermi-contact and dipolar shift contributions are considered in discussions of observed paramagnetic shifts.

2.6 Nuclear Spin Relaxation

2.6.1 Spin-Lattice Relaxation

Once the system has been perturbed by the applied RF field, it will return to thermal equilibrium by a process known as longitudinal or spin-lattice relaxation. The time constant that governs this relaxation is termed \( T_1 \), and can vary greatly depending on the local environment of the spin system being measured. The relaxation can be monitored by the exponential buildup of magnetization along the z-axis (\( M_z \)) as a function of time relative to the magnetization measured at equilibrium (\( M_{ze} \)) (Equation 2-31).
The total relaxation \( T_{1r}^{-1} \) is facilitated by a combination of the interactions with the local surroundings including, dipolar coupling \( T_{1p}^{-1} \), quadrupolar coupling \( T_{1q}^{-1} \), chemical shift anisotropy \( T_{1csa}^{-1} \) as well as spin-rotation \( T_{1sr}^{-1} \) (Equation 2-32).

\[
T_{1r}^{-1} = T_{1p}^{-1} + T_{1q}^{-1} + T_{1csa}^{-1} + T_{1sr}^{-1}
\]  

Equation 2-32

In the solid-state, the first three terms are more important, as the spins are fixed in a crystalline lattice. Moreover, for spin \( \frac{1}{2} \) nuclei, the quadrupolar term is dropped. For the paramagnetic systems investigated in this thesis, there is an additional relaxation contribution from the hyperfine coupling \( T_{1H}^{-1} \) as shown in Equation 2-33.

\[
T_{1H}^{-1} = \frac{2S(S+1)A_H^2}{3\hbar^2} \left[ \frac{\tau_{e2}}{1 + (\omega_I + \omega_S)^2 \tau_{e2}^2} \right]
\]  

Equation 2-33

Where \( \tau_{e2} \) is the sum of the electron exchange rate and electron transverse relaxation rate, and \( \omega_I \) and \( \omega_S \) are the nuclear and electron resonance frequencies, respectively. Overall, the dipolar term has the largest contribution, as the electron-nuclear couplings are significantly larger than any CSA, \( C_q \), and even \( A_H \) contributions. This leads to measured \( T_{1r} \) times on the \( \mu s - ms \) timescale in the paramagnetic systems investigated where in diamagnetic analogues, lattice relaxation times would range from seconds to hundreds of seconds.
When nuclei in different environments undergo site-exchange, there is the observed averaging of the spin-lattice relaxation times. This is the case for $^{6,7}$Li nuclei where the Li ions hop from one crystallographic site to another. Chapter 3 outlines selective inversion experiments used to separate the ion exchange dynamics from the inherent $T_1$ times such that information regarding the local Li environments is accessed.

### 2.6.2 Spin-Spin Relaxation

Similar to longitudinal relaxation along the $z$-axis, transverse relaxation in the $xy$-plane is also observed. This relaxation has a time constant, termed $T_2$.

The importance of this term is highlighted by its influence on the line-width of isotropic resonances of nuclear spins. The FWHM of a peak is defined by $1/T_2$ which for paramagnetic systems, has a dependence on both the hyperfine coupling as well as the spin-lattice relaxation of the electron spins ($T_{1e}$) (Equation 2-34),

$$FWHM = T_2^{-1} = T_{2N}^{-1} + \left( \frac{A_H}{\hbar} \right)^2 \left( \frac{T_{1e}}{8} \right)$$

where $T_{2N}^{-1}$ is the contribution to the linewidth from diamagnetic effects that are largely outweighed by effects of the Fermi-contact dominated hyperfine coupling.

### 2.7 Summary

The nuclear and electron resonance properties outlined in this chapter will serve to better explain the spectroscopic features that arise in the measurement of $^{6,7}$Li, $^{31}$P, and $^{19}$F environments of cathode materials studied in subsequent chapters. Chapter 3 details
specific NMR experiments used throughout this thesis that probe the structural and dynamics origins of the many spectral features observed in these materials.
2.8 References


Chapter 3: Introduction to Solid-State NMR Techniques Used in This Thesis

3.1 Introduction

This chapter outlines specific NMR techniques used throughout this thesis to characterize the structure and dynamics of cathode materials presented in Chapter 1. Rotational-echo, double-resonance (REDOR) measurements are used to reintroduce heteronuclear dipolar couplings that have been averaged by MAS. Measurements of this type allow for relative heteronuclear internuclear distances to be determined and assist in assignment of Li environments. Two-dimensional exchange spectroscopy (2D EXSY) of either $^6$Li or $^7$Li nuclei allow for ion-hopping pairs to be identified in samples having more than one non-equivalent crystallographic environment. Application of these experiments over a variable time and temperature range identifies Li ion hopping pairs and subsequent determination of timescales and energy barriers to be determined. This work is complemented by one-dimensional selective inversion studies (1D SI), which are a simpler means to probe ion dynamics than 2D EXSY studies and require considerably smaller amounts of spectrometer time. Overall, the determined ion-hopping timescales are compared between the materials presented in Chapter 1 where a set of structural parameters observed to enhance or inhibit ion mobility is considered.
3.2 REDOR Measurements

3.2.1 Introduction & Motivation

Assignment of $^6_7$Li NMR resonances to the crystallographic Li sites in paramagnetic materials is an important step towards understanding ion mobility pathways in a host framework. While the Fermi-contact interaction, based on the Goodenough-Kanamori rules, can be used to rationalize the observed shifts using the crystallographic data, NMR experimental tools can be employed to support the assignment.\(^1\)\(^-\)\(^4\) Rotational-echo, double-resonance (REDOR) experiments probe the relative internuclear distance between a heteronuclear spin pair, correlating the Li ions to atoms in the host framework.\(^5\)\(^,\)\(^6\) REDOR in this thesis is also used to measure Li ion dynamics in LiFePO\(_4\), as changes to the Li-P dipolar couplings are attributed to mobility of the Li ion within the framework.\(^7\) In this chapter, $^6$Li\{$^3$P\} REDOR measurements of LiFePO\(_4\) will be used as an illustrative example, where $^6$Li is the observed spin and $^3$P is the dephased nucleus. However, for the Li-fluorophosphate material, Li\(_2\)VPO\(_4\)F, studied in Chapter 6, $^6$Li\{$^{19}$F\} REDOR measurements are used to support resonance assignments made initially from the Fermi-contact interaction.

3.2.2 $^6$Li\{$^{19}$F\} and $^6$Li\{$^3$P\} REDOR Experiments

The basis of the REDOR experiment is the measurement of spectral signal intensity before and after the perturbation of a dipolar coupled heteronuclear partner. Figure 3.1 shows the dipolar interaction between the local fields of a $^3$P-$^6$Li spin pair separated by a distance, $r$. Here the $z$-component of the local field of the P nuclei ($B_{loc}^z$)
is influenced by the Li-spin, (and vice-versa) whereby perturbation of one (in this case $^{31}\text{P}$) using a 180° ($\pi$) pulse results in a change of sign of the $^{31}\text{P}$ local field felt at the $^6\text{Li}$ spin. The resulting $^6\text{Li}$ signal is attenuated relative to its magnitude in the absence of $^{31}\text{P}$ perturbation.

**Figure 3.1** – Illustration styled after a figure from Gullion *et al.* showing the influence of the $^{31}\text{P}$ local field on the $^6\text{Li}$ spin. Application of a $\pi$-pulse on the $^{31}\text{P}$ spin changes the direction of the local field at the $^6\text{Li}$ spin, causing an attenuation of the $^6\text{Li}$ magnetization aligned along the z-direction.

Initial Spin-Echo, DOuble-Resonance (SEDOR) measurements were applied to stationary samples, where the spins being detected (in our case $^6\text{Li}$) are measured first using a spin-echo sequence without perturbation to the heteronuclear spin partner (i.e. $^{31}\text{P}$) giving rise to a spectrum with intensity $S_0$ (**Figure 3.2**, top). The $^6\text{Li}$ environment is then measured again, but this time with a train of $\pi$ pulses applied to the $^{31}\text{P}$ spins giving rise to a $^6\text{Li}$ spectrum with intensity, $S$ (**Figure 3.2**). The duration between the $\pi$-pulses is stepped over a series of experiments to probe dipolar coupling constants of different magnitudes (and therefore a range of internuclear distances). Rotational-Echo, DOuble Resonance measurements were later introduced as an expansion of SEDOR to systems
where sample rotation was necessary.\textsuperscript{5,6} This is true for our case where MAS is needed to resolve the different crystallographic Li sites. This however averages the orientation dependence of the dipolar couplings. REDOR therefore synchronizes the spacing of the $^{31}$P $\pi$-pulses as integer multiples (N) of the rotor-period ($\tau_R$) which reintroduces the dipolar coupling lost through MAS, while still allowing for distinction between the $^6$Li peaks.

Figure 3.2 – Example of a $^6$Li-$^{31}$P REDOR experiment.

Over a series of experiments, the normalized difference in $^6$Li signal intensity ($[S_0-S]/S_0$) is measured as a function of the dipolar evolution time ($N\tau_R$). The result is a REDOR buildup curve, shown in Figure 3.2, where the strength of the buildup is proportional to the strength of the dipolar coupling. For multi-site materials, this provides a relative...
picture of which Li resonances have the shortest and longest Li-P or Li-F contacts, and thus assists in the assignment of Li resonances to crystallographic sites in the host framework.

3.2.3 Simulations Using SIMPSON

REDOR experiments are most often used to measure the internuclear distances in materials where crystallographic data is unavailable (such as glasses). This is determined by modeling REDOR buildup curves for a given spin system, using a program such as SIMPSON. This program allows the user to refine spin systems, nuclear interactions, RF irradiation, etc. to generate simulated REDOR curves allowing for comparison to the experimental data.

For very complicated spin systems where there is more than one dipolar coupling pair, accurate modeling in SIMPSON presents a challenge. It was shown by Bertmer et al., that SIMPSON curves are multi-spin and geometry independent in the initial portion of the buildup curve, where \(0 \leq [S_0-S]/S_0 \leq 0.3\). Moreover, it was later shown that limiting the simulated curve to this region also excluded complications from pulse imperfections and finite pulse length. Therefore, for spin systems studied in this thesis, only the \(0 \leq [S_0-S]/S_0 \leq 0.3\) region of the experimental curve will be considered.

3.2.4 REDOR Measurements of Paramagnetic Materials

A complication that arises in \(^6\text{Li}^{31}\text{P}\) REDOR experiments of paramagnetic materials, is that the broad resonances of the \(^{31}\text{P}\) and \(^{19}\text{F}\) nuclei are often not completely

63
excited by the applied $\pi$-pulses. This is demonstrated in Figure 3.2 where the REDOR buildup of a paramagnetic material is compared with its simulated SIMPSON curve. Even in the $0 \leq [S_0-S]/S_0 \leq 0.3$ there is considerable deviation of the experimental results from the idealized curve. We therefore only consider REDOR results as relative to one another within a single experiment and do not make absolute determinations of dipolar coupling values and or internuclear distances.

Very short $T_2$ and $T_1$ times of paramagnetic resonances leads to loss of magnetization of the perturbed and measured spins at long dipolar evolution times. This further warrants the exclusion of data found beyond the $0 \leq [S_0-S]/S_0 \leq 0.3$ limit, as magnetization at longer dipolar evolution times is less coherent.

3.2.5 REDOR for Studying Ion Dynamics

Previous studies in our group have evaluated site specific dynamics in monoclinic Li$_3$V$_2$(PO$_4$)$_3$. The study was performed in a temperature range where Li site exchange was known to be “frozen” out based on activation energies determined from 2D NMR exchange studies. The observed attenuation of the $^6\text{Li}\{^{31}\text{P}\}$ REDOR curve from the static simulated case was therefore attributed to site-specific rattling rather than from Li diffusion. In this thesis, $^6\text{Li}\{^{31}\text{P}\}$ REDOR measurements were performed on samples of LiFePO$_4$ in a temperature range where thermally activated Li ion diffusion (rather than site rattling) is observed in other Li intercalation compounds. By evaluating this temperature range, thermally activated Li ion mobility in LiFePO$_4$ is monitored as a
weakening of the Li-P dipolar couplings resulting in attenuated REDOR buildup curves at higher temperatures.

3.3 $^{6,7}$Li MAS Two Dimensional Exchange Spectroscopy

3.3.1 Introduction & Motivation

Two-dimensional exchange spectroscopy (2D EXSY) is used throughout this thesis to identify ion hopping pairs in materials having more than one crystallographically distinct Li environment. These measurements allow for the timescales and energy barriers of the hopping processes to be determined leading to a better understanding of the structural constraints that enhance or inhibit ion mobility. This section provides an introduction to 2D NMR measurements and how they can be used to identify ion hopping pairs and quantify the timescales and energy barriers of the exchange processes.

3.3.2 2D NMR Measurements

Two dimensional NMR measurements were first introduced by Kumar et al. in 1975. Since then, the field of multi-dimensional NMR spectroscopy has found widespread application in a large range of materials and biomaterials. The basic principle of the 2D NMR experiments is the measurement of two time variables, $t_1$ and $t_2$, constituting the observed signal, $s$, which is Fourier transformed to yield a 2D spectrum with two frequency dimensions, $\omega_1$ and $\omega_2$, respectively. The duration of the two
time variables is best described by partitioning the 2D experiment into three parts as shown in Figure 3.3.22

![Figure 3.3](image)

**Figure 3.3** – Schematic showing the partitioning of the time axis in a 2D NMR experiment.

The preparatory period allows the system to adjust to an appropriate set of initial conditions. During the evolution period, the system evolves under the first Hamiltonian, $\hat{H}_1$, which defines the time domain, $t_1$. For the detection period, the spins develop further under the second time domain, $t_2$, with Hamiltonian, $\hat{H}_2$. During this time the transverse magnetization, $M_{xy}(t_1, t_2)$ (or $s(t_1, t_2)$) is detected and Fourier transformed giving the spectral signal, $S(\omega_1, \omega_2)$. The detection of $t_2$ is stepped over a series of experiments where $t_1$ is varied. The resulting 2D spectrum shows $t_1$ transformed into the indirect dimension (or F1 dimension) and $t_2$ producing the F2 or direct dimension.

### 3.3.3 2D NMR to Study Chemical Exchange

To study Li ion hopping in the materials presented in Chapter 1, the 2D Exchange Spectroscopy (EXSY) experiment, proposed by Jeener *et al.*24 was used (Figure 3.4).
Figure 3.4 – Pulse sequence for a 2D EXSY experiment. 90° pulses are shown as black rectangles.

This experiment is an expansion of the 2D NMR experiment outlined in the previous section but has an added time domain, referred to as the mixing period ($\tau_{\text{mix}}$), where the chemical exchange processes are allowed to evolve. The first 90° pulse creates initial transverse magnetization where the spins then evolve at their characteristic precession frequency during $t_1$ and are stored with their respective “spin label”. The second 90° places the magnetization back onto the longitudinal axis, where during the mixing period, the chemical exchange processes take place and the spins acquire the precessional frequency of their new environment. The third 90° places the magnetization back on the $xy$-plane where detection of the new frequency takes place under $t_2$. The initial spin label, stored under $t_1$, gives rise to a 2D spectral signal of $S(\omega_1, \omega_1)$, identified as a diagonal peak. The signal detected after the mixing period has a 2D spectral signal of $S(\omega_1, \omega_2)$ and is referred to as a crosspeak (Figure 3.5). Crosspeaks appear on both sides of the diagonal with spectral coordinates of both $S(\omega_1, \omega_2)$ and $S(\omega_2, \omega_1)$. If no exchange takes place, then no crosspeaks evolve under $\tau_{\text{mix}}$. 
Figure 3.5 – Schematic of a 2D EXSY spectrum for a 3-site material, A, B, and C. Diagonal peaks of the A, B, and C signals stored during F1 are shown as red, yellow, and blue circles. Crosspeaks evolving from A-C and B-C exchange are shown as green and purple circles on either side of the diagonal region.

A drawback of 2D EXSY measurements appears in systems having slow exchange where single-stage hops are difficult to distinguish from multi-site hops at long mixing times. This is not a problem for two-site materials undergoing a single exchange process, but for the three site example of Figure 3.5, at longer mixing times, exchange between A and B could arise from a site hop from A to B to C making an accurate, quantitative determination of the exchange rates difficult. For the present thesis this is not considered an issue as the mixing times in the paramagnetic solids are limited by the short spin-lattice relaxation of the Li ions. It is a more likely scenario in the regime of

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68
slow exchange, that analysis is made less accurate by loss of signal intensity at longer mixing times.

3.3.4 Quantification of Ion-Hopping Timescales using 2D EXSY

To determine the timescales of chemical exchange from 2D EXSY measurements in systems undergoing fast ion exchange (such as Li$_3$Fe$_2$(PO$_4$)$_3$, Chapter 5), the mixing time is stepped over a series of experiments and the volume of the crosspeak measured. An exponential buildup of crosspeak volume as a function of mixing time is fit to yield a correlation time, $\tau_c$, of the exchange process. An Arrhenius or Eyring analysis of the inverse correlation times over a variable temperature range produces the energy barrier.

Previous work has used 2D $^6,^7$Li 2D EXSY as a means to understand and quantify timescales of Li ion exchange of intercalation materials that include Li$_4$SiO$_4$, LiMn$_2$O$_4$, Li$_3$V$_2$(PO$_4$)$_3$, and more recently Li$_3$VF$_6$.

Qualitative $^6$Li 2D EXSY measurements are used in Chapters 6, 7, and 8, to identify hopping pairs in Li$_2$VPO$_4$F, Li$_2$VOPO$_4$, and Li$_3$V(PO$_4$)$_2$F$_2$, respectively. A quantitative analysis of these systems using 2D EXSY was made difficult by the slower exchange times between the ion sites. The short $T_1$ times of the $^6,^7$Li spins limit the mixing times to regions where sufficient buildup of crosspeak intensity as a function of mixing time cannot be reached. While extension of the mixing period beyond the longest $T_1$ value of the spins is possible, it leads to a more complicated determination of the hopping rates and subsequent energy barriers. The next section outlines a set of one-
dimensional experiments that overcome this limitation and are a more simplified approach to determining timescales of ion hopping in materials of this type.

3.4 $^{6,7}$Li One-Dimensional Selective Inversion Measurements

3.4.1 Introduction & Motivation

The 2D EXSY experiments provide a clear and visually convincing measurement of ion exchange. However, along with the complications imposed by short spin-lattice relaxation, generating enough data to determine the timescales and energy barriers of ion exchange requires hundreds of hours of spectrometer time. It was therefore a goal of this thesis to apply more time and cost effective methods for determining timescales of ion mobility where the short $T_1$ and $T_2$ times placed fewer limitations on the data analysis. This led to the use of 1D $^{6,7}$Li Selective Inversion (SI) experiments as a means to expand the determination of ion-hopping timescales to more slowly exchanging materials, and also reduce the required spectrometer time to approximately one-fifth what is needed for 2D EXSY experiments. In the 1D measurements, the relaxation of a selectively inverted spin is monitored as function of both the inherent $T_1$ properties as well as the exchange processes taking place with non-inverted spin(s). Conversely, non-inverted spin(s) showed attenuation of signal intensity as a function of time during the period where ion exchange was the dominant mechanism for relaxation of the inverted spin.$^{29,30}$ The experimental data is modeled in a program such as CIFIT to yield accurate exchange
timescales. CIFIT is a C program based on McClung’s SIFIT (Selective Inversion FIT) and is introduced in sub-section 3.4.3.\textsuperscript{32}

This section outlines the principles of relaxation of selectively inverted spins as well as highlights the mathematical model used by CIFIT to fit the experimental data and separate the rate constant of exchange from the inherent $T_1$. \textsuperscript{6}Li 1D selective inversion experiments are applied to quantify the timescales of ion-hopping in Li$_2$VPO$_4$F, Li$_2$VOPO$_4$, and Li$_5$V(PO$_4$)$_2$F$_2$ (Chapters 6, 7, and 8, respectively). This is the first application of the SI measurement to paramagnetic systems and subsequently expands the range of materials whose dynamics can be measured. Comparison of timescales arising from different frameworks gives a more comprehensive picture of the structural parameters that enhance or inhibit ion mobility in these electrochemically active materials.

3.4.2 One-Dimensional Selective Inversion Experiments

One-dimensional \textsuperscript{6}Li Selective Inversion methods are relaxation-type experiments that monitor the effect of a chemical exchange process (or processes) on the magnetization’s return to equilibrium. This experiment works by selectively inverting a site known to undergo exchange ion exchange with other spins in the lattice. The return to equilibrium of the inverted site is measured as a function of time (in this study it is termed the mixing time, $\tau_{\text{mix}}$). In a multi-spin system, a selectively inverted spin ($i$) will relax (R) due to the combined effects of inherent spin-lattice ($T_1$) relaxation time as well as the sum of the
rate constants \( (k) \) associated with each exchange process taking place with the measured spin (Equation 3-1).$^{33}$

\[
R_i = \frac{1}{T_{1i}} + \sum_{i \neq j} k_{ij}
\]

Conversely, the non-inverted spin(s) \( (j) \) will experience an attenuation of signal intensity as a function of mixing time during the period where chemical exchange is taking place. This results in a characteristic “transient” curve for the non-inverted spin. This is shown in Figure 3.6 for the selective inversion experiment of a two site, A-B system. Here A is the inverted site with both signals measured over a mixing time range of 5 µs to 150 ms.

Figure 3.6 – Example of data collected using \(^6\)Li SI experiments over a variable mixing time range. Inversion of Peak A (highlight in green) returns to equilibrium due to the combined effects of inherent \( T_1 \) as well as exchange with Peak B (highlighted in purple). This results in a characteristic “transient” curve for Peak B (left). Error bars on the integration values are within the size of the data points.
The initial portions of the buildup and transient curves are governed by the rate of the ion hopping process. The latter portion of the curves is dominated by the inherent $T_1$ of the spins. The rate information is separated from the $T_1$ properties by fitting the data to a simulated curve generated through a program such as CIFIT.\textsuperscript{33} The mathematical model utilized by CIFIT for accurate determination of these parameters is outlined in section 3.4.3.

The experimental picture of a selective inversion measurement is illustrated in Figure 3.7. The initial inversion step is followed by a mixing period where the chemical exchange processes take place, similar to 2D EXSY measurements. Signals from both the inverted and non-inverted sites are measured as a function of mixing time over a series of 1D experiments. In this thesis, two pulse sequences having different inversion methods were used for measurement of timescales and energy barriers of ion hopping in a series of materials. The details of these methods are given in sections 3.4.4.1 and 3.4.4.2.

**Figure 3.7** – Schematic showing the basic principle of a selective inversion experiment. The selective inversion period creates the initial conditions where one of the environments known to undergo ion-exchange is selectively inverted. This is followed by the mixing period where the return to equilibrium of the inverted peak is measured as a function of time. Detection of the signal at different mixing times gives rise to a buildup curve of the inverted site and transient curve(s) for non-inverted spin(s).
3.4.3 CIFIT

CIFIT takes a table of observed intensities for all spins as a function of mixing time and determines a key set of parameters: the jump rate \( k \) of each chemical exchange process, spin-lattice relaxation times in the absence of chemical exchange \( T_1 \), and the magnetization values from initial to equilibrium conditions (i.e. from \( M_i(0) \) to \( M_i(\infty) \)). The primary mathematical model used by the CIFIT program is a rate matrix describing the relaxation of magnetization for a system with \( n \) sites (Equation 3-2).

\[
\begin{pmatrix}
M_1(\infty) - M_1(t) \\
\vdots \\
M_n(\infty) - M_n(t)
\end{pmatrix} = \exp(-At)
\begin{pmatrix}
M_1(\infty) - M_1(0) \\
\vdots \\
M_n(\infty) - M_n(0)
\end{pmatrix}
\]

Equation 3-2

where,

\[
A = \begin{pmatrix}
R_{11} & -k_{21} & -k_{31} & \cdots & -k_{n1} \\
-k_{12} & R_{22} & -k_{32} & \cdots & -k_{n2} \\
-k_{13} & -k_{23} & R_{33} & \cdots & -k_{n3} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
-k_{1n} & -k_{2n} & -k_{3n} & \cdots & R_{nn}
\end{pmatrix}
\]

Equation 3-3
and where the relaxation \( R_{mn} \) is defined as the \( T_1 \) of the \( n^{th} \) spin plus the sum of the rates for each exchange process in which that spin participates (Equation 3-1).

To simplify this analysis for the 2-spin example of an ion hopping process, introduced in Figure 3.6, we will first define both the exchange process and the equilibrium expression (Equation 3-4 and Equation 3-5, respectively).

\[
A \xrightarrow[k_{AB}]{k_{BA}} B \quad \text{Equation 3-4}
\]

\[
K = \begin{bmatrix} B \\ A \end{bmatrix} \quad \text{Equation 3-5}
\]

where \( k_{AB} \) is the rate constant for the forward hop from A to B, and \( k_{BA} \) describes the reverse hop. The solution to the exchange matrix is now simplified to give Equation 3-6

\[
\begin{bmatrix} M_A(\infty) - M_A(t) \\ M_B(\infty) - M_B(t) \end{bmatrix} = \exp(A_{AB}t) \begin{bmatrix} M_A(\infty) - M_A(0) \\ M_B(\infty) - M_B(0) \end{bmatrix} \quad \text{Equation 3-6}
\]

where,

\[
A_{AB} = \begin{bmatrix} -\frac{1}{T_{1(A)}} - k_{AB} & k_{BA} \\ k_{AB} & -\frac{1}{T_{1(B)}} - k_{BA} \end{bmatrix} \quad \text{Equation 3-7}
\]
When the concentrations of the two spins are equal, and the system has reached equilibrium, the rates of the forward and reverse processes are equal. The rate constants \(k_{AB}\) and \(k_{BA}\), therefore, will be equal as well. It is now more convenient to evaluate the exchange process from the standpoint of the equilibrium constant \((K)\) rather than the rate constants themselves. The solution to the exchange matrix can then be written where T\(_1\) relaxation is now ignored and the rate is fit as a single parameter (Equation 3-8).

\[
\frac{\partial}{\partial t} \begin{pmatrix}
M_A(\infty) - M_A(t) \\
M_A(\infty) - M_A(t)
\end{pmatrix} = -k_{AB} \begin{pmatrix}
K & -1 \\
-K & 1
\end{pmatrix} \begin{pmatrix}
M_A(\infty) - M_A(t) \\
M_B(\infty) - M_B(t)
\end{pmatrix}
\]

Equation 3-8

CIFIT works to adjust this mathematical model until the sum of the squares of the differences between the experimental and modeled data is minimized.

### 3.4.4 Experimental Methods For Selective Inversion

In this thesis, two experimental methods were used to selectively invert \(^6\)Li spins known to undergo ion hopping with non-equivalent Li partners. The first inversion method evaluated is referred to as 1D EXSY and is limited to 2-site exchange systems. It is the method applied to determine the timescales and energy barriers of ion hopping in the 2-site \(\text{Li}_2\text{VPO}_4\text{F}\) (Chapter 6). The second method uses a Gaussian Shaped Pulse (SP) which is placed on resonance to a site chosen for selective inversion. This method is applicable to multi-exchange systems and is therefore used to study ion hopping timescales in the 3-site \(\text{Li}_2\text{VOPO}_4\) (Chapter 7) and 6-site \(\text{Li}_5\text{V(PO}_4\text{)}_2\text{F}_2\) (Chapter 8).
3.4.4.1 $^6\text{Li} \text{ 1D EXSY}$

Figure 3.8 illustrates the pulse sequence for selective inversion using the 1D EXSY method. Selective inversion is accomplished during the $90^\circ - \tau_1 - 90^\circ$ step where the carrier frequency is set on-resonance to the site chosen for inversion ($i$). The delay period, $\tau_1$, is dependent on the frequency difference between the site of inversion ($i$) and its exchange partner ($j$) (specifically, $1/[2\Delta \nu_{ij}]$).$^{29,30,34}$ The on-resonance spin is selectively inverted following the second $90^\circ$ pulse, while its exchange partner is placed along the $+z$-axis. The mixing time ($\tau_{\text{mix}}$) is stepped over a series of experiments with the latter delay time being long enough to ensure relaxation back to equilibrium. Due to the dependence of $\tau_1$ on the frequency difference between the two spins, it is not possible to extend this inversion technique beyond a 2-site, 1-exchange process system, as the initial conditions of a third site are not established. The next section discusses an inversion method that allows for systems having a higher number of ion-hopping processes to be measured.

![Figure 3.8](image)

Figure 3.8 – Schematic showing the pulse sequence for a 1D EXSY experiment.
3.4.4.2 Selective Inversion Using Shaped Pulse

A second inversion method, familiar to the solution-state NMR community, is used to expand SI experiments to materials studied in this thesis that have multiple-exchange pairs.\textsuperscript{31,33,35,36} Here the initial $90^\circ - \tau_1 - 90^\circ$ of the 1D EXSY sequence, is replaced with one long, soft, Gaussian pulse, placed on-resonance to the site chosen for inversion (Figure 3.9). The bandwidth of the Gaussian pulse ensures inversion of only one of the sites undergoing ion exchange, leaving all other sites unperturbed. This experimental approach will be referred to as the Shaped Pulse (SP) method. A drawback to this method is that the shaped pulse can become very long (500 $\mu$s to 1 ms) for the desired bandwidth to be reached. In paramagnetic systems these pulse lengths are on the order of the relaxation time of the spin-chosen for inversion, and competition between complete inversion and relaxation results. Chapter 7 elaborates on this topic through the $^{6}$Li 1D SP study of Li$_2$VOPO$_4$ and the comparative $^{6}$Li 1D EXSY versus $^{6}$Li 1D SP study of Li$_2$VPO$_4$F
Figure 3.9 – Schematic showing the pulse sequence for selective inversion where a shaped pulse is employed to selectively invert an on-resonance pulse.

Chapter 7 uses the 3-site material, Li\(_2\)VOPO\(_4\), to illustrate how the AB, AC, and BC hopping rates constant can be determined accurately from separate experiments where either A, B or C is inverted. Chapter 8 extends the method to a more complicated spin system, Li\(_5\)V(PO\(_4\))\(_2\)F\(_2\) where due to low resolution, only one site in an exchange pair can be selectively inverted.

Overall, the use of selective inversion experiments results in the timescales and energy barriers to be determined in materials that are of considerable interest for battery applications.

3.5 Summary

In this thesis, a combination of the three experimental methods described above is used to identify and quantify the structural and dynamic features of cathode materials for
Li ion batteries. Gathering this information for a series of Li-intercalation materials allows for a comparison of key parameters that inhibit or enhance Li ion mobility. These parameters include ion internuclear distance, area of the bottleneck for diffusion, as well the bond sum valence of the ions. $^6\text{Li}\{^{31}\text{P}\}$ and $^6\text{Li}\{^{19}\text{F}\}$ REDOR measurement are employed for Li site assignments as well providing a qualitative look at changes to dipolar couplings brought on by ion mobility in Li$_2$VPO$_4$F and LiFePO$_4$, respectively. $^6,^7\text{Li}$ 2D EXSY experiments are used to identify and quantify timescales of ion exchange in many of the multi-Li site materials including Li$_3$Fe$_2$(PO$_4$)$_3$. Lastly, 1D $^6,^7\text{Li}$ selective inversion measurements are investigated for quantification of timescales of exchange in Li$_2$VPO$_4$F, Li$_2$VOPO$_4$, and Li$_5$V(PO$_4$)$_2$F$_2$. This is shown to be a more accurate and time efficient method for determining these values than analogous 2D EXSY experiments.
3.6 References


(2) Kanamori, J. *Progress in Theoretical Physics* 1957, 17, 177.


Chapter 4: Solid-State NMR Studies of the Olivine Family of Phosphate Cathode Materials

4.1 Introduction

This chapter is compromised of three sections that all together present results from $^6$Li and $^{31}$P MAS NMR measurements of olivine LiMnPO$_4$ and Li$_x$FePO$_4$ ($x = 0, 0.5, 1.0$). The first section details a comparison of the $^7$Li and $^{31}$P MAS spectra of LiMnPO$_4$ and LiFePO$_4$ phases where the different electron configurations at the transition metal center give very different spectra for these isostructural materials. The second section briefly discusses the challenges encountered when determining properties of ion mobility in the olivine phases as only a single crystallographic Li site is present and these phases are highly paramagnetic. The last section details the characterization of Li environments and phase transformations in 50% delithiated 0.5LiFePO$_4$:0.5FePO$_4$. Here, the transformation of a biphasic 0.5LiFePO$_4$:0.5FePO$_4$ material to the solid solution Li$_{0.5}$FePO$_4$ at high temperature is shown using $^{31}$P static measurements.

The bulk of this latter section was published in Physical Chemistry Chemical Physics (2011, 13, 5171-5177) with co-authors I. Heinmaa, B. L. Ellis, L.F. Nazar, and G.R. Goward. Brian Ellis prepared samples of LiFePO$_4$ ($x = 0.0, 0.5, 1.0$) in the research lab of Prof. Nazar at the University of Waterloo. Ivo Heinmaa supervised NMR collection at the National Institute of Chemical Physics and Biophysics (NICPB) in Tallinn, Estonia. Prof. Goward was the principal investigator of this project.
4.2 Experimental

4.2.1 Sample Preparation

Samples studied in this thesis were prepared at McMaster University and also by collaborators at the University of Waterloo. Samples prepared at the University of Waterloo include Li$_x$FePO$_4$ (where $x = 0.0, 0.5, 1.0$). Here natural abundance olivine LiFePO$_4$ (92.58% $^7$Li, 7.42% $^6$Li) samples were prepared via a modified hydrothermal synthesis first described by Yang et al.$^1$ Briefly, $(\text{NH}_4)_2\text{Fe}($SO$_4)_2$$\cdot$6H$_2$O (Alfa Aesar), H$_3$PO$_4$ (Fisher), LiOH•H$_2$O (Alfa Aesar) and ascorbic acid (Sigma Aldrich) were combined in a 1:1:3:0.1 molar ratio and the reagents were stirred in a sealed 45 ml Parr autoclave at $190^\circ$C for 8 hours. The ascorbic acid acts as an in situ reducing agent.$^2$ The solid product was filtered and dried under vacuum at $90^\circ$C for 18 hours. The as-prepared LiFePO$_4$ was oxidized to various compositions of xLiFePO$_4$:(1-x)FePO$_4$ ($x = 0.5, 0.0$) using $x$ NOBF$_4$. The reagents were stirred in acetonitrile under an inert atmosphere for one hour. X-ray diffraction was performed on a Bruker D8-Advance powder diffractometer using Cu-Kα radiation ($\lambda = 1.5405$Å) from $2\theta = 10$ to 70 degrees at a count rate of 1 sec per step of 0.02°. The reflections were indexed using DICVOL91 software. LiFePO$_4$ samples were gold coated and examined in a LEO 1530 field emission scanning electron microscope (FESEM) instrument equipped with an energy dispersive X-ray spectroscopy (EDX) attachment. Images were recorded at 15 kV with a back-scatter electron detector.
LiMnPO$_4$ and $^6$Li enriched LiFePO$_4$ for $^6$Li$^{31}$P REDOR measurements were prepared at McMaster University via the hydrothermal methods of Yang et al.$^1$ The starting materials, MnSO$_4$·H$_2$O, FeSO$_4$·7H$_2$O (98% Sigma Aldrich), H$_3$PO$_4$ (85% Fisher), LiOH ($^6$Li enriched, 99 %), and ascorbic acid (Aldrich) were combined in a ratio of 3:1:1:0.1 with water added to make a 67% filled volume. $^6$Li-enriched samples were prepared using $^6$LiOH prepared in house (Cambridge isotopes $^6$Li metal). The concentration of MSO$_4$·xH$_2$O was 0.75 M to ensure smaller particle size.$^3$ Samples were sealed in a 23 ml Parr reactor and placed in an oven for 5 hours at 190°C. Final products were collected by vacuum filtration and dried at 60 °C under vacuum. Samples were characterized using a PANalytical diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å). Data was collected from 15 – 70 ° in 2θ step size of 0.008 with a step time of 100 s. The reflections were indexed in agreement with the literature.$^4$

4.2.2 Solid-State NMR

NMR measurements were carried out at both McMaster University and the National Institute for Chemical Physics and Biophysics (NICPB) in Tallinn, Estonia. Measurements carried out at McMaster University include room temperature 1D $^7$Li and $^{31}$P MAS measurements of LiFePO$_4$ and LiMnPO$_4$ presented in Sections 4.3.1, 4.3.4, and 4.3.4.1. Here, a Bruker AV300 spectrometer was used with $^{31}$P and $^7$Li Larmor frequencies of 121.8 MHz and 116.64 MHz, respectively. MAS measurements were made using a custom-built 1.8 mm probe with spinning speeds of 25 or 40 kHz. $^7$Li and $^{31}$P 1D spectra were acquired using a Hahn-echo pulse sequence ($90^\circ – \tau – 180^\circ$) with 90° pulses ranging from 2.0 to 2.5 µs and recycle delays of 50-200 ms. Spin-lattice
relaxation times were acquired using a spin inversion recovery pulse sequence, with a variable delay list stepped over 16 experiments from 5 µs to 150 ms.

$^6\text{Li}\{^{31}\text{P}\}$ REDOR (section 4.3.2) and $^{31}\text{P}$ static high temperature experiments (section 4.3.3) were carried out at the NICPB on a Bruker AMX200 spectrometer. For the REDOR measurements a custom-built double resonance wide bore probe supporting 1.8 mm rotors capable of MAS frequencies up to 45 kHz was used. $^6\text{Li}\{^{31}\text{P}\}$ REDOR spectra of LiFePO$_4$ were collected at MAS = 25.021 (± 0.002) kHz with a $^{31}\text{P}$ 180° pulse of 3.5 µs and $^6\text{Li}$ 90° pulse length of 3 µs. Spectra were collected with 600 scans and recoupling times ($N\tau_R$) incremented in 4 rotor period steps starting at $N = 4$ up to $N = 256$. This gave a maximum recoupling time of 10 ms. The $^{31}\text{P}$ CSAs were determined using the DMFIT program$^5$ with the result confirmed using a Herzfeld-Berger analysis program developed by K. Eichele and R. Wasylishen.$^6,7$ REDOR buildup curves were simulated using the SIMPSON (version 1.1.1) simulation program.$^8$

High temperature static $^{31}\text{P}$ measurements were carried out on a custom built wide-bore, static, solid-state NMR probe able to reach temperatures up to 500 °C. Samples were sealed in a quartz ampoule and heated under flowing nitrogen. Temperatures were calibrated using Pb(NO$_3$)$_2$ as described elsewhere.$^9$ For all experiments, $^7\text{Li}$ shifts were referenced to 1M LiCl (0 ppm) and $^{31}\text{P}$ shifts were referenced to 85% H$_3$PO$_4$ (0 ppm). Due to the width of the total resonance being considerably larger than the excitation bandwidth of the $^{31}\text{P}$ pulse, the $^{31}\text{P}$ spectra were frequency-stepped over a total range of 450 kHz with a step size of 50 kHz with 16000 scans and SW of 1 MHz for each sub-spectrum. The sub-spectra were added in Topspin 2.1 to give the total spectrum.
4.3 Results and Discussion

4.3.1 $^7\text{Li}$ and $^{31}\text{P}$ MAS NMR of LiMnPO$_4$ and LiFePO$_4$.

In this section, the $^7\text{Li}$ and $^{31}\text{P}$ MAS spectra of both LiMnPO$_4$ and LiFePO$_4$ are presented. The olivine phase of cathode materials, LiMPO$_4$ (M = Mn, Fe), have received significant attention as the most commercially viable cathode materials for low-cost Li ion battery applications. Since its introduction in 1997, the landmark communication outlining the synthesis and electrochemical cycling of LiFePO$_4$ has been referenced in well over 1500 publications. The high theoretical capacity, excellent reversibility, and low environmental impact make it a promising material for battery applications. As outlined in Chapter 1, the high thermal and electrochemical stability results from the strong covalent bonding of oxygen within the PO$_4^{3-}$ moieties leaving very open channels for Li ion diffusion. LiMnPO$_4$ offers higher ion conductivity as well as a higher redox potential of 4.1 V when compared to LiFePO$_4$. However, the Jahn-Teller distortions around Mn$^{3+}$ lead to poor reversibility making LiMnPO$_4$ the less preferred material for electrochemical applications.

Figure 4.1 shows the $^7\text{Li}$ MAS spectra of LiMnPO$_4$ and LiFePO$_4$ at MAS speed of 25 kHz. For LiMnPO$_4$ a higher $^7\text{Li}$ MAS paramagnetic shift (75 ppm) and larger spinning sideband manifold ($\Omega = 440$ kHz) is attributed to an additional unpaired electron in the $t_{2g}$ orbital as compared to LiFePO$_4$ which has $\delta_{\text{iso}} = -11$ ppm and $\Omega = 275$ kHz.
Figure 4.1 - $^7$Li MAS NMR (25 kHz) of isostructural LiMnPO$_4$ (top) and LiFePO$_4$ (bottom). Asterisks denote spinning sidebands. This figure illustrates the changes to the Li environment when the redox center changes from a t$_{2g}^4$e$_g^2$ (LiFePO$_4$) to a t$_{2g}^3$e$_g^2$ (LiMnPO$_4$)

The Full-Width at Half-Maximum (FWHM) of the isotropic peak for LiMnPO$_4$ is 500 Hz whereas for LiFePO$_4$ it is much more broad at 9500 Hz. As outlined in Chapter 2, the lineshape in paramagnetic systems has contributions from both the hyperfine coupling value ($A/h$) and the spin-lattice relaxation of the electrons ($T_{1e}$) to which the nucleus is coupled. This relationship is presented here again in Equation 4-1.$^{13,14}$

$$FWHM = \frac{1}{T_{2N}} = \frac{1}{T_{2a,b}} + \frac{(A/h)^2 T_{1e}}{8}$$

Equation 4-1

The first portion of Equation 4-1, (1/$T_{2a,b}$), is governed by the the transverse relaxation terms arising from effects other than those induced by interaction with a
paramagnetic metal center. This has a significantly smaller contribution than the portion containing terms associated with the unpaired electron spin density sitting on the metal center ($T_{1e}$, and the hyperfine coupling constant, $A/\hbar$).\textsuperscript{14} Previous studies have measured the hyperfine coupling constants for both LiMnPO$_4$ and LiFePO$_4$ (0.86 \times 10^6 \text{ rad/s} and -0.48 \times 10^6 \text{ rad/s}, respectively).\textsuperscript{15} The larger $A/\hbar$ value for LiMnPO$_4$ does not appear to affect the FWHM as this would lead to a broader resonance in the Mn materials over the Fe analogue. Therefore, the greater resolution in the LiMnPO$_4$ $^7$Li spectrum is due to the shorter $T_{1e}$ times of the spin density on the metal center as compared to LiFePO$_4$.

Similar trends for $\delta$, FWHM, and $\Omega$, were observed in the $^{31}$P MAS spectra of the Mn and Fe phases (Figure 4.2). An isotropic $^{31}$P shift of 7600 ppm is observed in LiMnPO$_4$ at almost 4000 ppm higher frequency than LiFePO$_4$ with $\delta = 3800$ ppm. The LiMnPO$_4$ $^{31}$P FWHM is 7600 Hz while the span of the manifold, $\Omega$, is 450 kHz. The LiFePO$_4$ $^{31}$P MAS spectrum has a larger FWHM of 11600 Hz but a smaller sideband manifold of 300 kHz. Again, the $T_{1e}$ dominates the isotropic lineshape while the total electron spin density dominates the sideband manifolds and paramagnetic shift.
**Figure 4.2** – $^{31}\text{P}$ MAS spectra of LiFePO$_4$ (top) and LiMnPO$_4$ bottom, with MAS speed of 25 kHz. Isotropic shifts values are given for each phase with sidebands denoted with asterisks.

### 4.3.2 Studying Li Dynamics in the Olivine Phases.

Here the ion dynamics in LiFePO$_4$ are investigated using $^6\text{Li}$$^{31}\text{P}$ REDOR measurements of $^6\text{Li}$ enriched samples of LiFePO$_4$. Extracting timescales of Li ion mobility is an important step towards understanding the conductivity restrictions within these phases however, many challenges are present when trying to identify and quantify Li ion mobility in the olivine phases. Firstly, the presence of a single crystallographic site means that ion mobility measurements that rely on the movement of the Li ions from one crystallographic site to another are not possible. This includes the 2D EXSY and 1D selective inversion measurements used extensively in subsequent chapters, where
materials having more than one crystallographic Li site are studied. In diamagnetic systems, dynamics of single-site materials can be quantified by measuring changes in the FWHM (or $1/T_2$) mobile ion lineshape as a function of temperature.\footnote{16} This relationship is presented in (Equation 4-2).

$$k = \frac{1}{\pi T_2^*}$$ 

Equation 4-2

Where the rate constant, $k$, is proportional to $1/T_2^*$ which is the FWHM of a resonance with the inhomogeneity of the magnetic field taken into account. The contributions to $T_2^*$ in a diamagnetic system include heteronuclear and homonuclear dipolar couplings meaning that changes in the FWHM reflect changes to the average homo- or heteronuclear internuclear distances brought on by dynamics of the mobile species. As demonstrated previously, the FWHM in paramagnetic systems has contributions from both $T_{1e}$ and the hyperfine coupling between the nucleus measured and the unpaired electron spin density on the transition metal center (Equation 4-1). The temperature dependent changes of the hyperfine coupling (due to Curie-Weiss changes to the magnetic susceptibility)\footnote{17} means that any observed changes in the FWHM of a paramagnetic resonance are likely arising not only due to changes in the nuclear dipolar couplings but also due to changes in the magnetic susceptibility of the metal center.

For the olivine phases, alternative methods to probe changes to the heteronuclear couplings resulting from movement of the mobile ion were investigated and some
preliminary results are presented here. As outlined in Chapter 3, $^{6}\text{Li}\{^{31}\text{P}\}$REDOR reintroduces $^{6}\text{Li}-^{31}\text{P}$ dipolar couplings that are averaged out through MAS. The observed nucleus ($^{6}\text{Li}$) is measured using a spin-echo sequence with (S) and without ($S_0$) the application of a series of $\pi$ pulses on the dephased nucleus ($^{31}\text{P}$). The normalized difference in $^{6}\text{Li}$ signal intensity ($[S_0-S]/S_0$) is then plotted as a function of the dipolar evolution time ($N\tau_R = \text{number of rotor periods times the rotor period}$). This experiment is more often used to determine internuclear distances in systems where diffraction studies are not possible. For our purposes, this technique is applied over a variable temperature range to monitor changes to the $^{6}\text{Li}-^{31}\text{P}$ dipolar coupling brought on by mobility of the Li ion. Previous studies in our group have evaluated site specific dynamics in the cathode material Li$_3$V$_2$(PO$_4$)$_3$.$^{18}$ The study of Li$_3$V$_2$(PO$_4$)$_3$ was performed in a temperature range where Li site exchange was known to be “frozen” out based on activation energies determined from 2D NMR exchange studies.$^{18,19}$ The observed attenuation of the $^{6}\text{Li}\{^{31}\text{P}\}$ REDOR curve from the static simulated case was therefore attributed to site specific rattling rather than from Li diffusion. For the present study, $^{6}\text{Li}\{^{31}\text{P}\}$ REDOR measurements were performed in a temperature range where thermally activated Li ion diffusion (rather than site-rattling) is observed in related Li-intercalation compounds.$^{19-21}$

Experimental $^{6}\text{Li}\{^{31}\text{P}\}$ REDOR curves were therefore measured over a temperature range of 250 K to 350 K with MAS of 25 kHz. Several complications arise from the broad paramagnetic $^{31}\text{P}$ resonance which must be accounted for within this set of experiments. A 1D $^{31}\text{P}$ MAS spectrum was collected for each temperature at which a $^{6}\text{Li}\{^{31}\text{P}\}$ REDOR experiment was acquired. It is clear from Figure 4.3 that the $^{31}\text{P}$
isotropic shift moves to lower frequency as the temperature is increased. This is consistent with Curie-Weiss changes to the magnetic susceptibility in paramagnetic materials where, in this temperature range, there is a near linear dependence (Figure 4.3 inset) of the shift on sample temperature.\textsuperscript{17}

![Figure 4.3](image)

**Figure 4.3** – Changes to the $^{31}$P MAS resonance of LiFePO$_4$ as a function of temperature.

Due to the migration of the resonance, the frequency of the $^{31}$P $\pi$ pulse was adjusted for each REDOR experiment such that the excitation was on resonance (Table 4.1). **Figure 4.4** shows the $^6$Li$_{^{31}}$P REDOR buildup curves acquired over a variable temperature range (250 K to 350 K).
Table 4.1 - Summary of changes to transmitter frequency due to migration of the $^{31}$P resonance as temperature is increased.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$^{31}$P π transmitter frequency (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>81.3173770</td>
</tr>
<tr>
<td>298</td>
<td>81.3060000</td>
</tr>
<tr>
<td>310</td>
<td>81.2870000</td>
</tr>
<tr>
<td>330</td>
<td>81.2667129</td>
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<tr>
<td>340</td>
<td>81.2615890</td>
</tr>
<tr>
<td>350</td>
<td>81.2579238</td>
</tr>
</tbody>
</table>

Figure 4.4 – $^6$Li{$^{31}$P} REDOR curve of LiFePO$_4$ over a variable temperature range. The static simulated curve from SIMPSON is also shown as the data points connected by a line.

Overall, there are no observable changes to the $^6$Li{$^{31}$P} REDOR buildup curve as the temperature is increased. It is difficult to assess whether this is from an inherent lack of Li ion diffusion below 350 K or if a systematic error is present within the experiment.
The shortest Li–P contact of 2.659 Å gives rise to dipolar coupling value of 381 Hz which is 2.4 % of the FWHM of the isotropic (16000 Hz at 300 K) and 0.2 % of the total $^{31}\text{P}$ signal (250000 Hz over the entire sideband manifold). The transmitter frequency is chosen by identifying the frequency at which the maximum intensity of isotropic signal is found. Based on the width of the isotropic peak being close to 16000 Hz, if a 1% error is allotted to this selection then the error on the transmitter frequency would be $\pm 160$ Hz. This constitutes close to 50% of the total dipolar coupling value and illustrates how changes to the measured couplings may fall within the error values of experimental parameters.

Changes in the magnetic susceptibility of the Fe center over a variable temperature range may also introduce a systematic error within this experiment. As the temperature is raised, the magnetic susceptibility decreases and the paramagnetic character of the resonances decreases. This leads not only to the migration of the isotropic shift towards the diamagnetic region of the spectrum, (Figure 4.3) but also to a narrowing of the resonance. This is not a problem if the total signal falls within the bandwidth of the pulse as 100% of the signal is excited regardless of span. However, in the highly paramagnetic systems studied here, the width of the signal (250 kHz) is larger than the bandwidth of the applied pulse (142 kHz) and incomplete excitation of the $^{31}\text{P}$ signal occurs. Previous studies have shown that a base attenuation of the REDOR buildup is observed and related to this incomplete excitation of the $^{31}\text{P}$ signal. This base attenuation is not a problem at measurements carried out over a single temperature, but for a variable temperature range where changes to the REDOR buildup indicate mobility.
of the Li ions, a narrowing of the shift leads to more complete excitation of the $^{31}$P signal meaning stronger REDOR buildup curve are measured at higher temperatures. This increase in REDOR buildup from improved excitation may offset the weakening of the REDOR buildup from movement of the mobile ion, making interpretation of the results non-trivial. While neutron diffraction results have shown that there is limited lithium diffusion below 620 K (prior to the onset of solid solution formation)\(^{22}\) it is unclear if the REDOR results presented here can be interpreted to support this claim. It is therefore the focus of ongoing work to measure nuclei whose full signal falls within the bandwidth of the applied pulse such that narrowing of the resonances brought on by susceptibility changes has no effect on the total excitation. This includes use of $^6$Li{$^7$Li} REDOR and $^7$Li{$^6$Li} REDOR measurements where dephasing of the narrower $^7$Li and $^6$Li resonances has fewer complications from excitation disparities over a variable temperature range.

4.3.3 Phase Transformation in Li\(_x\)FePO\(_4\) (x = 0.5)

The section details the solid solution formation at high temperature in biphasic 0.5LiFePO\(_4\):0.5FePO\(_4\) characterized using static $^{31}$P measurements. To date, the conductivity restrictions in the olivine phases are ascribed to a one-dimensional Li ion diffusion pathway coupled with limited electronic conduction owing to small polaron hopping conductivity.\(^{22-24}\) This results in a two-phase redox reaction during electrochemical cycling and a voltage plateau corresponding to the phase transition between them.\(^{10,11,25-28}\) In order to enhance the cycling capabilities, particularly for LiFePO\(_4\), generation of single phase or “solid-solution” properties at temperatures
amenable to the operation of the Li ion battery have been investigated either through chemical or mechanical manipulation of the parent compound.\textsuperscript{27-32}

The present work evaluates the temperature driven formation of solid solution phases in samples of partially delithiated Li\textsubscript{x}FePO\textsubscript{4} using static \textsuperscript{31}P variable temperature NMR experiments. The \textsuperscript{31}P paramagnetic shift proves to be an ideal tool for monitoring electronic changes taking place at the Fe redox center as it has a very strong hyperfine coupling to the unpaired electrons on the transition metal center.\textsuperscript{15} The use of static NMR measurements in this case provides access to a broad temperature range, such that the phase transformation can be performed \textit{in-situ} providing a complementary NMR picture to the previous \textit{in-situ} diffraction and Mossbauer studies of Li\textsubscript{x}FePO\textsubscript{4}.\textsuperscript{28,29} For this study, Li\textsubscript{0.5}FePO\textsubscript{4} was the chosen composition as it allows for well-balanced \textsuperscript{31}P signal intensity from the separate FePO\textsubscript{4} and LiFePO\textsubscript{4} domains.

\subsection{XRD of 0.5LiFePO\textsubscript{4}:0.5FePO\textsubscript{4}}

Complete chemical and electrochemical oxidation of triphylite Li\textsubscript{x}FePO\textsubscript{4} produces orthorhombic FePO\textsubscript{4} (heterosite), while partial oxidation to \(x = 0.5\) results in mixtures of the two end-members. The diffraction pattern of biphasic 0.5LiFePO\textsubscript{4}:0.5FePO\textsubscript{4}, produced by the oxidation of LiFePO\textsubscript{4} with a stoichiometric amount of NOBF\textsubscript{4} by collaborators at the University of Waterloo is shown in \textbf{Figure 4.5}. The lattice parameters of LiFePO\textsubscript{4} were indexed to be \(a = 10.323 \text{ Å}, b = 6.002 \text{ Å}, c = 4.696 \text{ Å}\) with a unit cell volume of 291.0 \(\text{Å}^3\), in good accord with several other reports of LiFePO\textsubscript{4} bulk crystallites. The lattice parameters of the oxidized phase were determined to be \(a = 9.833\text{ Å}\).
Å, $b = 5.801$ Å, $c = 4.771$ Å with a unit cell volume of $272.1$ Å$^3$, also in good accord with previous reports.

An SEM micrograph (inset Figure 4.5) shows the particle size of the crystallites to be 200-500 nm in dimension.

![Figure 4.5 - Powder X-ray diffraction pattern of biphasic Li$_{0.5}$FePO$_4$ prepared from chemical oxidation of LiFePO$_4$. Selected reflections of LiFePO$_4$ (triphylite, T) and FePO$_4$ (heterosite, H) are indexed. Inset: SEM micrograph of the Li$_{0.5}$FePO$_4$ material which consists of uniform sub-micron sized particles, with a narrow particle size distribution.]

**4.3.3.2 $^{31}$P MAS NMR of 0.5LiFePO$_4$:0.5FePO$_4$**

The sample of half-delithiated, hydrothermally prepared, 0.5LiFePO$_4$:0.5FePO$_4$ was first evaluated using $^{31}$P MAS NMR. Figure 4.6 (bottom) shows the room
temperature $^{31}$P MAS NMR spectrum of 0.5LiFePO$_4$:0.5FePO$_4$ where two distinct domains with resonances centered around $\sim$ 3800 and 5800 ppm are observed. Figure 4.6 also shows the $^{31}$P MAS NMR spectrum of fully lithiated LiFePO$_4$ and with an Fe$^{2+}$ electron configuration of $t_{2g}^4 e_g^2$ giving a $^{31}$P isotropic resonance centered at 3800 ppm. In contrast, for the $^{31}$P MAS spectrum of FePO$_4$, where the oxidation state of the iron center is raised to Fe$^{3+}$ giving a $t_{2g}^3 e_g^2$ electron configuration, the paramagnetic shift increases to 5800 ppm (Figure 4.6 top). This shift information is in agreement with previous reports of the olivine Li$_x$FePO$_4$ family.$^{15,33,34}$ The cause of this increase in paramagnetic shift is similar to what was observed for the LiMnPO$_4$ - LiFePO$_4$ comparison in Section 4.3.1. The unpairing of an electron in the $t_{2g}$ orbital of both FePO$_4$ and LiMnPO$_4$ (which both have a d$^5$ electron configuration of $t_{2g}^3 e_g^2$) leads to an increased amount of unpaired electron spin density able to delocalize onto the phosphorus nucleus and hence an increased paramagnetic shift relative to LiFePO$_4$. 
Although LiMnPO$_4$ and FePO$_4$ are isoelectronic, the overall higher shift observed in LiMnPO$_4$ is attributed to slightly better orbital overlap within this phase. Figure 4.7 shows the P environment found within the olivine phases. Five metal centers coordinate to the P atom via the oxygen atoms creating both edge- and corner-sharing geometries between the phosphate tetrahedra and metal octahedra. Table 4.2 lists the P-O-M orbital overlap angles where the edge shared geometries give the best overlap angles ranging from 92.05° for LiMnPO$_4$ to 94.75° for FePO$_4$. The higher $^{31}$P paramagnetic shift for LiMnPO$_4$ is attributed to this phase having an overlap angle closer to 90° than FePO$_4$. Moreover, this highlights how the geometry dependent contact shift dominates the observed paramagnetic shift, as the pseudo-contact interaction would be near equivalent in these materials.

Figure 4.6 - $^{31}$P MAS NMR of FePO$_4$ (top), LiFePO$_4$ (middle) and biphasic 0.5LiFePO$_4$:0.5FePO$_4$ (bottom) all at room temperature. Isotropic shifts for FePO$_4$, LiFePO$_4$ found at 5800 and 3800 ppm respectively. Asterisks denote spinning sidebands.
Figure 4.7 – Schematic showing the P environment as coordinated via oxygen to the metal centers (either Mn or Fe) in the olivine phases of LiMnPO$_4$, LiFePO$_4$ and FePO$_4$.

<table>
<thead>
<tr>
<th>O Label</th>
<th>LiFePO$_4$ Fe-O-P Angle (°)</th>
<th>FePO$_4$ Fe-O-P Angle (°)</th>
<th>LiMnPO$_4$ M-O-P Angle (°)</th>
</tr>
</thead>
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<tr>
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</table>

4.3.3.3 *In-Situ* $^{31}$P NMR Study of the Thermally Driven Solid Solution in Li$_{0.5}$FePO$_4$

The sensitivity of the $^{31}$P resonance to changes at the redox center allow for an *in-situ* $^{31}$P NMR study of the thermally driven phase transformation from biphasic 0.5LiFePO$_4$:0.5FePO$_4$ to solid solution Li$_{0.5}$FePO$_4$. In order to reach temperatures where full electron delocalization occurs (~ 400 °C), NMR experiments were acquired in the
absence of magic angle spinning. The static $^{31}$P NMR spectra (Figure 4.8) were collected as a series of frequency stepped sub-spectra and added. The room temperature spectrum (Figure 4.8, bottom 26 °C) clearly shows the separate domains of phosphorous nuclei near Fe$^{3+}$ and Fe$^{2+}$ similar to that observed in the MAS NMR experiments. When the temperature is raised to 250 °C, there is a loss of resolution between the two phases consistent with the expected onset of electron and lithium delocalization leading to a larger phase interface region.$^{28,29}$ The migration of the FePO$_4$ and LiFePO$_4$ resonances to lower frequency with increased temperature results from to Curie-Weiss behaviour of paramagnetic resonances whereby the overall magnetic susceptibility of each metal center decreases as the temperature is raised. This leads to a decrease in the hyperfine coupling constant and thus a lower chemical shift.$^{17}$ When temperatures of 400 °C are reached, a single resonance centered at 3200 ppm appears. The $^{31}$P nuclei now “see” the Fe transition metal in a single, average oxidation state due the complete delocalization of electrons of the solid solution phase.
The sample was then cooled in small increments to observe the re-emergence of the two domains. Between temperatures of 400 °C and 270 °C, the sample retains single phase features but with slight broadening. At this stage it is difficult to determine whether this is caused by the slowing of electron mobility or increased paramagnetism at lower temperatures. At 250 °C, where reappearance of the separate domains is expected, the spectrum continues to appear single phase. Figure 4.9 shows two sub-spectra with the excitation frequency set to 81.28 MHz collected at 250 °C before and after the solid

Figure 4.8 – $^{31}$P static solid-state NMR spectra under variable temperature conditions. Frequency stepped sub-spectra (grey) added to yield total spectrum (black).
solution was formed. The pre-solid solution sub-spectrum shows features that indicate that two domains are present. For the same sub-spectrum collected 24 hours after formation of the solid solution, these features are no longer present and only single phase Li$_{0.5}$FePO$_4$ is observed. Upon cooling and allowing the sample to sit at room temperature for 72 hours, the separation into two domains is apparent (Figure 4.8 top 26 °C). This separation however, is not as well defined as the 26 °C spectrum collected prior to heat treatment and thus suggests that there is a considerable increase in the number of P nuclei residing at the phase interface following treatment at high temperature.

Figure 4.9 – Static $^{31}$P sub-spectra of Li$_{0.5}$FePO$_4$ at 250 °C measured before and after the solid solution phase was reached. The two-phase features observed before the solid solution was formed do not reappear in the cooled sample on a timescale of 24 hr following heat treatment.
4.3.4 $^7$Li MAS NMR Investigation of Phase Boundary Regions in Nanoparticles

Here, detailed information regarding the FePO$_4$/LiFePO$_4$ phase interface is obtained from room temperature $^7$Li MAS NMR spectra of biphasic Li$_{0.5}$FePO$_4$ that has not undergone any heat treatements. For comparison, a $^7$Li MAS NMR spectrum of pristine, fully lithiated, LiFePO$_4$ is also presented which shows a single isotropic resonance centered at -11 ppm (Figure 4.10 a) consistent with previous reports.$^{15,34}$ The isotropic lineshape has a FWHM of 9500 Hz. Following chemical delithiation, the $^7$Li MAS NMR spectrum of biphasic Li$_{0.5}$FePO$_4$ (Figure 4.10 b) shows an isotropic resonance centered at -12 ppm which deconvolutes to 5 peaks labelled as A, B, C, D, and E. The deconvolution resulting in the appearance of multiple peaks is somewhat surprising as only the LiFePO$_4$ domain should contain observable Li. The FePO$_4$ domain is not expected to give rise to any Li signals. These newer peaks are therefore resulting either from Li ion disorder and/or Li belonging to the LiFePO$_4$ domain but sitting at the interface with the FePO$_4$ domain. The deconvolution presented here is the minimum number of peaks needed to obtain a goodness of fit of 95% in the Topspin 2.1 program. Peak A is broad with parameters similar to that of the $^7$Li MAS NMR spectrum of pristine LiFePO$_4$ (Table 3) and is thus confidently assigned as Li sitting in the fully lithiated domain. Peak B is very narrow and centered at -7 ppm. This peak does not contribute to the lineshape of the spinning sidebands meaning it is a non-paramagnetic Li environment (possibly a Li-salt impurity arising from the oxidation of LiFePO$_4$ with NO$_2$BF$_4$). Peaks C, D, and E, deconvolute with varying degrees of broadening and also appear in the 1$^{st}$ order sidebands suggesting these resonances belong to paramagnetic phases. Peaks C and D have
chemical shifts slightly higher than the LiFePO$_4$ domain ($-8$ ppm and $-6$ ppm, respectively).

\[ \text{Figure 4.10} \quad \text{a) } ^7\text{Li MAS NMR spectra of LiFePO}_4 \text{ (top, MAS = 40 kHz) and biphasic Li}_{0.5}\text{FePO}_4 \text{ (0.5LiFePO}_4\text{:0.5FePO}_4 \text{) (bottom, MAS = 40 kHz). Asterisks denote spinning sidebands. b) Deconvolution of biphasic Li}_{0.5}\text{FePO}_4 \text{ with MAS = 40 kHz. Fitted spectrum (grey) sits on top of experimental spectrum (black). Deconvoluted peaks shown in black.} \]
Table 4.3 - Summary of deconvolution parameters for the $^7$Li MAS NMR spectrum of biphasic Li$_{0.5}$FePO$_4$ (Figure 4.10)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Chemical shift (ppm)</th>
<th>FWHM (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-12</td>
<td>9998</td>
</tr>
<tr>
<td>B</td>
<td>-7</td>
<td>114</td>
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<tr>
<td>C</td>
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<td>427</td>
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<td>E</td>
<td>65</td>
<td>9827</td>
</tr>
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</table>

The narrowness and appearance in higher order sidebands suggests that these resonances arise due to their closeness to an Fe$^{3+}$ environment (i.e. proximity to the phase interface as purely Fe$^{3+}$ regions would have no Li ions present). This conclusion is made in consideration of the through-space nuclear-electron spin interactions for paramagnetic materials. Increasing the unpaired electron spin density significantly impacts not only the paramagnetic shifts, but also the span of the chemical shift anisotropy (CSA) and the broadness of the isotropic resonance.\textsuperscript{37,38} Li sitting close to Fe$^{3+}$ experiences a larger electron-nuclear dipolar coupling as compared to Li sitting close to Fe$^{2+}$. This leads to a larger CSA which is now observed for biphasic Li$_{0.5}$FePO$_4$ (span of the CSA is now close to $^7$Li 8000 ppm). There is also a characteristic narrowness to the $^7$Li lineshapes that we have assigned to Li near Fe in oxidation 3+. This is justified based on the contributions from both the hyperfine coupling value ($A/\hbar$) and the spin-lattice relaxation of the electrons ($T_{1e}$) to which the nucleus is coupled on the FWHM of paramagnetic resonance identified in (Equation 4-1). In the LiFePO$_4$:FePO$_4$ system, the increase in chemical shift from -11 ppm for Li in a Fe$^{2+}$ environment to -6 ppm for Li near Fe$^{3+}$ is due to a modest increase in the $A/\hbar$ value. This increase alone would then lead to broadening of the resonance for any Li near Fe$^{3+}$. However, the opposite trend is observed in this system.
(Figure 4.10) thus indicating that the changes in the linewidth are governed, rather, by the $T_{1e}$ term. As the redox charge is raised from Fe$^{2+}$ to Fe$^{3+}$ (or as the spin number goes from $S = 2$ to $S = 5/2$) the $T_{1e}$ decreases, resulting in the observed narrower resonances. This trend was also observed when comparing the $^7$Li MAS spectra of LiFePO$_4$ and LiMnPO$_4$ (Figure 4.1). In LiMnPO$_4$, all Li nuclei are surrounded by transition metals with a spin state of $S = 5/2$ (isoelectronic with Fe$^{3+}$). The resultant $^7$Li MAS NMR spectrum (with $\delta = 75$ ppm, FWHM of $\sim 500$ Hz, Figure 4.1) strongly resembles the new, narrower resonances, assigned to Fe$^{3+}$ Li environments in biphasic 0.5LiFePO$_4$:0.5FePO$_4$.

Overall, there is sufficient evidence to confirm that a fraction of the Li nuclei are sitting close to a more paramagnetic Fe$^{3+}$ ($t_{2g}^3e_g^2$) center. This thereby results in phase interface Li being observable in these materials. However, due to the large number of possible Li sites that could be produced, caution is emphasized when attempting site specific assignments of the remaining deconvoluted peaks (C, D, and E). Figure 4.11 shows the local lithium environment in LiFePO$_4$ where each Li ion is connected via O to 6 Fe atoms. Two of the Fe atoms have Li-O-Fe overlap angles close to 90° while the other 4 Fe atoms overlap at angles of either 110° or 120°. Oxidation of an Fe atom involved in the 90° orbital configuration (Figure 4.11 left) would lead to the greatest increase in the paramagnetic shifts based on the geometry dependent delocalization of unpaired electron spin density discussed previously. Alternatively, oxidation of Fe atoms in the 110° or 120° configurations (Figure 4.11 right) would have a less significant impact on the paramagnetic shift but through-space effects including changes to the CSA
would still be observed. These represent the two extreme cases of numerous possible combinations of Fe$^{2+}$/Fe$^{3+}$ neighbours to the crystallographic Li site. Together these lead to a large number of Li environments with varying degrees of paramagnetic shift and broadness.

Figure 4.11 – Schematic detailing the local Li environment with respect to Fe transition metal center proximity. **Left.** Oxidation of Fe centers that have orbital overlap close to 90° leading to Li environments with high paramagnetic shift. **Right.** Oxidation of Li environments with orbital overlap of 110-122° leading to a smaller impact on paramagnetic shift but similar impact on lineshape and breadth of CSA.

An exception is made for Peak E which was deconvoluted with a shift of 65 ppm and large FWHM of ~9800 Hz. While the paramagnetic shift is considerably higher, the linewidth is virtually unchanged from the parent LiFePO$_4$ thus suggesting that this Li environment is still in an Fe$^{2+}$ environment. This peak is therefore assigned as a Li environment generated where there is a larger number of Fe$^{2+}$ atoms in the Li-coordination sphere. This scenario is best represented by the anti-site defect commonly
generated in this system.\textsuperscript{39,40} \textbf{Figure 4.12} shows the local Li environment generated if an Fe is found along the diffusion channel. The Li ion now has 7, rather than 6, Fe\textsuperscript{2+} in its coordination sphere where the defect Fe\textsuperscript{2+} (Fe_{defect}) edge shares with the Li-atom at two Li-O-Fe overlap angles of 87.5 and 92.2°. Due to the additive nature of the Fermi-contact interaction, this would lead to the observed increase in the Li-paramagnetic shift value but with minimal changes to the lineshape. This anti-site defect was not observed in the fully lithiated parent compound. This is attributed to the the difficulty in deconvolution of such a broad isotropic resonance which is made worse by the increased concentration of Li in the crystallographic, -11 ppm, environment. Future work will look to overcome this obstacle through the use of \textsuperscript{6}Li MAS NMR on enriched samples of Li\textsubscript{1-x}FePO\textsubscript{4}.

\textbf{Figure 4.12} – Schematic detailing the new Li environment generated if a Fe atom was found along the Li diffusion channel. The Fe_{defect}-O-Li orbital overlap angles are very close to 90° resulting in a further increase of the paramagnetic shift value.
4.3.4.1 $^7$Li MAS NMR Investigation of Phase Boundary Regions in Microparticles

Confirmation of the influence of particle size on the ability to detect the phase boundary following delithiation is provided through parallel studies of electrochemically cycled LiFePO$_4$. It is shown that observation of phase boundary lithium is limited as the particle size increases. Figure 4.13 shows $^7$Li MAS spectra of large particle (1-1.5 µm) LiFePO$_4$ before and after cycling to a composition of Li$_{0.43}$FePO$_4$. The post-cycled spectrum is unchanged relative to the parent material and, no new Fe$^{3+}$ environment is observed. Therefore, although the material is delithiated to an equivalent, or slightly greater degree than the nanoparticles studied above, there is not sufficient lithium in the interface region to allow detection by NMR. Similarly in a recent report from, Cabana et al.,$^{33}$ a $^6$Li MAS NMR spectrum of chemically delithiated, large particle (>2 µm) LiFePO$_4$ did not reveal features of phase boundary Li.

![Figure 4.13 - $^7$Li MAS NMR (40 kHz) of micro-diameter LiFePO$_4$ before (top) and after (bottom) electrochemically cycling to a composition of Li$_{0.43}$FePO$_4$. Asterisks denote spinning sidebands. Inset is SEM image of pristine particles.](image-url)

\[LiFePO_4\]
\[Li_{0.43}FePO_4\]
In both cases, there is certainly Li residing at the FePO₄/LiFePO₄ interface, however because of the larger particle diameter, the fraction of this lithium (relative to Li in the fully lithiated LiFePO₄ domain) would be significantly smaller. The interface regions are proposed to be only a few nanometers thick.¹⁰ In smaller diameter particles, these few nanometers carry greater significance than in particles of micrometer diameter. From a $^7$Li NMR standpoint, signals arising from Li residing in the fully lithated domain would overtake the NMR spectrum in the microdiamater samples making the small region of interface Li unobservable. Due to the larger relative impact of the interface in nanodimension particles, both the fully lithiated domain as well as interface Li is observed.

4.4 Concluding Remarks

Significant differences in paramagnetic shift, isotropic lineshape and sideband manifold were observed when comparing the $^7$Li and $^{31}$P MAS spectra of LiMnPO₄ and LiFePO₄. This is attributed to the different electron configurations at the transition metal center of these isostructural compounds where LiMnPO₄ has a $d^5$, $t_{2g}^3e_g^2$ configuration while LiFePO₄ has a $d^6$, $t_{2g}^4e_g^2$ configuration. This sensitivity of the nuclear spins to electron configuration is exploited to characterize phase transformations and phase interface environments in Li₀.₅FePO₄ where room temperature MAS and static $^{31}$P spectra show the presence of two distinct domains arising from the Fe$^{3+}$PO₄ and LiFe$^{2+}$PO₄ domains. The P nuclei show extreme sensitivity to electronic changes taking place at the transition metal center yielding $^{31}$P paramagnetic shifts of 5800 ppm and 3800 ppm, respectively. At 400 °C, these resonances coalesce into a single P-site centered at 3200
ppm. This is due to complete electron delocalization resulting in a single, average Fe oxidation state. Upon cooling back to room temperature, the two domains of FePO$_4$ and LiFePO$_4$ are not as clearly resolved suggesting that some P nuclei continue to sit in an environment where the average Fe oxidation state is between 2+ and 3+. $^7$Li MAS NMR spectra of biphasic Li$_{0.5}$FePO$_4$ (or 0.5LiFePO$_4$:0.5FePO$_4$) reveal phase interface regions as sites deconvolute into resonances attributable to the distribution of Fe$^{3+}$ and Fe$^{2+}$ around a lithium center. This is based on the extent of orbital overlap, and the resulting magnitude of the chemical shift at one extreme, and alternatively, the lack of orbital overlap, but the significant influence of $T_{1e}$, on the narrowness of the lineshape. These details allow for a clear distinction between NMR spectra of samples with larger particle size from those with submicron particle sizes. The latter uniform, small particles have been shown to have excellent electrochemical performance, and the utility of NMR in elucidating properties of the lithiated/delithiated phase boundary will provide ongoing insight into the development of similar phases.
4.5 References


(7) Eichele, K.; Wasylischen, E. *Dalhousie University and Universität Tübingen 2006*.


Chapter 5: Quantification of Li Ion Mobility in $\alpha$–Li$_3$Fe$_2$(PO$_4$)$_3$ using Variable Temperature $^6$Li 2D EXSY Measurements

5.1 Introduction

This chapter is divided into two studies detailing the ion dynamics and electrochemical performance of the monoclinic $\alpha$-Li$_3$M$_2$(PO$_4$)$_3$ ($M = V, Fe$) family of cathode materials. The first study elucidates timescales of Li-mobility in Li$_3$Fe$_2$(PO$_4$)$_3$ using $^6$Li 2D EXSY measurements. Three crystallographically unique Li sites were resolved under magic angle spinning (25 kHz) with paramagnetic shifts arising at 45 ppm, 102 ppm, and 216 ppm. These resonances were assigned to the crystallographic positions based on the degree of the Fermi-contact interaction with the paramagnetic iron center. $^6$Li 2D exchange NMR experiments were performed under variable temperature conditions in order to determine the activation energies for hopping between lithium sites. Activation energies ranged from 0.59 (± 0.05 ) eV to 0.81 (± 0.04 ) eV, where shorter Li internuclear distances, yet larger Li-O bottlenecks, yielded higher activation energies. These results are opposite in trend from the previous study of isostructural Li$_3$V$_2$(PO$_4$)$_3$ which showed that increased internuclear distance and constricted bottlenecks yield larger energy barriers for Li-Li exchange. In the Fe-case, the geometry of the polyhedral faces of the Li environments plays a more critical role in the ion dynamics as there is a blocking of the diffusion pathway by the Fe atoms in the edge-shared geometries. This latter result is better illustrated through evaluation of bond valence sum maps which reveal a large amount of bond valence density in the lone edge-shared geometry giving
this pair the highest energy barrier for hopping. This work was published in *Chemistry of Materials* (2010, 22, 769-775) with co-authors I. Heinmaa, and G. R. Goward. For this work, NMR data was collected at the National Institute of Chemical Physics and Biophysics in Tallinn Estonia, under the supervision of Dr. Ivo Heinmaa. All data was processed at McMaster University with supervision from Prof. Goward.

The second part of this chapter studies changes to Li ion mobility in Li$_x$V$_2$(PO$_4$)$_3$ using variable temperature $^6$Li MAS NMR as it is electrochemically cycled from $x = 3$ to $x = 2$. Preliminary results show the Li ion mobility is slowed in the cycled product relative to the as-prepared Li$_3$V$_2$(PO$_4$)$_3$ phase.
5.2 Experimental

5.2.1 Sample Preparation.

Li$_3$Fe$_2$(PO$_4$)$_3$ was prepared by solid state reaction as described by Padhi et al.$^1$ Stoichiometric amounts of NH$_4$H$_2$PO$_4$ (Sigma Aldrich, 99%), $^6$LiOH (prepared in house using Cambridge isotopes $^6$Li metal), and Fe$_2$O$_3$ (Sigma Aldrich, 99%) were ground together and heated to 250 °C to drive off ammonia and water. The mixture was reground and fired again, this time bringing the sample to 850 °C over a period of 24 hours and then holding for 2 days. The sample was reground, pelletized, and sintered at 930 °C for 24 hours.

Li$_3$V$_2$(PO$_4$)$_3$ was prepared by solid state reaction described by Yin et al.$^2$ Stoichiometric amounts of $^6$Li enriched Li$_2$CO$_3$ (Sigma Aldrich, 95% atom $^6$Li), V$_2$O$_5$ (Alfa Aesar, 99.6% ), and NH$_4$H$_2$PO$_4$ (Sigma Aldrich, 99%) were ground together and heated to 300°C for 3 hours. The mixture was reground and fired at 850°C for 12 hours under a flow of 5% H$_2$/N$_2$.

Synthesized samples were characterized using a PANalytical diffractometer with Cu K$\alpha_1$ radiation ($\lambda = 1.5406$ Å). Data was collected from 10 – 90 ° in 2θ step size of 0.016 with a step time of 100 s. The reflections were indexed in agreement with the literature.$^2,^3$
5.2.2 Solid-State NMR.

For the SSNMR study of Li$_3$Fe$_2$(PO$_4$)$_3$, variable temperature 1D $^6$Li MAS NMR and 2D EXSY spectra were acquired at a Larmor frequency of 29.4 MHz on a Bruker AMX 200 spectrometer. A custom-built double resonance probe supporting 1.8 mm rotors capable of MAS frequencies of 25 kHz up to 45 kHz was used. Temperatures were calibrated using Pb(NO$_3$)$_2$ as described elsewhere.$^4$ The spectra were referenced to 1 M $^6$LiCl (aq) (0 ppm). $^6$Li 1D spectra were acquired using a Hahn-echo pulse sequence with a 90° pulse of 2.5 µs and recycle delay of 50 ms. $T_1$ relaxation times were determined using a standard saturation recovery sequence. 2D exchange spectra were acquired using mixing times from 100 µs to 8 ms. The number of slices in the indirect dimension was 512. Phase-sensitive detection in $t_1$ was achieved through the use of States-TPPI.$^5$

For the variable temperature study of electrochemically cycled Li$_3$V$_2$(PO$_4$)$_3$, $^6$Li MAS spectra were acquired at a Larmor frequency of 44.1 MHz on a Bruker AV300 spectrometer. A custom-built double resonance probe supporting 1.8 mm rotors capable of MAS frequencies of 25 kHz up to 45 kHz was used. Temperatures were calibrated using Sm$_2$Sn$_2$O$_7$ as described elsewhere.$^6$ The spectra were referenced to 1 M $^6$LiCl (aq) (0 ppm). $^6$Li 1D spectra were acquired using a Hahn-echo pulse sequence with a 90° pulse of 2.5 µs and recycle delay of 200 ms.

5.2.3 Electrochemical Measurements

The positive electrode material was prepared by combining the active material (Li$_3$V$_2$(PO$_4$)$_3$) in a 75:15:10 weight ratio with carbon black (CB) and polyvinylidene
fluoride (PVDF). This mixture was made into a slurry with N-methyl-2-pyrrolidine (NMP) (Sigma Aldrich) as a solvent and cast onto Al foil. Cathode discs of 1.27 cm in diameter were assembled in coin cell casings with LiPF$_6$ as the electrolyte (1M LiPF$_6$ in a 1:1 wt% ethylene carbonate:dimethylcarbonate solvent, Novolyte) and Li-metal as the negative electrode. Cells were cycled on a VMP multichannel potentiostat at a rate of C/100 using a Galvanostatic Intermittent Titration Technique (GITT).

5.2.4 Bond Valence Density Maps

Bond valence density maps were generated for each crystal structure using the VALMAP program developed by Gonzalez-Platas et al. This program takes the crystallographic input data including unit cell parameters and atomic coordinates, and calculates the bond valences density within a three-dimensional unit cell using the empirical parameters of Brown et al. In this work, two-dimensional planes of bond valence density were extracted using the atomic coordinates of atoms defining a Li ion diffusion pathway. For each map, a 1.5 Å radius is shown with a bond valence density contour level increment is 0.485.
5.3 Results and Discussion

5.3.1 \(^{6}\text{Li} \text{2D EXSY Study of Li}_3\text{Fe}_2(\text{PO}_4)_3\)

The iron phosphate family of materials including the olivine LiFePO_4,\(^{10}\) NASICON Li_3Fe_2(PO_4)_3,\(^{11}\) and monoclinic Li_3Fe_2(PO_4)_3,\(^{1,12}\) have been an exceptional point of interest due to their low cost and low environmental impact. The appreciable redox potentials of the Fe\(^{3+}/\text{Fe}^{2+}\) redox couple for these materials occur at approximately 3.43, 3.55, and 2.8 V vs. Li\(^{+}\), respectively. Despite the advantages of using the iron phosphate materials, overall these compounds exhibit surprisingly poor electronic and ionic conductivity, which has limited their commercial success. Lithium NMR is well known to be an in-depth tool for studying structural and dynamic factors that can lead to poor electrochemical performance.\(^{13-16}\) Lithium in these materials is directly involved in the electrochemical process and moreover, shows sensitivity to electronic changes that may take place in the surrounding lattice during lithium extraction, making it an interesting nucleus for solid-state NMR studies.

Li_3Fe_2(PO_4)_3 crystallizes in a structure similar to the open framework NASICON structure with space group \(P2_1/n\).\(^3\) The structure is a three dimensional framework of FeO_6-octahedra and PO_4-tetrahedra (Figure 5.1). There are three crystallographically unique Li sites where Li1 occupies the tetrahedral position and Li2 and Li3 both occupy the distorted trigonal bipyramidal sites.
Figure 5.1 - Unit cell of monoclinic Li$_3$Fe$_2$(PO$_4$)$_3$ along the a-axis. FeO$_6$ octahedra (blue) are connected to PO$_4^{3-}$ tetrahedra (yellow) at oxygen vertices. Li1 (orange), Li2 (pink) and Li3 (green) sit in channels formed by the PO$_4$ and FeO$_6$ units.

5.3.1.1 $^6$Li MAS NMR and Site Assignment of Li$_3$Fe$_2$(PO$_4$)$_3$

The three Li crystallographic positions of Li$_3$Fe$_2$(PO$_4$)$_3$ (Figure 5.1) were resolved in the 1D $^6$Li NMR spectrum with MAS of 25 kHz (Figure 5.2). Resonances which arise at 45 ppm, 102 ppm, and 216 ppm, are designated as sites A, B, and C, respectively. An assignment of the $^6$Li resonances to the crystallographic positions was made based on the geometry dependent electron spin density transfer from the paramagnetic iron center to the Li and P atoms.$^8,17$ Note that the assignment presented here differs from the assignment made in the original manuscript.$^{18}$ This amendment is made in light of the density functional results of Kim et al. as well as the assignment presented by Castets et al.$^{19,20}$
The assignment of the Li shifts is rationalized based on the Fermi-contact rules outlined in Chapter 2. For Li$_3$Fe$_2$(PO$_4$)$_3$, the Fe$^{3+}$ has an electron configuration of high spin $t_{2g}^3e_g^2$. The overall chemical shift range (Table 2) for the three Li crystallographic sites of Li$_3$Fe$_2$(PO$_4$)$_3$ is significantly higher (45 – 216 ppm) than that of the vanadium analogue (17-107 ppm)$^{2,13}$ This is consistent with the addition of one more unpaired electron in the $t_{2g}$ orbitals and the assertion that the delocalization mechanism is often dominant over the polarization mechanism.$^{21}$ Therefore, the 1D $^6$Li MAS NMR spectrum was assigned based on the crystallographic data, using a similar approach to the Li$_3$V$_2$(PO$_4$)$_3$ case.$^{13}$ The highest chemical shift, C, is assigned to Li2 which showed orbital interactions with the strongest 90° overlap (90.28° and 89.47°) (Table 5.1). The lowest resonance, A, at 45 ppm is assigned to Li3 which has the poorest Li-O-Fe overlap.
Site B is therefore assigned to the four coordinate Li1 site which has two sites close to 90° (93.98° and 92.61°).

**Table 5.1** – Summary of crystallographic data for Li₃Fe₂(PO₄)₃ with assignment to the A, B, and C, resonance provided.²²

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<tr>
<th>Li Site</th>
<th>O label</th>
<th>Li-O Distance (Å)</th>
<th>Li-Fe Distance (Å)</th>
<th>Li-O-Fe Angle</th>
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<tr>
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5.3.1.2 ⁶Li 2D EXSY Over a Variable Temperature Range

⁶Li 2D EXSY experiments were used for determining the timescales and activation energies of ion hopping in Li₃Fe₂(PO₄)₃. As outlined in Chapter 3, in a 2D EXSY experiment each spin is frequency labeled during the evolution period, t₁. The exchange processes are allowed to take place during the following mixing period of set length, τₘ. Through successive experiments, the integrated volume of the cross peaks plotted as a function of mixing time yields a correlation time for the exchange process. Since the mixing period is limited by the spin-lattice relaxation time (T₁) of the spins, the increased number of unpaired electrons had a profound effect on the T₁ times when
comparing the Fe and V compounds. For Li$_3$V$_2$(PO$_4$)$_3$, $^7$Li relaxation times for all three resonance were on the order of 6.0 ± 0.2 ms. For Li$_3$Fe$_2$(PO$_4$)$_3$, $^7$Li T$_1$ times for all resonances were shortened significantly to 1.1 ± 0.2 ms due to the addition of 3 unpaired electrons at the Fe metal center. In order to achieve a first-order exponential buildup to extract an accurate correlation time, mixing times longer than 1 ms were needed. A smaller quadrupole moment and lower magnetogyric ratio for $^6$Li gives weaker dipolar coupling values than the $^7$Li counterpart, resulting in longer T$_1$ relaxation values. Therefore, samples of Li$_3$Fe$_2$(PO$_4$)$_3$ were prepared with $^6$Li enriched LiOH which increased T$_1$ times for all three sites to 8.0 ± 0.2 ms and allowed for longer mixing times to be used.

**Figure 5.3** shows $^6$Li 2D EXSY spectra acquired at 311 K at two different mixing times. For the shorter mixing time of 0.5 ms, exchange was not observed (**Figure 5.3.a**). When the mixing time was increased to 3.0 ms (**Figure 5.3.b**), exchange is observed between all three resonances giving AB, BC, and AC crosspeaks.
Hopping rates for each exchange pair were determined by measuring the cross peak intensity (normalized to the sum of the intensities of the diagonal peaks) as a function of mixing time (Figure 5.4). By fitting this data to a first order exponential function, correlation times, $\tau_c$, and jump rates (k) were extracted at each temperature (Table 5.2).
Figure 5.4 – Normalized cross peak volume as a function of mixing time for exchange pair AB (□), BC (○), and AC (△) for Li$_3$Fe$_2$(PO$_4$)$_3$. Clockwise from top left acquisition temperatures for each data set are 283 K, 292 K, 302 K, and 311 K. Due to $T_1$ limitations, plateaus, for lower temperature data sets were not achieved.

Table 5.2 – Summary of exchange rates determined from $^6$Li 2D EXSY measurements over a variable temperature range for Li$_3$Fe$_2$(PO$_4$)$_3$.

<table>
<thead>
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<th>Temperature (K)</th>
<th>$k_{AB}$ (s$^{-1}$)</th>
<th>$k_{BC}$ (s$^{-1}$)</th>
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<tr>
<td>283</td>
<td>8 ± 16</td>
<td>100 ± 50</td>
<td>100 ± 50</td>
</tr>
<tr>
<td>292</td>
<td>200 ± 100</td>
<td>150 ± 50</td>
<td>200 ± 100</td>
</tr>
<tr>
<td>302</td>
<td>700 ± 200</td>
<td>600 ± 100</td>
<td>600 ± 100</td>
</tr>
<tr>
<td>311</td>
<td>1000 ± 200</td>
<td>800 ± 200</td>
<td>1000 ± 200</td>
</tr>
</tbody>
</table>
The large relative error on the lowest temperature rate (283 K) for the AB exchange pair is due to the linear appearance of the cross peak build-up prior to the onset of $T_1$ relaxation (Figure 5.4 top left). Due to the dynamic limitations within this material, the range of temperatures for the exchange experiments was limited. At temperatures below 283 K, the dynamics were too slow for a sufficient buildup curve to be attained within the limits of the $T_1$ times. At higher temperatures, the three resonances began to coalesce due to fast mobility making accurate integration of the crosspeaks difficult. The jump rates from multiple integrations were averaged and error determined at the 95% confidence level. This error was insignificant as compared to the error from the first order exponential fit and therefore this latter error was propagated into the Arrhenius analysis.

The activation energies, $E_a$, for each exchange pair were determined by plotting natural log of the rates as a function of $1000/T$ in an Arrhenius analysis (Figure 5.5). Errors for the $E_a$ values were calculated from the standard error of the slope from the regression analysis. Exchange between sites AC and BC is the most energetically favourable having activation energies of 0.63 ($\pm$0.03) eV and 0.59 ($\pm$ 0.05) eV. A higher energy barrier is observed for the AB exchange pair, however it is noted that a poor linear fit is found when the low temperature data point (carrying the large error) is used. The energy barrier was therefore calculated again but this time with the AB 283 K data point set to the uppermost limit of the error bound. The result is a better linear fit and an activation energy of 0.81 ± 0.04 eV that is still considerably higher than the AC and BC ion hops.
Figure 5.5 – Arrhenius analysis for determination of activation energies for Li-Li hopping between exchange pairs AB (top), AC (middle), and BC (bottom). For the AB exchange pair (top), the large error bar of the lowest temperature data point (283K) obscures the fit significantly. The analysis was therefore performed with the 283 K data point set to the uppermost limit of the error bar to yield a better linear fit (open squares with dashed linear fit (top)).
5.3.1.3 Correlating $E_a$ to Structural Constraints in Li$_3$Fe$_2$(PO$_4$)$_3$

The energy barriers observed in Li$_3$Fe$_2$(PO$_4$)$_3$ were evaluated in relation to structural constraints present in the host framework. In the previous report of the ion dynamics in Li$_3$V$_2$(PO$_4$)$_3$, the energy barriers of the ion hopping were found to be higher in ion pairs where longer internuclear distances coupled with smaller bottlenecks of diffusion (summarized in Table 5.3). Bottlenecks of diffusion in both Li$_3$Fe$_2$(PO$_4$)$_3$ and Li$_3$V$_2$(PO$_4$)$_3$ were defined as the area created by O vertices of PO$_4$ and FeO$_6$ polyhedra that were found along the pathway of a Li-Li exchange pair.

Table 5.3 - Summary of activation energy values for the three Li-Li exchange pairs as well as the calculated Li-O bottlenecks of diffusion for Li$_3$V$_2$(PO$_4$)$_3$.

<table>
<thead>
<tr>
<th>NMR Sites</th>
<th>Li Site</th>
<th>$E_a$ (eV)</th>
<th>Li-O bottleneck (Å$^2$)</th>
<th>Li-Li distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>Li1-Li2</td>
<td>0.83 ± 0.01</td>
<td>3.69</td>
<td>3.43(3)</td>
</tr>
<tr>
<td>AB</td>
<td>Li1-Li3</td>
<td>0.73 ± 0.01</td>
<td>4.10</td>
<td>3.08(3)</td>
</tr>
<tr>
<td>AC</td>
<td>Li2-Li3</td>
<td>0.79 ± 0.01</td>
<td>3.79</td>
<td>3.28(3)</td>
</tr>
</tbody>
</table>

For Li$_3$Fe$_2$(PO)$_3$, no such correlation exists. Rather, the highest energy barrier observed has the most open bottleneck area and the shortest internuclear distance (Table 5.4).

Table 5.4 - Summary of activation energy values for the three Li-Li exchange pairs as well as the calculated Li-O bottlenecks of diffusion for Li$_3$Fe$_2$(PO$_4$)$_3$.

<table>
<thead>
<tr>
<th>NMR Sites</th>
<th>Li Site</th>
<th>$E_a$ (eV)</th>
<th>Li-O bottleneck (Å$^2$)</th>
<th>Li-Li distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>Li1-Li2</td>
<td>0.59 ±0.05</td>
<td>3.96</td>
<td>3.139</td>
</tr>
<tr>
<td>AC</td>
<td>Li1-Li3</td>
<td>0.63 ±0.03</td>
<td>3.61</td>
<td>3.417</td>
</tr>
<tr>
<td>AB</td>
<td>Li2-Li3</td>
<td>0.81 ±0.04</td>
<td>4.22</td>
<td>3.110</td>
</tr>
</tbody>
</table>

To better explain the observed trends of the energy barriers within Li$_3$Fe$_2$(PO$_4$)$_3$, the influence that bond valence sum (BVS) values have on ion mobility was investigated. BVS values are a measure of how tightly bound a Li ion is within its crystallographic
position. High BVS values indicate a tightly bound Li environment while more loosely bound Li will have lower BVS values.\(^9,23\) In Li\(_3\)Fe\(_2\)(PO\(_4\))\(_3\) the BVS values of each Li ion at the crystallographic positions fall very close to one another with Li1, Li2, and Li3 BVS values of 1.054, 0.952, and 0.989, respectively and subsequently do not shed light on the observed trends in exchange energy barriers. Bond valence density maps were therefore calculated for each of the exchange pathways given in Table 5.4. In these maps, regions of high bond valence density are less amenable to Li ion diffusion while low bond valence density leads to favourable pathways for Li mobility.\(^23,24\)

**Figure 5.6** shows the bond valence density maps where for a given exchange pair, a plane was defined by the coordinates of the O-atoms that create the faces of each ion that are directed towards one another. Using Li1-Li2 exchange as an example, the face of the Li1 atom directed towards the Li2 face is defined by atoms O1, O11, and O3. The O3 atom is shared with the Li2 polyhedron with O7 and O12 atoms completing the Li2 face. By calculating the midpoint between the unshared oxygen atoms arising from each face (i.e. the midpoints between the O1-O12 atoms and the O7-O11 atoms) a plane between the Li1 and Li2 faces is defined (**Figure 5.6** left column). In each BVS map, lines are drawn on the bond valence map to show the angles at which the diffusion region extends from the shared atoms to the coordinates of the mid-point for the unshared atoms.
Figure 5.6 – Bond valence maps (right column) for the Li1-Li2 (top), Li1-Li3 (middle), and Li2-Li3 (bottom) exchange pathways. The maps shown were defined by the plane of the vertices of the faces of the Li-polyhedra orientated towards each other for exchange, with a 1.5 Å radius and contour increment of 0.485. A schematic showing how these panes were defined is shown in the right column for the Li1-Li2 (top), Li1-Li3 (middle), and Li2-Li3 (bottom) exchange pathways. On each map the coordinates of shared atoms and midpoints are given with lines radiating from shared atoms to midpoints of unshared atoms.
The geometries of the Li1-Li2 and Li1-Li3 pathways have an appreciable region of low bond valence density available for the Li ions to diffuse. The similarity in appearance of the bond valance maps corresponds well to these two ion hopping pairs having energy barriers equivalent within error (0.59 ±0.05 and 0.63 ± 0.03 for Li1-Li2 and Li1-Li3, respectively). For Li2-Li3 on the other hand, the anchoring of the Li2 and Li3 atoms to the edge of a Fe octahedral environment (via O4 and O1), leads to a high-density region dominating the diffusion pathway which does not have the “open” features observed in the Li1-Li2 and Li1-Li3 maps. This highlights why a higher energy barrier is found for the Li2-Li3 exchange process. Moreover, the position of the edge-shared Fe octahedron relative to the Li ions (as shown in the spherical representation of the Li ions) shows the Fe obstruction along the Li-pathway **Figure 5.7**. For the corner-shared geometries, the prominence of the Fe atoms along the pathway is less severe.

**Figure 5.7** - Schematic showing the geometries of the shared polyhedra of the Li ion sites undergoing ion exchange in Li$_3$Fe$_2$(PO$_4$)$_3$, Li1-Li2 left, Li1-Li3 middle and Li2-Li3 left.

Correlation of the exchange information of Li$_3$Fe$_2$(PO$_4$)$_3$ to the available electrochemical data remains the focus of ongoing work. While these results show that the dynamics in the parent Li$_3$Fe$_2$(PO$_4$)$_3$ compound are more energetically favourable
than in the parent Li$_3$V$_2$(PO$_4$)$_3$ material, overall the Fe intercalation cathode is not as interesting from a commercial standpoint as the vanadium analogue. Not only does Li$_3$V$_2$(PO$_4$)$_3$ have an overall higher operating potential with three reversible voltage plateaus of 3.59, 3.67, and 4.06 V but it also has one of the highest theoretical capacities of all the phosphates (about 197 mAh/g).$^{25,26}$ In the case of Li$_3$V$_2$(PO$_4$)$_3$, results from the 2D EXSY study correlated well to the order in which the Li ions are extracted from the parent material. In the case of Li$_3$Fe$_2$(PO$_4$)$_3$, the potential of the Fe$^{3+}$/Fe$^{4+}$ redox pair lies well outside the operating voltage window of a typical Li ion battery meaning that extraction of Li1, Li2, and Li3 from the iron material studied here is not possible for electrochemical applications. Instead, electrochemists exploit the Fe$^{3+}$/Fe$^{2+}$ redox pair through insertion of fourth and fifth lithium ions into the structure, giving two voltage plateaus at 2.65 V and 2.85 V. Therefore, a direct correlation of the activation energies for ion hopping in the parent material to electrochemical extraction of lithium is not possible for Li$_3$Fe$_2$(PO$_4$)$_3$. Rather, we anticipate significant changes in local lithium dynamics upon chemical or electrochemical insertion of excess lithium.

5.3.2 $^6$Li MAS Study of Electrochemically Cycled Li$_x$V$_2$(PO$_4$)$_3$

Here preliminary results demonstrating changes to ion mobility in Li$_x$V$_2$(PO)$_3$ as it is electrochemically cycled from $x = 3$ to $x = 2$ are presented. Previous reports have linked the ion dynamics of the as-prepared phase to the order in which the Li ions are extracted from the lattice, giving rise to new, intermediate phases. Specifically, Yin et al. showed the existence of new, single phases, when Li$_x$V$_2$(PO$_4$)$_3$ was cycled to points found
midway between voltage plateaus. These results showed that Li3 is extracted first while Li1 and Li2 are more energetically costly and therefore removed as second and third sites, respectively. This analysis agreed well with the energy barriers found from the 2D EXSY work of Cahill et al. and highlighted how the dynamics of the as-prepared phase influences the electrochemical performance.

Here $^6$Li MAS NMR measurements are used to characterize Li environments in Li$_x$V$_2$(PO$_4$)$_3$ after being electrochemically cycled to points along the voltage plateaus (not midway between). Figure 5.8 shows the Galvanostatic Intermittent Titration Technique (GITT) experiments used to extract 0.8 Li from Li$_3$V$_2$(PO$_4$)$_3$. GITT experiments have current applied for a set time before being switched off to allow the system to reach equilibrium. This method ensures a 1:1 Li:electron removal. In this experiment, due to the low sample size of electrochemically cycled cathode materials, two separate coin cells were combined after being cycled to near equivalent compositions (Figure 5.8, left). The MAS spectra of the pristine and cycled samples are shown in Figure 5.8, right. There is an observed narrowness of the cycled peaks not observed in the as-prepared sample. We attribute this to a mixing of the active material with carbon black and binder as this same narrowing was observed in a $^6$Li NMR spectrum of the uncycled cast (Figure 5.9 middle). There is no observed change to the paramagnetic shift of the cycled sample indicating that no new Li environments have emerged in spite of electron changes at the transition metal center. This is not entirely unexpected as the flat voltage plateau indicates a two-phase extraction and although removal may be initiated from a preferred site, the fast ion exchange allows the sites to equilibrate over the crystallographic
positions. The cycled sample with $x = 2.2$ is therefore more accurately described as the two-phase $0.73\text{Li}_3\text{V}_2(\text{PO}_4)_3:0.27\text{V}_2(\text{PO}_4)_3$.

![Figure 5.8](image)

**Figure 5.8** – Right: GITT experiments of the two coin cells combined for NMR measurements. Cells were each cycled to $x \sim 2.2$. Left: $^6\text{Li}$ MAS spectra of the as-prepared $\text{Li}_3\text{V}(\text{PO}_4)_3$ (bottom) and the cycled material.

The sample size from the two coin cells was too small for quantitative methods such as 2D EXSY to be used for determination of ion dynamics. Therefore, a preliminary qualitative picture of the ion dynamics was made through variable temperature $^6\text{Li}$ 1D MAS measurements of the pristine sample as compared to the uncycled cast and the cycled material (**Figure 5.9**).
Figure 5.9 – $^6$Li MAS spectra under variable conditions of as-prepared Li$_3$V$_2$(PO$_4$)$_3$, an unycled cast of Li$_3$V$_2$(PO$_4$)$_3$ with carbon black and PVDF (middle) and a sample cycled to $x = 2.2$ giving 0.73Li$_3$V$_2$(PO$_4$)$_3$:V$_2$(PO$_4$)$_3$

For the as-prepared Li$_3$V$_2$(PO$_4$)$_3$, the coalescence of the three environments gives a resonance with single site features at 315 K. Two small diamagnetic impurities centered at 0 and 20 ppm are also observed but do not interact with the phase of interest and are therefore ignored. When Li$_3$V$_2$(PO$_4$)$_3$ is cast with CB and PVDF to form a positive electrode, the dynamics slow, and single site features do not definitively appear until 320 K. This result is presumably from increased grain boundary effects due to the introduction of the additives. After the material has been cycled to a composition of $x \sim 2.2$, the dynamics are slowed further, where complete coalescence has not been reached by 320 K. A diamagnetic peak is also observed here at ~ 0 ppm and is attributed to residual electrolyte from the battery casing. The slowing of the ion mobility in the
cycled sample is surprising result, as the presence of a larger number of Li site vacancies is expected to increase the ion mobility. Slow dynamics may arise from immobility of the phase interface regions, which is a known problem in the phosphate family of cathode materials. Studies are currently underway to investigate this system further including measurements of samples cycled to lower Li content and applying more quantitative measurements of the ion dynamics.

5.4 Summary and Outlook

This chapter presents the first study of Li$^+$ dynamics in monoclinic Li$_3$Fe$_2$(PO$_4$)$_3$. Exchange between the crystallographic Li sites was found to be on the millisecond timescale. By plotting the change in jump rate as a function of temperature the activation barriers for Li ion exchange were determined. The activation energies, ranging from 0.59 ($\pm$ 0.05) eV to 0.81 ($\pm$ 0.04) eV, did not correlate to Li-Li internuclear distances nor the Li-O bottlenecks along the diffusion pathway. The energy barriers were more simply described by the bond valence density found along the plane defining the midpoint between the faces of the Li polyhedra undergoing ion exchange.

This chapter also presents preliminary results on the ion dynamics of Li$_3$V$_2$(PO$_4$)$_3$ as it is cycled to lower Li content using GITT experiments. Here, coalescence data showed a slowing of the ion mobility as the Li ions were removed from the host framework. Due to the low sample size of the cathodes used in the current coin cell design, 2D EXSY measurements are not possible for quantification of ion hopping timescales. Future studies could not only increase the number of cathodes that are combined for an experiment, but also utilize 1D selective inversion methods which are a more time-
efficient method for determining ion hopping rates than 2D EXSY. Details of the selective inversion experiments and how they can be applied to paramagnetic systems are outlined in the next chapter.
5.5 References


Chapter 6: Structural Features and Li Ion Hopping Timescales in Li\textsubscript{x}VPO\textsubscript{4}F from \textsuperscript{6}Li MAS Measurements

6.1 Introduction

In this chapter \textsuperscript{6,7}Li MAS NMR measurements are used to characterize Li environments in three samples of Li\textsubscript{x}VPO\textsubscript{4}F (where x = 1.0, 1.5, or 2.0). Timescales of ion hopping are quantified in the final phase, Li\textsubscript{2}VPO\textsubscript{4}F, using \textsuperscript{6}Li 1D Selective Inversion (SI) measurements over a variable temperature range.

The tavorite-based LiVPO\textsubscript{4}F was first reported by Barker et al. as a high capacity (155 mAh/g) 4.1 V positive electrode material for Li ion batteries.\textsuperscript{1} Intercalation of a second lithium to create Li\textsubscript{2}VPO\textsubscript{4}F takes place with a V$^{3+}$–V$^{2+}$ redox potential of 1.8 V.\textsuperscript{2} Our collaborators at the University of Waterloo have chemically prepared L\textsubscript{x}VPO\textsubscript{4}F (x = 1.0, 1.5, 2.0) and used powder XRD to characterize the structural changes of the host framework as LiVPO\textsubscript{4}F transforms from triclinic space group P -1 (isostructural to many known fluorophosphates)\textsuperscript{3,4} to monoclinic Li\textsubscript{2}VPO\textsubscript{4}F (space group C 2/c). This structure is proposed to have three-dimensional conduction pathways which is considerably advantageous over more well-known cathode materials including olivine LiFePO\textsubscript{4} which is restricted to 1D tunnels for conduction.\textsuperscript{5} Here we evaluate the new Li environments generated through lithiation using \textsuperscript{6,7}Li MAS NMR and determine the propensity for 3D diffusion within the reduced phase.
This thesis also introduces the use of one-dimensional selective inversion (1D SI) methods to determine the ion hopping rates in the fully lithiated, Li$_2$VPO$_4$F, phase. As outlined in Chapter 3, 1D SI experiments monitor the return of magnetization to equilibrium conditions following the selective inversion of a single lithium environment. The ion relaxation is governed not only by the inherent spin-lattice relaxation of the nuclei, but also by the rate of ion exchange with non-inverted spins. Conversely, non-inverted spin(s) show attenuation of signal intensity as a function of time during the period where ion exchange is the dominant mechanism for relaxation of the inverted spin.$^{6,7}$ By fitting the experimental data in a program such as CIFIT, timescales of ion exchange can reliably be separated from inherent T$_1$ properties$^{8,9}$. These 1D experiments are more efficient in terms of spectrometer time as compared to their 2D counterparts and thus warrant investigation. Moreover, this method reveals timescales of ion hopping in materials where the Li ions exchange slowly relative to their T$_1$ spin-lattice relaxation. As was shown in the $^6$Li 2D EXSY study of Chapter 5, considerable error was introduced in the EXSY buildup curves as the dynamics slowed and the mixing times were limited to the longest T$_1$. This situation is particularly relevant to cathode materials for lithium ion batteries, where the unpaired electrons of the transition metal centers provide a dominant mechanism for rapid relaxation. The aim of the remainder of this thesis is to expand the use of 1D selective inversion experiments to allow for ion hopping timescales to be quantified in a larger range of materials that were previously excluded due to T$_1$ limitations.
The results of this chapter were published in two different manuscripts. The first paper was submitted to the journal, *Chemistry of Materials* (2011, in press, cm-2011-01773n.R1) with authorship of B. Ellis, T. N. Ramesh, L. J. M. Davis, G. R. Goward, L. F. Nazar. Researchers from Prof. Nazar’s group at the University of Waterloo, B. Ellis and T.N. Ramesh, prepared samples of \( \text{Li}_x\text{VPO}_4\text{F} \) (\( x = 0, 1.5, 2.0 \)). Electrochemical measurements as well as Rietveld analysis of crystallographic data were also carried out in the Nazar group. All NMR measurements and analysis was carried out at McMaster University under the supervision of Prof. Goward. A second manuscript of the \(^6\text{Li} 1\text{D EXSY measurements on Li}_2\text{VPO}_4\text{F} \) was submitted to the *Journal of Physical Chemistry C*, (2011, in press, DOI 10.1021/jp2059408). The authorship on this work was L.J.M. Davis, B. L. Ellis, T. N. Ramesh, L. F. Nazar, A. D. Bain, G. R. Goward. Here, I collected and analyzed all NMR data under the supervision of Prof. Bain and Prof. Goward. Members of Prof. Nazar’s research group, B. L. Ellis and T. N. Ramesh, prepared the samples studied in this work.
6.2 Experimental

6.2.1 Sample Preparation

Samples of Li$_x$VPO$_4$F were prepared by collaborators at the University of Waterloo. Briefly, LiVPO$_4$F was prepared by the method reported by Barker et al.$^1$ V$_2$O$_5$ (Aldrich, 99%+), NH$_4$H$_2$PO$_4$ (BDH, 99%) and carbon black were mixed in a 0.5:1:1.5 molar ratio and fired at 750 °C under a flowing Ar atmosphere to produce carbon-coated VPO$_4$. VPO$_4$ and LiF were combined in stoichiometric amounts and milled with zirconia milling media for 4-6 hours. The powder was fired at 600 °C for 1 hour under an Ar atmosphere to form LiVPO$_4$F. LiVPO$_4$F was then stirred with a stoichiometric amount of LiAlH$_4$ in tetrahydrofuran in an argon-filled glove box for 44 hours. The final product, Li$_2$VPO$_4$F, was washed with tetrahydrofuran and stored under argon.

6.2.2 Solid State NMR.

All experiments with the exception of the $^6$Li{$^{19}$F} REDOR and $^6$Li 1D EXSY measurements were carried out at field strength of 7.0 T with $^6$Li and $^7$Li Larmor frequencies of 44.1 and 116.6 MHz on a Bruker AV300 spectrometer. A custom built probe supporting 1.8 mm rotors was used with MAS frequencies ranging from 25-40 kHz. By adjusting spinning speeds from 25 kHz to 40 kHz, a temperature range of 303 K to 330 K was available. Both $^6$Li and $^7$Li 1D spectra were acquired using 90° pulse lengths ranging from 2.0 to 2.5 µs and recycle delay of 100 ms. Spin-lattice relaxation times (T$_1$) were determined using the standard inversion recovery sequence included in
the Bruker software package. Two-dimensional exchange (EXSY) spectra were acquired using mixing times ranging from 2 ms to 17 ms. The number of slices in the indirect dimension was 2048. Phase-sensitive detection in $t_1$ was achieved through the use of States-TPPI.\textsuperscript{10}

$^6\text{Li}\{^{19}\text{F}\}$ REDOR studies were carried out on a Bruker AV500 spectrometer (11.7 T) with $^6\text{Li}$ and $^{19}\text{F}$ Larmor frequencies of 73.6 MHz and 469.5 MHz, respectively. The same 1.8 mm probe as described above was used for these experiments with the $^1\text{H}$ channel modified to allow for $^{19}\text{F}$ dephasing. A $^{19}\text{F}$ $\pi$ pulse length of 4.40 $\mu$s was used.

1D $^6\text{Li}$ EXSY was also performed on a Bruker AV500 spectrometer with a Bruker MAS probe supporting 2.5 mm rotors. 1D EXSY experiments were performed using a $90^\circ$ - $\tau_1$ - $90^\circ$ - $\tau_{\text{mix}}$ - $90^\circ$ sequence, also with a $90^\circ$ pulse of 2.5 $\mu$s, recycle delay of 200 ms, and 10240 scans for each slice. For our two-site system, selective inversion of the lower frequency A spin was accomplished using a $90^\circ$ pulse, set on resonance to spin A. During the first [$90^\circ$ - $\tau_1$ - $90^\circ$] portion of the sequence, where $\tau_1$ is set to $1/(2\Delta\nu_{AB})$, the on-resonance spin is selectively inverted following the second $90^\circ$ pulse. Mixing times ($\tau_{\text{mix}}$) were stepped over a series of 16 experiments from 5 $\mu$s to 100 ms (the latter delay time being well beyond the relaxation rates of both spins to ensure that both spins had magnetization measured at equilibrium). Nonselective Inversion (NSI) experiments were performed using the standard inversion-recovery sequence. The same variable delay list was used in the NSI as was used in the 1D EXSY experiments. In both the SI and NSI studies, a digital filter was applied to allow for acquisition and analysis of the centerband region only.
All spectra were referenced to 1 M $^6$LiCl (aq) (0 ppm), and CFCl$_3$ for $^{19}$F experiments. Temperatures were calibrated using Sm$_2$Sn$_2$O$_7$ as described elsewhere.$^{11}$

### 6.2.3 1D EXSY Data Analysis

In each data set, slices for each mixing time/variable delay were extracted and baseline corrected. After integrating both spins involved in the exchange process, these values were normalized to the integration value of the slice collected at the longest mixing time/variable delay (where the magnetization of each spin was fully relaxed). The data was fit using the CIFIT program developed by A.D. Bain.$^{12}$ This program utilizes a table of observed intensities for all spins as a function of mixing time and determines a key set of parameters: the jump rates (k) of each chemical exchange process, spin-lattice relaxation times in the absence of chemical exchange ($T_1$), and the magnetization values from initial to equilibrium conditions (i.e. from $M_i(0)$ to $M_i(\infty)$). The rate matrix used to describe spin relaxation under the influence of chemical exchange is the primary mathematical model used by the CIFIT program and is described in greater detail elsewhere.$^{9,12,13}$ CIFIT adjusts the free parameters, $T_1$, k, $M_i(0)$ and $M_i(\infty)$, using a Levenberg-Marquardt algorithm until the sum of the squares of the differences between the experimental and calculated data is minimized. Error values of the exchange rates were approximated in the CIFIT program by the variance-covariance matrix of the fit to the data.$^{12}$
6.2.4 Bond Valence Density Maps

Bond valence density maps were generated for each crystal structure using the VALMAP program, developed by Gonzalez-Platas et al.\textsuperscript{14} This program takes crystallographic data including unit cell parameters and atomic coordinates, and calculates the bond valences density within a three-dimensional unit cell using the empirical parameters of Brown \textit{et al.}\textsuperscript{15,16} In this work, two-dimensional planes of bond valence density were extracted using the atomic coordinates of atoms defining a Li ion diffusion pathway. For each map, a 2 Å radius is shown with a bond valence density contour level increment is 0.485.
6.3 Results and Discussion

6.3.1 $^6$Li MAS NMR of Li$_x$VPO$_4$F ($1 \leq x \leq 2$)

The single crystallographic site for LiVPO$_4$F was resolved in the $^7$Li MAS NMR spectrum collected at 330 K (MAS = 40 kHz) with a paramagnetic shift centered at 111 ppm (Figure 6.1). The high value for the observed shift is attributed to the geometry dependent hyperfine coupling of the Li nuclei with the unpaired electron density sitting on the V$^{3+}$ transition metal center. The relatively short spin-lattice relaxation time ($T_1$) of this resonance ($6.5 \pm 0.2$ ms) also reflects the paramagnetic nature of the Li-resonance.

![Figure 6.1](image)

Figure 6.1 – $^7$Li MAS (40 kHz, 330 K) spectra of Li$_x$VPO$_4$F at various stages of lithiation resulting in single site LiVPO$_4$F (bottom), two-phase 0.5LiVPO$_4$F:0.5Li$_2$VPO$_4$F (middle), and single-phase Li$_2$VPO$_4$F (top)

The isotropic resonance of LiVPO$_4$F deconvoluted to reveal a small shoulder at higher frequency (Figure 6.2). This is consistent with the Rietveld refinement results.
performed by our collaborators at the University of Waterloo. Here they refined the splitting of the Li site in LiVPO$_4$F as a Li1:Li2 occupancy of 0.18:0.82 (Figure 6.3). Our NMR results deconvoluted to similar values however we assign an error of ± 0.1 giving an approximate Li1:Li2 ratio of 0.2:0.8. This site splitting is commonly observed in other lithium fluorophosphates materials as the large octahedral environments yield high thermal parameters for the Li atoms.$^{3,19}$

**Figure 6.2** – Deconvolution of $^7$Li MAS isotropic resonance of LiVPO$_4$F (MAS 40 kHz, 330 K). The Li1:Li2 sites integrate in a ratio of 0.2(±0.1):0.8(±0.1).

**Figure 6.3** – Schematic showing the split site in LiVPO$_4$F which both Rietveld refinement and NMR showed to be a Li1:Li2 0.18:0.82 occupancy.
Upon 50% lithiation of LiVPO$_4$F to \( x = 1.5 \), two new resonances emerge (Figure 6.1 middle). The first is centered at 50 ppm and the second at -52 ppm (at 330 K) (herein referred to as sites A and B, respectively). The peak belonging to the parent LiVPO$_4$F phase remains but broadens slightly. A resonance centered at 0 ppm is also observed and is attributed to a diamagnetic Li impurity as it has a considerably longer \( T_1 \) relaxation time (> 60 s). After lithiation to Li$_2$VPO$_4$F, a slight amount of the parent LiVPO$_4$F remains but resonances belonging to the A and B sites now dominate the spectrum. Over the entire sideband manifold, a 1:1 integration for the A:B sites is found and clearly correspond to the two independent lithium ions in the fully reduced phase. The phase at \( x = 1.5 \) therefore is better described as biphasic 0.5LiVPO$_4$F:0.5Li$_2$VPO$_4$F.

The $^7$Li spin lattice relaxation times for sites A and B were 3.2 ± 0.2 ms and 2.0 ± 0.2 ms, respectively. The lower times vis à vis the parent LiVPO$_4$F are consistent with the increase in unpaired electron spin density observed in these systems that leads to stronger electron-Li dipolar coupling values (Table 6.1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parent LiVPO$_4$F</th>
<th>$T_1$ times (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>LiVPO$_4$F</td>
<td>6.5 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>Li$_2$VPO$_4$F</td>
<td>-</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0 ± 0.2</td>
</tr>
</tbody>
</table>
6.3.2 \(^6\)Li 2D EXSY Measurements of Li\(_2\)VPO\(_4\)F

Exchange of the Li\(^+\) between these two sites was explored using \(^6\)Li 2D EXSY experiments. In these studies, each spin is frequency labeled during the evolution period, \(t_1\). The exchange processes are allowed to take place during a mixing period of set length, \(\tau_m\) which is limited by the \(T_1\) times of the nuclei. Cross peaks appear at off-diagonal sites corresponding to the sites involved in the exchange process. Samples partially enriched with \(^6\)Li (which has an inherently longer \(T_1\), see Table 6.1 and Table 6.2) were used for the exchange experiments in order to probe mixing times long enough for exchange processes to occur. Spin-lattice relaxation times of both spins were determined at room temperature for \(^6\)Li using a nonselective inversion recovery experiment, and found to be 22.7 ± 0.5 ms and 16.3 ± 0.5 ms for sites A and B respectively (Table 6.2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parent LiVPO(_4)F</th>
<th>(T_1) times (ms) A</th>
<th>(T_1) times (ms) B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_{1.5})VPO(_4)F</td>
<td>44.2 ± 0.5</td>
<td>22.9 ± 0.5</td>
<td>16.8 ± 0.5</td>
</tr>
<tr>
<td>Li(_2)VPO(_4)F</td>
<td>-</td>
<td>22.7 ± 0.5</td>
<td>16.3 ± 0.5</td>
</tr>
</tbody>
</table>

Figure 6.4.a shows \(^6\)Li 2D EXSY spectra acquired at 303 K for the 0.5LiVPO\(_4\)F:0.5Li\(_2\)VPO\(_4\)F sample. Although no ion exchange between the crystallographic sites takes place at this temperature, crosspeaks between the A and B sites are clearly evident at 330 K (Figure 6.4.b). The mixing time in these experiments was extended to 15 ms, which provided sufficient time for the exchange process to take place. This confirms that the two new resonances appearing in the reduced compound belong to the same phase and undergo thermally activated chemical exchange. The
timescales and energy barriers of this observed ion hopping were quantified using $^6\text{Li}$ 1D EXSY measurement in Section 6.3.4.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_4.png}
\caption{$^6\text{Li}$ 2D EXSY spectrum over a variable temperature range shows evidence of thermally activated chemical exchange in the Li$_2$VPO$_4$F phase. On left a) T = 303 K (MAS = 25 kHz) and b) T = 330 K (MAS = 40 kHz). For both experiments, $\tau_{\text{mix}} = 15$ ms}
\end{figure}

6.3.3 Site Assignment of Li$_2$VPO$_4$F

6.3.3.1 Site Assignment Based on the Fermi-Contact Interaction

To answer the question of which Li sites in the Li$_2$VPO$_4$F structure correlate to the A and B resonances, the geometry dependent hyperfine coupling between the unpaired electron spin density and the Li atoms was analyzed.$^{17,18}$ There are two mechanisms for electron spin density transfer which are found to be most effective when the Li-O-V (or Li-F-V) orbitals overlap at angles close to 90° or 180°.$^9,10$ Since Li$_2$VPO$_4$F has orbital overlap angles closer to 90°, the 180° interactions are ignored. For the mechanisms involving 90° orbital overlap, unpaired electron spin density sitting in the $t_{2g}$ orbital of V in an octahedral environment is able to delocalize onto the Li s orbital leading to an increase in the paramagnetic shift. Comparison of the local Li environments of Li1 and
Li2 in reference to the V centers clearly shows that Li1 has a larger number of Li-O-V angles closer to 90° than does Li2 (Table 6.3). A greater amount of electron density spin density is localized onto the Li nucleus meaning a higher paramagnetic shift is observed. Therefore resonance A is assigned to Li1. Conversely, Li2 has much poorer Li-O-V and Li-F-V overlap and gives rise to the lower frequency resonance labeled B.

Table 6.3 - Summary of Li-X-V bond angles for the Li1 and Li2 environments in Li2VPO4F.

<table>
<thead>
<tr>
<th>Li1-X-V</th>
<th>Angle (°)</th>
<th>Li-V Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1-O1a-V1a</td>
<td>108.30</td>
<td>3.681</td>
</tr>
<tr>
<td>Li1-O1b-V1b</td>
<td>89.61</td>
<td>3.046</td>
</tr>
<tr>
<td>Li1-O2b-V1b</td>
<td>91.45</td>
<td>3.046</td>
</tr>
<tr>
<td>Li1-O1c-V1c</td>
<td>135.00</td>
<td>4.268</td>
</tr>
<tr>
<td>Li1-F1-V1d</td>
<td>146.35</td>
<td>4.006</td>
</tr>
<tr>
<td>Li1-F1-V1e</td>
<td>87.86</td>
<td>2.904</td>
</tr>
<tr>
<td>Li1-O2e-V1e</td>
<td>87.72</td>
<td>2.904</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Li2-X-V</th>
<th>Angle (°)</th>
<th>Li-V Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2-F1a-V1a</td>
<td>123.77</td>
<td>4.074</td>
</tr>
<tr>
<td>Li2-F1a-V1b</td>
<td>73.10</td>
<td>2.764</td>
</tr>
<tr>
<td>Li2-O1b-V1b</td>
<td>83.86</td>
<td>2.764</td>
</tr>
<tr>
<td>Li2-O2b-V1b</td>
<td>84.05</td>
<td>2.764</td>
</tr>
<tr>
<td>Li2-F1c-V1c</td>
<td>134.62</td>
<td>3.643</td>
</tr>
<tr>
<td>Li2-F1c-V1d</td>
<td>86.92</td>
<td>2.724</td>
</tr>
<tr>
<td>Li2-O1d-V1d</td>
<td>66.15</td>
<td>2.724</td>
</tr>
<tr>
<td>Li2-O2d-V1d</td>
<td>86.99</td>
<td>2.724</td>
</tr>
</tbody>
</table>

It is unclear however, why the Li2 resonance falls at such a low shift value of \(-52\) ppm. We therefore turn to more experimental evidence to support the assignment of Li1 to resonance A, and Li2 to resonance B, which includes \(^6\text{Li}\{^{19}\text{F}\}\) REDOR measurements and determination of the \(^7\text{Li}\) CSA parameters for each of the resonances.
6.3.3.2 Site Assignment in Li$_2$VPO$_4$F from $^{6}$Li-$^{19}$F REDOR NMR

The assignment made using the Fermi-contact interaction was further confirmed by correlating each of the Li sites to the single F environment using $^{6}$Li-$^{19}$F rotational echo, double resonance (REDOR) measurements. As outlined in Chapter 3, $^{6}$Li-$^{19}$F REDOR reintroduces $^{6}$Li-$^{19}$F dipolar couplings that are averaged through MAS. The observed nucleus ($^{6}$Li) is measured using a spin-echo sequence with (S) and without ($S_0$) the application of a series of $\pi$ pulses on the dephased nucleus ($^{19}$F). The normalized difference in $^{6}$Li signal intensity ($[S_0-S]/S_0$) is then plotted as a function of the dipolar evolution time ($N_\tau_R = \text{number of rotor periods times the rotor period}$). Stronger REDOR buildup curves arise from stronger dipolar couplings ($D_{ij}$) which are inversely dependent on the internuclear distance between the two spins ($i$ and $j$) (Equation 2.4-11). Figure 6.5 shows the $^{6}$Li-$^{19}$F REDOR curves observed for resonances A and B.

![Figure 6.5](image)

**Figure 6.5** – $^{6}$Li-$^{19}$F REDOR buildup curves for resonances A (triangles) and B (circles). MAS = 35 kHz

The stronger REDOR buildup for the B resonance (Li2) is consistent with this site having one short Li-F internuclear distance of 1.82 Å, and a second Li-F contact at 2.49 Å.
The single Li1-F distance of 2.06 Å gives rise to the weaker REDOR buildup curve for resonance A (Li1).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Ligand</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>F1</td>
<td>2.062</td>
</tr>
<tr>
<td></td>
<td>O2e</td>
<td>2.071</td>
</tr>
<tr>
<td></td>
<td>O2b</td>
<td>2.135</td>
</tr>
<tr>
<td></td>
<td>O1b</td>
<td>2.183</td>
</tr>
<tr>
<td></td>
<td>O1a</td>
<td>2.399</td>
</tr>
<tr>
<td></td>
<td>O1c</td>
<td>2.479</td>
</tr>
<tr>
<td>Li2</td>
<td>F1c</td>
<td>1.824</td>
</tr>
<tr>
<td></td>
<td>O2d</td>
<td>1.826</td>
</tr>
<tr>
<td></td>
<td>O1b</td>
<td>1.994</td>
</tr>
<tr>
<td></td>
<td>O2b</td>
<td>2.008</td>
</tr>
<tr>
<td></td>
<td>F1a</td>
<td>2.492</td>
</tr>
<tr>
<td></td>
<td>O1d</td>
<td>2.759</td>
</tr>
</tbody>
</table>

6.3.3.3 Site Assignment Using $^7$Li Sideband Manifolds of 0.5LiVPO$_4$F:0.5Li$_2$VPO$_4$F

For a more detailed analysis of the Li environments within this system, the sideband manifolds belonging to the different Li sites were isolated and the respective CSA parameters determined. A $^7$Li MAS spectrum showing the full sideband manifold of Li$_{1.5}$VPO$_4$F is shown in Figure 6.6. Using the DMFit program, the sideband manifolds of each Li site were modeled. This allowed for determination of the chemical shift anisotropy ($\Delta_{cs}$), axial symmetry ($\eta$), and span ($\Omega$) of each site (Table 6.5). The substantial increase in the span of the sideband manifolds of A and B ($\Omega = 2400$ and 2700 ppm, respectively) as compared to the parent LiVPO$_4$F ($\Omega = 1350$ ppm) is consistent with the increase in electron spin density sitting on the transition metal center. This increase leads to stronger electron-Li dipolar coupling interaction which largely
governs the span of CSA in paramagnetic systems. When comparing the Li1 and Li2 sites, the larger anisotropy of the Li2 site vs the Li1 site ($\Delta_{cs} = 1205$ ppm vs 705 ppm) is expected as Li1 is a six coordinate site (LiO5F), whereas the Li2 sits in a much more asymmetric environment composed of a five coordinate LiO$_3$F$_2$ polyhedron with an additional long Li-O bond of 2.759 Å (Table 6.4).

**Figure 6.6** – Deconvolution of sideband manifold for $^7$Li MAS spectrum of 0.5LiVPO$_4$F:0.5Li$_2$VPO$_4$F. Experimental spectrum shown on left. Sideband manifolds for each of the crystallographic Li sites (as modeled in DMfit) on right from top to bottom—Parent LiVPO$_4$F, A site, and B site. Asterisks denote spinning sidebands.
Table 6.5 - Summary of CSA parameters for individual sites of Li_{1.5}VPO_{4}F

<table>
<thead>
<tr>
<th>Li site</th>
<th>Ω (ppm)</th>
<th>Δcs (ppm)</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent LiVPO_{4}F</td>
<td>1350 (± 20)</td>
<td>440 (± 20)</td>
<td>0.80 (± 0.05)</td>
</tr>
<tr>
<td>A</td>
<td>2400 (± 20)</td>
<td>740 (± 20)</td>
<td>0.50 (± 0.05)</td>
</tr>
<tr>
<td>B</td>
<td>2700 (± 20)</td>
<td>1200 (± 20)</td>
<td>0.75 (± 0.05)</td>
</tr>
</tbody>
</table>

6.3.4 Quantification of Ion Dynamics in Li_{2}VPO_{4}F Using $^{6}$Li 1D EXSY

Our earlier investigations confirmed the lithium ion dynamics within the Li_{2}VPO_{4}F, using a qualitative 2D EXSY experiment, where the expected cross peaks were observed for the doubly lithiated phase, whereas no cross peak between the doubly and singly lithiated phases was detected, confirming the two-phase nature of the lithiation process (Figure 6.4). To determine the timescales and energy barriers of exchange in the doubly lithiated phase, $^{6}$Li 1D EXSY experiments were applied over a variable temperature range. For the two-spin system found in Li_{2}VPO_{4}F, resonance A was chosen for inversion while resonance B was left unperturbed. Data collected from $^{6}$Li 1D EXSY experiments over a variable temperature range are shown in Figure 6.7 a. At all temperatures, the strong buildup of the inverted A spin, is accompanied by a transient “well” in the intensity of the B spin. This clearly shows the expected chemical exchange between the two sites.
Figure 6.7 – Results of the $^{6}$Li 1D EXSY experiments over a variable temperature range. Clockwise from the top left, 331 K, 337 K, 343 K and 350 K. The points represent measured values and the lines are the best fit to the data from the CIFIT program. The depth of the transient well increases with increasing temperature.

The effect of temperature, on both the buildup of the A spin as well as the transient well of the B spin, is better illustrated in Figure 6.8. Here the A and B curves are separated and then each plotted over the entire temperature range. This x-axis has been adjusted to show the shorter mixing times where the influence of the ion dynamics is more prominent. The lines drawn show the best fit to the data from the CIFIT program.
Figure 6.8 - Results of the $^6$Li 1D EXSY experiments over a variable temperature range. Plots are separated into the inverted A spin (left) and non-inverted B spin (right). Data points represent measured values and the lines are the best fit to the data from the CIFIT program.

As the temperature is raised from 331 K to 350 K, the exchange rate is increased from $24 \pm 1$ to $55 \pm 4$ Hz (Table 6.6). The lower limit of the temperature range in this experiment was governed by the ion dynamics of this material where no exchange was observed at temperatures below 330 K. The upper limit of the temperature range was governed by the instrumentation where 350 K was the highest possible temperature for the probe.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Exchange rate (Hz)</th>
<th>Correlation time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>331 K</td>
<td>24 ($\pm$ 1)</td>
<td>41 ($\pm$ 2)</td>
</tr>
<tr>
<td>337 K</td>
<td>30 ($\pm$ 1)</td>
<td>34 ($\pm$ 1)</td>
</tr>
<tr>
<td>343 K</td>
<td>40 ($\pm$ 2)</td>
<td>25 ($\pm$ 1)</td>
</tr>
<tr>
<td>350 K</td>
<td>55 ($\pm$ 4)</td>
<td>18 ($\pm$ 1)</td>
</tr>
</tbody>
</table>

Activation energy $0.44 \pm 0.06$ eV
The effectiveness of $^6$Li 1D EXSY experiments in separating rate information from inherent $T_1$ properties is demonstrated in Figure 6.9. Here $^6$Li 1D Nonselective Inversion (NSI) experiments, recorded over the same temperature range and mixing time period, are plotted beside the $^6$Li 1D SI counterparts. Only the A resonance is evaluated as it was the environment chosen for selective inversion in the $^6$Li 1D SI study. Figure 6.9 clearly shows that the initial portion of the EXSY buildup curves are influence by changes in the ion dynamics while the NSI data remains relatively unchanged. This further confirms that thermally driven chemical exchange is taking place between the two Li environments of Li$_2$VPO$_4$F.

**Figure 6.9** – Results of selective 1D $^6$Li EXSY (left) and nonselective inversion (NSI) recovery (right) experiments of the A resonance over the same temperature range. The x-axis is minimized to the time region where chemical exchange is expected to dominate the buildup curves. The 1D EXSY results show an increase in buildup intensity as the temperature is raised. The NSI recovery shows only a slight variation with temperature.

The NSI data however, cannot be taken as a true measurement of the inherent $T_1$ times of each environment. The $T_1$ values reported earlier, from the NSI experiments at
331 K (herein referred to a $T_1^{\text{NSI}}$) were $23 \pm 1$ ms and $18 \pm 1$ ms for spins A and B, respectively (note that these $T_1$ values were collected at a field of 11.7 T and differ from result given in Table 6.2 which were collected at 7.0 T). By fitting the 1D EXSY data (also at 331 K) using CIFIT, a new set of $T_1$ values (abbreviated as $T_1^{\text{SI}}$) were generated. These values were determined from single component fits as the primary mechanism of relaxation in $^6$Li MAS NMR is from dipolar coupling with the unpaired electrons sitting on the paramagnetic center. $T_{1Q}$ and spin diffusion have negligible effects on these values. For spins A and B, the fitted $T_1^{\text{SI}}$ values of $29 \pm 2$ ms and $11 \pm 1$ ms, respectively, were determined. The $T_1^{\text{SI}}$ are a more faithful representation of the inherent $T_1$ times of each environment in the absence of chemical exchange, which is further emphasized when the modeled $T_1^{\text{SI}}$ values are compared to the experimentally measured $T_1^{\text{NSI}}$ values. For the A spin, $T_1^{\text{SI}}$ is longer than the $T_1^{\text{NSI}}$ while for the B spin, the opposite is true: the $T_1^{\text{SI}}$ is shorter than the experimentally measured $T_1^{\text{NSI}}$ value. This is a result of equilibration of the spin-lattice relaxation times for spins undergoing chemical exchange and further emphasizes how the $T_1^{\text{SI}}$ values are a more accurate timescale of the spin-lattice relaxation in the absence of chemical exchange. The $T_1^{\text{SI}}$ values were therefore held as a constant in the CIFIT models of $^6$Li 1D EXSY data over the remaining variable temperature range.

Determination of jump rates for the Li1-Li2 exchange pair at different temperatures allowed for the calculation of the activation energy, $E_a$, as the natural log of the exchange rates was plotted as a function of inverse temperature in an Arrhenius plot (Figure 6.10). An energy barrier value of $0.44 \pm 0.06$ eV was calculated from the slope of
the graph, where the error bounds on the ln(k) values were included in the regression analysis. The error value of the energy barrier was calculated from the standard error of the slope from the regression analysis.

\[ \text{Figure 6.10} \quad \text{Arrhenius plot of ion exchange rates as a function of temperature for Li1-Li2 ion exchange in Li}_2\text{VPO}_4\text{F.} \]

6.3.5 Correlating the Timescales of Exchange to Structural Constraints

This activation energy was correlated to structural constraints within the lattice in a similar approach to the one taken in Chapter 5 for Li$_3$Fe$_2$(PO$_4$)$_3$ and to previous studies where mechanisms of Li-transport were identified.\textsuperscript{22-24} The lithiated tavorite structure has the two crystallographically unique Li sites, both of which were previously determined to be half occupied.\textsuperscript{2} \textbf{Figure 6.11} shows a simplified unit cell, where the two most probable pathways for Li ion hopping are identified as face shared geometries between the Li1-Li2 polyhedral environments.
**Figure 6.11** - Schematic of the simplified unit cell highlighting the two face-shared \text{Li}_1-\text{Li}_2 (orange-lilac) diffusion pathways. Each has a bottleneck area (shaded triangle) created by 1 F atom (green) and 2 O atoms (red). Depending on the population of the half occupancy \text{Li}_1 and \text{Li}_2 environments, the $\alpha$-bottleneck (red triangle) is present as either $\alpha1$ (\text{Li}_1a-\text{Li}_2a) or $\alpha2$ (\text{Li}_1a-\text{Li}_2b). Similarly, the $\beta$-bottleneck (blue triangle) exists as either $\beta1$ (\text{Li}_1b-\text{Li}_2b) or $\beta2$ (\text{Li}_1b-\text{Li}_2a). The coordination environments and pathways lend themselves to 3D ion transport.

The bottlenecks for diffusion along each pathway were quantified by calculating the area of the triangular face created by the 2 O atoms and 1 F atom shared by the two exchanging Li sites. The first triangular window which we term the $\alpha$-bottleneck (red triangle, **Figure 6.11**) has a smaller area of 3.92 Å$^2$. The second triangular window which we term the $\beta$-bottleneck (blue triangle, **Figure 6.11**) is more open with an area of 4.22 Å$^2$ (**Table 6.7**). The internuclear distances between the ions passing through the $\alpha$ and $\beta$ bottlenecks, is complicated by the half-occupancy of the Li environments. For each bottleneck there is one short and one long \text{Li}_1-\text{Li}_2 internuclear distance. For the case of the $\alpha$ bottleneck, the shorter \text{Li}_1-\text{Li}_2 distance of 1.938 Å is referred to as the $\alpha1$ pathway, whereas the longer 2.791 Å distance is the $\alpha2$-pathway (**Table 6.7**). Similarly for the $\beta$-
bottleneck, \( \beta_1 \) identifies the Li1-Li2 distance of 1.979 Å whereas \( \beta_2 \) indicates the pathway with a 2.993 Å Li1-Li2 distance. In order to minimize electrostatic repulsion between the Li environments, it is expected that a longer internuclear distance separates the Li ions. Based on this assumption, the two plausible exchange pathways occur such that the shorter internuclear distance is paired with the tighter bottleneck \( (\alpha_2 \text{ pathway}) \), as compared to the longer internuclear distance that is paired with the wider bottleneck \( (\beta_2 \text{ pathway}) \).

Table 6.7 - Summary of face-shared Li1-Li2 pathways in \( \text{Li}_2\text{VPO}_4\text{F} \) with the corresponding bottlenecks for diffusion and internuclear distances.

<table>
<thead>
<tr>
<th>Li1-Li2 pathway</th>
<th>Area of bottleneck (Å(^2))</th>
<th>Li1-Li2 distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_1 )</td>
<td>3.92</td>
<td>1.938</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>3.92</td>
<td>2.791</td>
</tr>
<tr>
<td>( \beta_1 )</td>
<td>4.22</td>
<td>1.979</td>
</tr>
<tr>
<td>( \beta_2 )</td>
<td>4.22</td>
<td>2.993</td>
</tr>
</tbody>
</table>

This makes differentiation between these two possible pathways non-trivial, and the single rate determined here at each temperature is attributable to either of these exchange routes. Bond valence maps of the \( \alpha_2 \) and \( \beta_2 \) faces also do not indicate a preferred pathway either, as they both show very similar density along the planes defined by the shared face of each pathway (Figure 6.12).
Figure 6.12 – Bond valence maps of the planes defining the shared face of the α2 (left) and β2 (right) pathways. Atoms that define the space are marked with an X.

Overall, the similarity between the pathways, which are fitted to a single ion exchange rate for the 1D EXSY data at each temperature, is a strong indication of the propensity for 3D ion transport in this material.

6.4 Conclusions

This work identifies new Li environments generated as Li$_x$VPO$_4$F is lithiated from $x = 1.0$ up to $x = 2.0$ and confirms that this takes place in a two-phase fashion. This chapter also presents the first quantitative study of Li$^+$ dynamics in tavorite Li$_2$VPO$_4$F. It also is the first quantitative study of ion dynamics in a solid-state paramagnetic system using 1D EXSY experiments. This is an example of a material where the spin-lattice relaxation rates are faster than the ion dynamics, and thus a 2D EXSY approach is non-trivial. Exchange between the two crystallographic Li sites was found to be on the millisecond timescale with an energy barrier of 0.44 ± 0.06 eV. Two pathways of ion exchange between Li1 and Li2 were identified, with similar structural constraints. The next chapter extends the use of 1D selective inversion methods to systems having
multiple exchange processes allowing this NMR tool to be expanded to systems with more complex ion conduction pathways.
6.5 References


Chapter 7: Expansion of $^6$Li 1D Selective Inversion Methods to Multi-Spin Systems

7.1 Introduction

In the previous chapter, $^6$Li 1D EXSY measurements were used to probe the timescales of ion hopping in Li$_2$VPO$_4$F, which had a single exchange process between its two crystallographically distinct Li environments. Here we expand the use of selective inversion techniques to paramagnetic materials that have more than one ion hopping pathway. The selective inversion method of Chapter 6 was 1D EXSY which uses a $90^\circ$−τ$_1$−$90^\circ$ sequence for selective inversion of a Li resonance undergoing site exchange. The first delay period, τ$_1$, is determined by the frequency difference between two resonances undergoing ion exchange which subsequently limits the experiment to probe the timescales of single exchange pair systems. To overcome this limitation, a second selective inversion method is used in this chapter where the $90^\circ$−τ$_1$−$90^\circ$ portion of 1D EXSY is replaced with a long, selective Shaped Pulse (SP). This work has been accepted to a special issue of the journal, *Solid State NMR (SSNMR-11-39)* with the authorship of X. (−J). He, L. J. M. Davis, A. D. Bain, and G. R. Goward. My contribution to this work was the collection of NMR data and supervision of undergraduate thesis student, Xuilan (Janice) He as she carried out the data analysis in CIFIT. Prof. Bain and Prof. Goward were the principal investigators of the project.

The two paramagnetic cathode materials chosen for analysis using the 1D SI methods are Li$_2$VPO$_4$F and Li$_2$VOPO$_4$. The first compound, monoclinic Li$_2$VPO$_4$F, is the
same reduced phase of the tavorite-based triclinic compound studied in Chapter 6.\textsuperscript{1,2,3} The two crystallographically unique lithium sites mean only a single exchange pair is present. Both selective inversion methods are applied to this simple exchange system in order to evaluate the agreement between the two methods. The second compound, Li\textsubscript{2}VOPO\textsubscript{4}, is the reduced phase of triclinic α−LiVOPO\textsubscript{4}, a structure first reported by Lavrov \textit{et al.}\textsuperscript{4} The V\textsuperscript{5+}/V\textsuperscript{4+} redox potential sits at 3.95 V with a reversible capacity of 100 mAh/g.\textsuperscript{5} Fewer details regarding the V\textsuperscript{4+}/V\textsuperscript{3+} redox potential and electrochemical performance are available at present and thus remain the focus of ongoing work. Lithiation to form the reduced phase results in three crystallographically unique Li environments with three ion-exchange pairs. The higher number of ion exchange pairs led to determination of timescales and energy barriers using the SP method only.

### 7.1.1 Selective Inversion Using 1D EXSY

As outlined in the previous chapter, 1D EXSY, uses a 90° - \(\tau_1\) - 90° - \(\tau_{\text{mix}}\) - 90° pulse sequence to selectively invert the on-resonance spin.\textsuperscript{6-8} The first delay period, \(\tau_1\), is set to a value governed by the frequency difference between the site of inversion (spin \(i\)) and its exchange partner (spin \(j\)) (specifically, \(1/(2\Delta\nu_{ij})\)). The on-resonance spin (\(i\)) is selectively inverted following the second 90° pulse, while its exchange partner, \(j\), is placed along the +z-axis. The mixing time (\(\tau_{\text{mix}}\)) is stepped over a series of experiments with the longest delay time set to ensure relaxation back to equilibrium. Due to the dependence of \(\tau_1\) on the frequency difference between the two of spins it is not
appropriate to extend this inversion technique beyond a 2-site, 1-exchange process and is therefore only applied to the monoclinic phase of Li$_2$VPO$_4$F.

7.1.2 Selective Inversion Using Shaped Pulses

A second inversion method is investigated and tested on both materials having either single or multiple-exchange processes. This second method replaces the initial 90° - $\tau_1$ - 90° of the 1D EXSY sequence, with one long, soft, Gaussian pulse, placed on-resonance to the site chosen for inversion. The bandwidth of the Gaussian pulse ensures inversion of only one of the sites undergoing ion exchange, leaving all other sites unperturbed. This experimental approach will be referred to as the Shaped Pulse (SP) method. Previous studies have shown this to be an effective technique for determining timescales in systems undergoing multiple chemical exchange processes in solution-state systems. This method is applied to the single-exchange material, Li$_2$VPO$_4$F, in addition to the 1D EXSY method in order to determine the agreement between the two methods. The SP method was then used to quantify the timescales of ion hopping in a multiple-exchange system, Li$_2$VOPO$_4$, over a variable temperature range.
7.2 Experimental

7.2.1 Sample Preparation.

Collaborators at the University of Waterloo provided samples of $^6\text{Li}$ enriched Li$_2$VPO$_4$F and Li$_2$VOPO$_4$.

7.2.2 Solid State NMR.

For both materials, a custom built 1.8 mm probe with MAS speed of 40 kHz was used for initial characterization of the $^6\text{Li}$ environments, at a Larmor frequency of 44.1 MHz. Li$_2$VPO$_4$F. Variable temperature experiments of Li$_2$VPO$_4$F were carried out using a Bruker 2.5 mm probe with MAS of 25 kHz at a Larmor frequency of 76.7 MHz. $^6\text{Li}$ 1D MAS spectra were acquired using a 90° pulse of 2.5 µs and recycle delay of 200 ms. Li$_2$VOPO$_4$. Variable temperature experiments of Li$_2$VOPO$_4$ were performed using a custom built probe supporting 1.8 mm rotors with MAS frequencies ranging from 25 – 40 kHz at a Larmor frequency of 44.1 MHz. $^6\text{Li}$ 1D MAS spectra were acquired using a 90° pulse of 3.5 µs and recycle delay of 300 ms.

7.2.3 1D EXSY.

$^6\text{Li}$ 1D EXSY experiments were performed using a 90° - $\tau_1$ - 90° - $\tau_{\text{mix}}$ - 90° sequence. Selective inversion was accomplished by setting the carrier frequency on-resonance to a chosen spin $i$ and setting $\tau_1$ to one-half the frequency difference with the resonance frequency of an ion-exchange partner ($1/[2\Delta\nu_i]$). This experiment was applied to Li$_2$VPO$_4$F with the mixing time ($\tau_{\text{mix}}$) stepped over a series of 16 experiments from 5 µs to 100 ms.
7.2.4 Shaped Pulse Experiments.

Shaped Pulse experiments used a $180^\circ - \tau_{\text{mix}} - 90^\circ$, where the $180^\circ$ pulse was a long (500 µs), soft, Gaussian pulse set on resonance to the site chosen for inversion. To calibrate the Gaussian pulse, the pulse length is fixed at 500 µs while the power level is adjusted to get maximum inversion of the on-resonance signal. The mixing time ($\tau_{\text{mix}}$) was stepped over a series of 16 experiments from 5 µs to 100 ms for Li$_2$VPO$_4$F and 5 µs to 200 ms for Li$_2$VOPO$_4$. For Li$_2$VPO$_4$F, the same variable/mixing time list used in the 1D EXSY experiments is used here in order to facilitate the comparison of the two methods. A hard, short, $90^\circ$ pulse was used to acquire the final magnetization.

7.2.5 Nonselective Inversion Recovery.

Nonselective Inversion (NSI) recovery experiments used a standard inversion-recovery sequence with the variable delay list set equivalent to the variable mixing time list of the SP and 1D EXSY experiments.

7.2.6 Data Analysis.

In each data set, slices for each mixing time/variable delay were extracted and baseline corrected. All spins involved in the exchange process, were integrated and normalized to data collected with longest mixing time/variable delay (where the magnetization of each spin was fully relaxed). The data was modeled using the CIFIT program developed by A.D. Bain of McMaster University.$^{10}$ This program takes the table of observed areas for all spins as a function of mixing time and determines a key set of parameters: the jump rates (k) of each chemical exchange process, spin-lattice relaxation
times in the absence of chemical exchange ($T_1$), and the magnetization values from initial ($M_i(0)$) to equilibrium conditions ($M_i(\infty)$). The rate matrix used to describe spin relaxation under the influence of chemical exchange is the primary mathematical model used by the CIFIT program and is described in greater detail elsewhere. CIFIT adjusts the free parameters, $T_1$, $k$, $M_i(0)$ and $M_i(\infty)$, using a Levenberg-Marquardt algorithm until the sum of the squares of the differences between the experimental and calculated data is minimized. Error values of the exchange rates were approximated in the CIFIT program by the variance-covariance matrix of the fit to the data.

7.3 Results and Discussion

Figure 7.1 shows the $^{6}\text{Li}$ MAS spectra of the two-site material, $\text{Li}_2\text{VPO}_4\text{F}$, and three-site compound, $\text{Li}_2\text{VOPO}_4$. For $\text{Li}_2\text{VPO}_4\text{F}$ the paramagnetic shifts arising at 46 ppm and $-47$ ppm were labeled A and B, respectively and integrated to give a 1:1 ratio over the entire sideband manifold. There is a small diamagnetic impurity centered at 0 ppm. The higher frequency resonance centered at $\sim 112$ ppm is the known parent phase of $\text{LiVPO}_4\text{F}$. In the $^{6}\text{Li}$ MAS spectrum of $\text{Li}_2\text{VOPO}_4$, the resonances centered at 190 ppm, 75 ppm and $-105$ ppm were labeled A, B, and C, respectively and integrated to give a 1:0.5:0.5 A:B:C occupancy over the entire sideband manifold. The lithiation process ($\text{LiVOPO}_4 \rightarrow \text{Li}_2\text{VOPO}_4$) is found to create two new, partially-occupied lithium environments, which is often seen in lithiation of cathode materials. Again, there is a diamagnetic impurity centered at 0 ppm along with a broad resonance centered
at 10 ppm. Neither of these resonances participates in ion exchange, as determined through the 2D EXSY data set, and were therefore omitted from the analysis.

![Figure 7.1](image)

**Figure 7.1** – $^6$Li MAS (25 kHz) spectra of Li$_2$VPO$_4$F (top) and Li$_2$VOPO$_4$ (bottom). Labeling of sites A, B, and C, indicate spins involved in ion hopping processes. The resonances at zero ppm arise from diamagnetic impurities from the lithiation process.

$^{6,7}$Li MAS 2D EXSY spectra of each sample confirm ion hopping between each of the labeled Li environments (Figure 7.2). For the $^6$Li 2D EXSY spectrum of Li$_2$VPO$_4$F, exchange between the A and B spins confirms that Li$_2$VPO$_4$F is a 2-site, 1-exchange process system. The $^7$Li 2D EXSY spectrum of Li$_2$VOPO$_4$ shows crosspeaks between the A-B, B-C, and A-C resonances, confirming a 3-site, 3-exchange system. The 2D EXSY spectra provided an initial indication that the timescales of ion mobility between the fluorophosphate Li$_2$VPO$_4$F and oxyphosphate Li$_2$VOPO$_4$ are significantly different. For the oxyphosphate, prominent cross peaks at MAS 40 kHz (calibrated to a temperature of 330 K), were observed with a mixing time of 6 ms. In contrast, for
Li$_2$VPO$_4$F, at an equivalent temperature, only weak crosspeaks appeared at an extended mixing time of 15 ms, indicating a more slowly exchanging system.

Figure 7.2 - 2D EXSY spectra of Li$_2$VPO$_4$F (left, $^6$Li MAS 40 kHz, $\tau_{mix} = 15$ ms) and Li$_2$VOPO$_4$ (right, $^7$Li MAS 40 kHz, $\tau_{mix} = 6$ ms). A 2-site, 1-exchange process system is shown in Li$_2$VPO$_4$F as crosspeaks between the A and B Li ion crystallographic positions are present. Similarly, a 3-site, 3-exchange process system in Li$_2$VOPO$_4$, is proven with observation of A–B, A–C, and B–C, crosspeaks.

Figure 7.3 shows the results of $^6$Li selective inversion of Li$_2$VPO$_4$F using both the 1D EXSY and SP methods. The magnetization of the selectively inverted site (the A resonance) from both the SP, and 1D EXSY experiments is also plotted alongside results from a NSI recovery experiment at the same temperature. The stronger buildup of both the selectively inverted curves, as compared to the NSI recovery, highlights the influence of chemical exchange on the relaxation of selectively inverted magnetization. Comparing the 1D EXSY and SP results only, a slightly stronger buildup of the A magnetization is
observed. The discrepancy between the data from the two methods is more evident when the transient curves of resonance B are examined (Figure 7.3, right). In this case, the transient of the 1D EXSY data is slightly deeper than the SP data. We attribute this difference to the timescales of the inversion processes leading to different initial conditions for selective inversion. For the 1D EXSY method, the total time of the $90^\circ - \tau_1 - 90^\circ$ inversion step is 78.3 µs whereas for the shaped pulse experiments, the length of the shaped pulse needed for inversion is 500 µs in length. Despite the differences in experimental timescales, CIFIT is able to fit the data from each experiment to yield comparable timescales of exchange. Li-hopping rates of $59 \pm 2 \text{ s}^{-1}$ and $64 \pm 4 \text{ s}^{-1}$, for the shaped pulse and 1D EXSY methods, respectively, are equivalent within error (Table 7.1). A complete analysis of the timescales of Li$_2$VPO$_4$F using the 1D EXSY method over a variable temperature range has been reported in the previous chapter.³

![Normalized Integration Value vs Time](image)

**Figure 7.3** – Selective inversion results of the 2-site, 1-exchange material, Li$_2$VPO$_4$F, at 360 K. Left: Comparison of NSI recovery, 1D EXSY, and SP experiments of the inverted A resonance. Right: 1D EXSY and SP results of the non-inverted B resonance.
Table 7.1 – Summary of Li-hopping rates in Li$_2$VPO$_4$F as determined from the SP and 1D EXSY inversion methods.

<table>
<thead>
<tr>
<th></th>
<th>$k_{AB}$ (s$^{-1}$) (T = 360 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP</td>
<td>$58 \pm 2$</td>
</tr>
<tr>
<td>1D EXSY</td>
<td>$64 \pm 4$</td>
</tr>
</tbody>
</table>

The equivalent results observed from the 1D EXSY and SP experiments of the single-exchange system, allows us to extend the SP method to systems with a higher number of exchange pairs. The timescales and energy barriers in the 3-site, 3-exchange model compound, Li$_2$VOPO$_4$, were measured using SP experiments over a variable temperature range (304 K – 327 K). For each exchange process, a forward and backward ion-hopping rate coefficient exists. For exchange between B and C, the populations of these sites is equal meaning that under a steady-state approximation, the forward and backward rate coefficients (labeled $k_{BC}$ and $k_{CB}$), respectively, are equal. For ion hopping between A and C, the 2:1 occupancy of A to C means that under steady-state conditions, $k_{AC}$ (forward) will not be equal to $k_{CA}$ (backward) (more specifically, $k_{CA} = 2k_{AC}$). A similar situation arises for A and B exchange where the population of A:B is also 1:0.5, meaning that again the reverse ($k_{BA}$) is twice that of the forward ($k_{AB}$) rate coefficient ($k_{BA} = 2k_{AB}$). In this study therefore, the CIFIT parameters were set such that only the three backward rates of ion-exchange, $k_{BA}$, $k_{CA}$, and $k_{CB}$ were determined for the exchange pairs, A-B, A-C and B-C, respectively, while the reverse rates $k_{AB}$, $k_{AC}$, and $k_{BC}$, were predicted, based on the site-populations. Details on the treatment of unequal populations in CIFIT is outlined in greater detail elsewhere.$^{16}$
Here, the rate coefficients for each exchange process were determined reproducibly from two separate experiments where either site in an exchange pair was selectively inverted. Therefore, a total of three experiments were carried out at each temperature where either A, B or C was inverted. To identify which site was inverted in each experiment, an $XY$ notation for the exchange pairs is used, where $X$ is the inverted site and $Y$ is the unperturbed, transient peak. As an example, for determination of ion exchange rate $k_{BA}$, the $\overline{AB}$ experiment indicates that results are from the inversion of A whereas the $A\overline{B}$ experiment is from the inversion of B. The results for inversion of A, B, and C, over a variable temperature range are shown in Figure 7.4. For all temperatures, there is a clear increase in the depth of the transient well as the temperature is raised. This is accompanied by an increase in the buildup of the inverted magnetization of each experiment. Results from CIFIT show agreement between the rates of ion exchange regardless of the site chosen for inversion (Table 7.2). The values of $k_{BA}$ at 304 K were determined from both $\overline{AB}$ and $A\overline{B}$ experiments, giving ion exchange rates of $63 \pm 7 \text{ s}^{-1}$ and $55 \pm 6 \text{ s}^{-1}$, respectively. Similarly for $k_{CA}$, values of $58 \pm 7 \text{ s}^{-1}$ and $64 \pm 5 \text{ s}^{-1}$ were found from $\overline{AC}$ and $A\overline{C}$ experiments, respectively. The equivalency of the ion hopping rates from different inversion sites will allow this inversion method to be extended to systems where only one of the exchange sites is well enough resolved for selective inversion.
Inversion of A

A

B

C

Inversion of B

B

A

C

Inversion of C

C

A

B

Figure 7.4 – $^6$Li SP results over a variable temperature range (304 K – 327 K) of the 3-site, 3-exchange material, Li$_2$VOPO$_4$. Top row shows results from the inversion of A with A, B, and C magnetization curves plotted from left to right. The middle row contains results from the inversion of B where the B, A, and C, magnetization curves are plotted from left to right. Results from the inversion of C are shown in the bottom row where from left to right the C, A, and B magnetization curves are given.
Table 7.2 – Summary of exchange rates determined from $^6$Li SP measurements of Li$_2$VOPO$_4$. Each rate of ion exchange was determined twice from separate inversion of each resonance involved in the ion exchange process. Example: $\overline{AB}$ indicates the results from inversion of A, whereas $A\overline{B}$ is from inversion of B.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$\overline{AB}$</th>
<th>$A\overline{B}$</th>
<th>$\overline{AC}$</th>
<th>$A\overline{C}$</th>
<th>$\overline{BC}$</th>
<th>$B\overline{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>63 ± 7</td>
<td>55 ± 6</td>
<td>58 ± 7</td>
<td>64 ± 5</td>
<td>90 ± 10</td>
<td>110 ± 10</td>
</tr>
<tr>
<td>311</td>
<td>110 ± 10</td>
<td>100 ± 10</td>
<td>130 ± 20</td>
<td>130 ± 10</td>
<td>320 ± 40</td>
<td>210 ± 30</td>
</tr>
<tr>
<td>319</td>
<td>200 ± 50</td>
<td>190 ± 30</td>
<td>230 ± 50</td>
<td>210 ± 30</td>
<td>750 ± 90</td>
<td>710 ± 90</td>
</tr>
<tr>
<td>327</td>
<td>290 ± 90</td>
<td>280 ± 70</td>
<td>300 ± 90</td>
<td>370 ± 60</td>
<td>1100 ± 200</td>
<td>900 ± 200</td>
</tr>
</tbody>
</table>

Jump rates for A-B, A-C, and B-C exchange pairs at different temperatures were determined making the calculation of the activation energy, $E_a$, possible. Figure 7.5 shows Eyring plots of the natural log of the averaged exchange rates over temperature plotted as a function of inverse temperature for the A-B, A-C, and B-C exchange pairs. The energy barriers were reported in three separate ways, to ensure accuracy between the different inversion methods (Table 7.3). For example, the energy barrier of the A–B hopping pair was determined first using the rates determined from experiments where A was inverted ($\overline{AB}$), then using the results from measurements where B was inverted ($A\overline{B}$), and lastly, using the average ion hopping rates from both experiments. Figure 7.5 shows only the Eyring plots using the latter, averaged results where the A–B, A–C, and B–C ion hopping energy barriers were 0.6 ± 0.1 eV, 0.6 ± 0.1 eV, and 0.9 ± 0.2 eV, respectively (Table 7.3). Refinement data from powder x-ray diffraction measurements is not yet available. Therefore correlation of these energy barriers and timescales to structural constraints within the lattice is ongoing.
Figure 7.5 - Eyring plots where the slope of the natural log of the averaged ion hopping rate over temperature plotted against inverse temperature gives the energy barrier for the A-B, (top), A-C (middle), and B-C (bottom) exchange processes.
Table 7.3 - Summary of activation energies for Li ion hopping from the variable temperature $^6$Li SP studies of Li$_2$VOPO$_4$.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>A-B hop $E_a$ (eV)</th>
<th>A-C hop $E_a$ (eV)</th>
<th>B-C hop $E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inversion of A</td>
<td>0.57 ± 0.04</td>
<td>0.7 ± 0.1</td>
<td>N/A</td>
</tr>
<tr>
<td>Inversion of B</td>
<td>0.62 ± 0.03</td>
<td>N/A</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>Inversion of C</td>
<td>N/A</td>
<td>0.63 ± 0.05</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>Average</td>
<td>0.6 ± 0.1</td>
<td>0.6 ± 0.1</td>
<td>0.9 ± 0.2</td>
</tr>
</tbody>
</table>

7.4 Conclusions

The present work compares the effectiveness of different inversion methods for accurate determination of timescale and energy barriers of Li ion hopping in solid-state paramagnetic Li-intercalation materials. Inversion using both 1D EXSY and SP methods was performed on a 2-site, 1-exchange example, Li$_2$VPO$_4$F. The 3-site, 3-exchange example, Li$_2$VOPO$_4$ was measured with the SP method only. As expected, in the 2-site, 1-exchange example, the 1D EXSY and SP methods gave equivalent timescales of exchange. However the longer duration of the inversion pulse in the SP method leads to different initial conditions of the inversion resulting in slightly different features of the transient well. For the 3-site, 3-exchange material, Li$_2$VOPO$_4$, only the SP method was applied with timescales of ion hopping determined over a variable temperature range. Ion hopping rates from AB, AC, and BC, experiments at 304 K were 55 ± 6 s$^{-1}$, 58 ± 7 s$^{-1}$, and 90 ± 10 s$^{-1}$, respectively. These rates increased at higher temperature (327 K) to $\overline{AB}$, $\overline{AC}$, and $\overline{BC}$, of 290 ± 90 s$^{-1}$, 300 ± 90 s$^{-1}$, 1100 ± 200 s$^{-1}$, respectively. These timescales were found to be equivalent within error to hopping rates determined from $\overline{AB}$, $\overline{AC}$, and $\overline{BC}$, experiments at all temperatures. An Eyring analysis of the averaged
ion hopping rates as function of temperature gave A–B, A–C, and B–C, energy barriers of 0.6 ± 0.1 eV, 0.6 ± 0.1 eV, and 0.9 ± 0.2 eV, respectively.
7.5 References


Chapter 8: Quantification of Li Ion Hopping Timescales in Li$_5$V(PO$_4$)$_2$F$_2$

8.1 Introduction

This chapter characterizes Li ion hopping rates and energy barriers in the novel layered phase, Li$_5$V(PO$_4$)$_2$F$_2$, using $^6$Li Selective Inversion (SI) NMR measurements. Li$_5$V(PO$_4$)$_2$F$_2$ has six crystallographically distinct lithium sites giving the possibility of fifteen exchange partners between non-equivalent lithium environments. Previous studies have qualitatively observed ion hopping in five pairs of ions using $^6$Li 2D EXSY measurements.\(^1\) Higher temperature and lower field $^6$Li 2D EXSY measurements presented in this chapter revealed a sixth ion hopping pair, confirming that ion hopping is found only between Li sites which have polyhedral sharing either through an edge or face geometry. $^6$Li 1D SI measurements over a variable temperature range were used to quantify the timescales and energy barriers of ion mobility for three of the six ion pairs observed to participate in ion hopping. Limiting the analysis to only three of the six pairs was brought on by the poor resolution of the exchanging sites found in the lower part of the $^6$Li MAS spectrum, making selective inversion a challenge.
8.2 Experimental

8.2.1 Sample Preparation.

Samples of $^6$Li enriched Li$_3$V(PO$_4$)$_2$F$_2$ were provided by collaborators at the University of Waterloo and is the same material studied in previous publications.$^1$

8.2.2 Bond Valence Density Maps

Bond valence density maps were generated for each crystal structure using the VALMAP program, developed by Gonzalez-Platas et al.$^2$ This program takes crystallographic data including unit cell parameters and atomic coordinates, and calculates the bond valences density within a three-dimensional unit cell using the empirical parameters of Brown et al.$^{3,4}$ In this work, two-dimensional planes of bond valence density were extracted using the atomic coordinates of atoms defining a Li ion diffusion pathway. For each map, a 2 Å radius is shown with a bond valence density contour level increment is 0.485.

8.2.3 Solid State NMR.

$^6$Li 2D EXSY spectra were acquired at a Larmor frequency of 29.4 MHz on a Bruker AMX 200 spectrometer at the National Institute of Chemical Physics and Biophysics (NICPB), Tallinn, Estonia. A custom-built double resonance probe supporting 1.8 mm rotors capable of MAS frequencies of 25 kHz up to 45 kHz was used. Temperatures were calibrated using Pb(NO$_3$)$_2$ as described elsewhere.$^5$ The spectra were referenced to 1 M $^6$LiCl (aq) (0 ppm). Two-dimensional exchange spectra were acquired.
with mixing time set to 2 ms, 608 scans, and a recycle delay of 50 ms. The number of slices in the indirect dimension was 512. Phase-sensitive detection in $t_1$ was achieved through the use of States-TPPI.\textsuperscript{6}

Variable temperature $^6$Li MAS NMR experiments were acquired at a Larmor frequency of 73.6 MHz on a Bruker AV500 spectrometer at McMaster University. Temperatures were calibrated using Sm$_2$Sn$_2$O$_7$ as described elsewhere.\textsuperscript{7} $^6$Li 1D MAS spectra were acquired with a 90° pulse length of 2.5 $\mu$s and recycle delay of 200 ms. 1D $^6$Li Selective Inversion (SI) experiments were performed using a 180° - $\tau_{\text{mix}}$ - 90° sequence. Selectivity for a particular resonance was accomplished using a soft, long, Gaussian pulse for the 180° pulse. The duration of the low power (0.159 W) shaped pulse was 1 ms. The mixing time ($\tau_{\text{mix}}$) was stepped over a series of 16 experiments from 5 $\mu$s to 100 ms (the latter delay time being well beyond the relaxation rates of both spins reached equilibrium). A recycle delay of 200 ms was used with a total of 2048 scans collected for each slice, Nonselective Inversion (NSI) experiments were performed using the standard inversion-recovery sequence included in the Bruker software package. The same variable delay list, scan number, and recycle delay, was used in the NSI as was used in the 1D SI experiments.

8.2.4 Data Analysis.

A Mathematica notebook developed by Darren Brouwer of Redeemer University was used for deconvolution and integration of the pseudo two-dimensional data sets.
produced by the arrayed 1D selective and non-selective inversion recovery experiments. The integrals were normalized to the integration value of the slice collected at the longest mixing time/variable delay (where the magnetization of each spin was fully relaxed). The experimental data was fit using the CIFIT program developed by A.D. Bain of McMaster University. CIFIT uses as an input table of observed integrated intensities for all spins as a function of mixing time and determines a key set of parameters: the jump rates (k) of each chemical exchange process, spin-lattice relaxation times in the absence of chemical exchange ($T_1$), and the magnetization values from initial to equilibrium conditions (i.e. from $M_0$ to $M_\infty$). The rate matrix used to describe spin relaxation under the influence of chemical exchange is the primary mathematical model used by the CIFIT program and is described in greater detail elsewhere. CIFIT adjusts the free parameters, k, $T_1$, $M_0$ and $M_\infty$ using a Levenberg-Marquardt algorithm until the sum of the squares of the differences between the experimental and modeled data is minimized. Error values of the exchange rates were approximated in the CIFIT program by the variance-covariance matrix of the fit to the data.
8.3 Results and Discussion

The six Li crystallographic positions in Li₅V(PO₄)₂F₂ (Figure 8.1) were resolved in the 1D °Li NMR spectrum with MAS of 25 kHz at a calibrated temperature of 312 K (Figure 8.2). Resonances centered at 110 ppm, 83 ppm, 49 ppm, 16 ppm, 11 ppm, and 7 ppm, were labeled as A-F in order of highest to lowest frequency. The assignment of these resonances to the crystallographic positions is detailed in a previous publication based on the Fermi-contact interaction with the transition metal as well as the exchange pathways observed from °Li 2D EXSY experiments.¹

Figure 8.1 – Structure of Li₅V(PO₄)₂F₂, which crystallizes in the monoclinic space group, P2₁/c. Corner shared vanadium octahedra (grey) and phosphate tetrahedra create a two-dimensional sheet that sandwiches layers of lithium ions (coloured spheres). Li₁A (pink) and Li₂B (blue) sit on the 2b and 2d Wyckoff positions, respectively, each with occupancy of 0.5. The remaining lithium environments, Li₃E (purple), Li₄C (red), Li₅F (orange), and Li₆D (green), all sit on the 4e Wyckoff position with full occupancy.¹¹
Figure 8.2 – Top: $^6$Li MAS NMR spectrum of $\text{Li}_5\text{V}(\text{PO}_4)_{2}\text{F}_2$ at MAS frequency of 25 kHz and temperature of 312 K. Deconvolution of the isotropic region is shown as the bottom spectrum. The experimental spectrum (black) was deconvoluted into the known six crystallographic sites (green). The difference map (blue) between the experimental (back) and modeled spectrum (red) is shown at the bottom of the spectrum.
Previous studies in our group identified five Li ion hopping pairs between Li$_3$E-Li$_5$F, Li$_3$E-Li$_6$D, Li$_4$C-Li$_5$F, Li$_4$C-Li$_6$D, and Li$_5$F-Li$_6$D, in Li$_5$V(PO$_4$)$_2$F$_2$, using $^6$Li 2D EXSY measurements at 327 K and magnetic field strength of 7.0 T. The sharing of the Li polyhedral environments for each exchange pair is summarized here (Table 8.2). The Li$_4$C-Li$_5$F and Li$_4$C-Li$_6$D polyhedra are face shared with internuclear distances of 2.749 Å and 2.831 Å, respectively. Triangular bottlenecks created by the O and F atoms along the ion hopping pathway have areas of 3.59 Å$^2$ and 3.43 Å$^2$, for the Li$_4$C-Li$_5$F, Li$_4$C-Li$_6$D pairs, respectively. For the exchange pairs with edge-shared Li polyhedra, extension of the Li bond radius from 2.80 Å to 3.00 Å in a crystal structure visualization software program such as xtaldraw, a pseudo-face-shared geometry can be visualized. This also allowed for bottleneck areas of, 3.80 Å$^2$, 3.70 Å$^2$, and 3.97 Å$^2$ to be calculated for exchange pairs Li$_3$E-Li$_5$F, Li$_3$E-Li$_6$D, and Li$_5$F-Li$_6$D, respectively. The corresponding internuclear distances for these pairs are 3.133 Å, 3.041 Å, and 3.027 Å, as listed in Table 8.1.

**Table 8.1** – Summary of the five exchange pairs/pathways in Li$_5$V(PO$_4$)$_2$F$_2$ identified previously in the Goward group using $^6$Li 2D EXSY measurements.$^1$

<table>
<thead>
<tr>
<th>Exchange pair</th>
<th>Geometry of Li Ion Polyhedra</th>
<th>Li-Li Internuclear Distance (Å)</th>
<th>Bottleneck Area (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$E-Li$_5$F</td>
<td>Edge</td>
<td>3.133</td>
<td>3.80</td>
</tr>
<tr>
<td>Li$_3$E-Li$_6$D</td>
<td>Edge</td>
<td>3.041</td>
<td>3.70</td>
</tr>
<tr>
<td>Li$_4$C-Li$_5$F</td>
<td>Face</td>
<td>2.749</td>
<td>3.59</td>
</tr>
<tr>
<td>Li$_4$C-Li$_6$D</td>
<td>Face</td>
<td>2.831</td>
<td>3.43</td>
</tr>
<tr>
<td>Li$_5$F-Li$_6$D</td>
<td>Edge</td>
<td>3.027</td>
<td>3.97</td>
</tr>
</tbody>
</table>

In this work, a $^6$Li 2D EXSY study carried out at lower field (4.7 T) with higher temperature of 349 K (Figure 8.3) revealed a sixth exchange pair between Li$_1$A-Li$_5$F.
This is another edge-shared geometry with internuclear distance of 2.988 Å. Extension of the Li bond radius to 3.1 Å for both Li$_{1A}$ and Li$_{5F}$, in the crystal structure drawing program, allows for pseudo-face geometry to be visualized with a calculated bottleneck area of 4.17 Å$^2$.

![Figure 8.3](image_url) – $^6$Li 2D EXSY spectrum of Li$_5$V(PO$_4$)$_2$F$_2$ collected at the NICPB. MAS = 40 K, T = 349 K, and $\tau_{\text{mix}} = 2$ ms.

While only six exchange pairs were observed from the $^6$Li 2D EXSY studies, a total of fifteen ion hopping pairs are possible between the six crystallographic positions within Li$_5$V(PO$_4$)$_2$F$_2$. All fifteen pairs are listed in (Table 8.2) along with their respective polyhedral sharing geometry, internuclear distance, and bottleneck area of diffusion (if
applicable). *Italicized* typeface indicates that exchange has been observed between that pair from $^6\text{Li}$ 2D EXSY measurements.

<table>
<thead>
<tr>
<th>Table 8.2 – Summary of all possible exchange pairs/pathways in Li$_2$V(PO$_4$)$_2$F$_2$. Pairs where ion exchange has been observed are presented in <em>italicized</em> typeface.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exchange pair</strong></td>
</tr>
<tr>
<td>Li$_1$A-Li$_2$B</td>
</tr>
<tr>
<td>Li$_1$A-Li$_3$E</td>
</tr>
<tr>
<td>Li$_1$A-Li$_4$C</td>
</tr>
<tr>
<td>Li$_1$A-Li$_5$F</td>
</tr>
<tr>
<td>Li$_1$A-Li$_6$D</td>
</tr>
<tr>
<td>Li$_2$B-Li$_3$E</td>
</tr>
<tr>
<td>Li$_2$B-Li$_4$C</td>
</tr>
<tr>
<td>Li$_2$B-Li$_5$F</td>
</tr>
<tr>
<td>Li$_2$B-Li$_6$D</td>
</tr>
<tr>
<td>Li$_3$E-Li$_4$C</td>
</tr>
<tr>
<td>Li$_3$E-Li$_5$F</td>
</tr>
<tr>
<td>Li$_3$E-Li$_6$D</td>
</tr>
<tr>
<td>Li$_4$C-Li$_5$F</td>
</tr>
<tr>
<td>Li$_4$C-Li$_6$D</td>
</tr>
<tr>
<td>Li$_5$F-Li$_6$D</td>
</tr>
</tbody>
</table>

This provides an opportunity to identify which structural constraints are most critical for ion exchange to take place. As was demonstrated in previous chapters, parameters that have strong influence on the probability of ion exchange include Li-Li internuclear distance, sharing geometry of the Li polyhedra site within an exchange pair (corner-, edge-, or face-shared), area of the bottleneck for face-sharing or pseudo-face sharing geometries, and bond valence density along the diffusion pathway. When evaluating Table 8.2, it is noted that ion exchange is not observed between Li polyhedra sharing only a corner (Li$_1$A-Li$_3$E, Li$_2$B-Li$_4$C, Li$_2$B-Li$_5$F, Li$_2$B-Li$_6$D, and Li$_3$E-Li$_4$C) or in
pairs where no common atoms are shared between their polyhedra (Li$_1^A$-Li$_2^B$). For the edge-shared interactions, ion exchange was observed between Li$_1^A$-Li$_5^F$, Li$_3^E$-Li$_5^F$, Li$_3^E$-Li$_6^D$, and Li$_5^F$-Li$_6^D$. Here the pseudo-face-sharing geometries have bottlenecks ranging from 3.70 Å$^2$ to 4.17 Å$^2$ and internuclear distances from 2.749 Å to 3.133 Å. For the non-exchanging Li$_2^B$-Li$_3^E$ edge-shared pair, the structural parameters (bottleneck of 3.47 Å$^2$ and Li-Li distance of 2.964 Å) fall within the range of pairs where exchange has been observed. Similarly for the non-exchanging Li$_1^A$-Li$_4^C$ pair, which has face-shared Li polyhedra, the structural constraints of the internuclear distance and bottleneck suggest that exchange is possible between these two Li sites. However, exchange has not been observed in either Li$_1^A$-Li$_4^C$ and Li$_2^B$-Li$_3^E$. We therefore turn to bond valence density maps to better explain why ion hopping is not observed in these otherwise promising pathways for ion diffusion. Figure 8.4 shows bond valence (BV) maps of Li$_1^A$-Li$_4^C$, Li$_1^A$-Li$_5^F$, Li$_2^B$-Li$_3^E$, Li$_3^E$-Li$_5^F$, Li$_3^E$-Li$_6^D$, Li$_4^C$-Li$_5^F$, Li$_4^C$-Li$_6^D$, and Li$_5^F$-Li$_6^D$ (from Table 8.2). The plane of each BV density map was defined by the atomic coordinates of the O and F atoms that create the bottleneck of diffusion for a given exchange pair.
Figure 8.4 – Bond valence maps of ion exchange pathways in Li$_5$V(PO$_4$)$_2$F$_2$ for the ion hopping pairs that have either face-shared (left) or pseudo-face-shared (right) Li polyhedral geometries.

The exchange pairs with face-shared Li polyhedra have pathways with higher BV density than the pairs with pseudo-face-shared polyhedra. As will be shown in the next section, the timescales of ion hopping between pairs with pseudo-face-shared polyhedra are considerably slower than the pairs having face-shared geometry. This is attributed to
the less direct pathway found in the pseudo-face-shared geometries created by the open edge. Therefore, the comparison of BV density is restricted to ion pairs with similar geometries of polyhedral sharing. For the Li exchange pairs with face-shared polyhedral environments, the map of the non-exchanging Li1A-Li4C pair has much higher bond valence density relative to the maps of the exchanging Li4C-Li5F and Li4C-Li6D pairs. Similarly in the maps of the exchange pairs with edge-shared (or pseudo-face-shared) Li polyhedra, the non-exchanging Li2B–Li3E has higher bond valence density when compared to the maps of Li1A-Li5F, Li3E-Li5F, Li3E-Li6D, and Li5F-Li6D, where exchange has been observed. Overall, there is a strong correlation between the BV density found along the diffusion pathway and the propensity for ion exchange to take place within a host framework.

8.3.1 Timescales of Ion Hopping Determined from \(^6\)Li SI Experiments

The influence of bond valence density on the timescales of ion exchange was investigated using \(^6\)Li 1D selective inversion measurements over a variable temperature range. Only Li1A and Li4C were chosen for selective inversion out of the six Li sites in Li5V(PO4)2F2. (Figure 8.2) as these resonances were the best resolved in the spectrum and observed to participate in chemical exchange from the 2D EXSY studies. Inverting Li1A allowed for the timescales and energy barriers of the exchange pair Li1A-Li5F, to be determined. Inversion of Li4C in a second set of experiments gave quantitative results for Li4C-Li5F, and Li4C-Li6D ion hopping. The exchange timescales in Li5F-Li6D, Li3E-
Li\(_5\)\(_F\), and Li\(_3\)\(_E\)-Li\(_6\)\(_D\) were not determined due to low resolution of the crystallographic sites within this set of exchange pairs (Figure 8.2). The CIFIT model was designed to include the ion hopping rate matrices from all six exchange pairs. However, because the Li\(_3\)\(_E\)-Li\(_6\)\(_D\), Li\(_3\)\(_E\)-Li\(_5\)\(_F\), and Li\(_5\)\(_F\)-Li\(_6\)\(_D\) hopping rates could not be measured experimentally, the influence that they have on the resolved Li\(_4\)\(_C\)-Li\(_5\)\(_F\), Li\(_4\)\(_C\)-Li\(_6\)\(_D\), and Li\(_1\)\(_A\)-Li\(_5\)\(_F\) rates is difficult to determine. Therefore, rates of the measureable Li\(_4\)\(_C\)-Li\(_5\)\(_F\), Li\(_4\)\(_C\)-Li\(_6\)\(_D\), and Li\(_1\)\(_A\)-Li\(_5\)\(_F\) were fit initially with the rates of Li\(_3\)\(_E\)-Li\(_6\)\(_D\) (k\(_{36}\)), Li\(_3\)\(_E\)-Li\(_5\)\(_F\) (k\(_{35}\)), and Li\(_5\)\(_F\)-Li\(_6\)\(_D\) (k\(_{56}\)) set to zero. The ion hopping rates of Li\(_4\)\(_C\)-Li\(_5\)\(_F\) (k\(_{45}\)) and Li\(_4\)\(_C\)-Li\(_6\)\(_D\) (k\(_{46}\)) at 348 K were then fit again with non-zero values input for k\(_{35}\), k\(_{36}\), and k\(_{56}\). A more detailed presentation of this latter strategy is given in section 8.3.1.3 while the results from the zero value fits are given herein.

### 8.3.1.1 \(^{6}\)Li Selective Inversion Results for Inversion of Li\(_1\)\(_A\)

Data collected from inversion of Li\(_1\)\(_A\) in the \(^{6}\)Li 1D SI experiments over a variable temperature range is shown in Figure 6.7. The magnetization curves of Li\(_3\)\(_E\), Li\(_4\)\(_C\), and Li\(_6\)\(_D\) do not have transient features that indicate ion exchange is taking place with the inverted Li\(_1\)\(_A\) site. Only Li\(_5\)\(_F\) shows transient features attributable to ion exchange, which is consistent with the \(^{6}\)Li 2D EXSY results of Figure 8.3.
Figure 8.5 – Results of the $^6$Li 1D selective inversion of Li$_1$A (resonance A) over a variable temperature range (312 K – 348 K as indicated on legend on each plot). Clockwise from the top left, magnetization curves of Li$_1$A, Li$_2$B, Li$_3$E, Li$_4$C, Li$_5$F and Li$_6$D. The points represent measured values and the lines are the best fit to the data from the CIFIT program. For the non-inverted resonances, the depth of the transient well increases with increasing temperature, as expected for the ion exchange process.

Li$_2$B does show a temperature dependent attenuation of its magnetization with inversion of Li$_1$A. This attenuation however, is not attributed to Li$_1$A-Li$_2$B exchange as these two sites are 5.912 Å apart and do not share any atoms between their respective polyhedral environments (Table 8.2). Rather, the attenuation is attributed to the proximity of the Li$_2$B resonance to the site selected for inversion. Figure 8.6 shows the slight inversion (~ 5%) of the Li$_2$B resonance at the lowest (312 K) and highest (348 K) experimental temperatures. As the temperature is raised, the paramagnetic resonances
migrate towards 0 ppm, (due to Curie-Weiss changes in the magnetic susceptibility)\textsuperscript{12} creating a less resolved spectrum. The attenuation of the neighbouring Li\textsubscript{2B} magnetization has now increased to \(\sim 15\%\) relative to the signal observed at a mixing time where all spins are at equilibrium.

Figure 8.6 – \(^{6}\)Li SI spectra showing the inversion of Li\textsubscript{1A} at different mixing times and temperatures. Left: inversion of Li\textsubscript{1A} at 312 K. Right: Inversion of Li\textsubscript{1A} at 348 K. The red spectra are at a mixing time of 100 ms, where complete relaxation of the inverted peak is accomplished. The black spectra are at mixing times of 5 µs where maximum inversion is observed.

The rate coefficients for the Li\textsubscript{1A}Li\textsubscript{5F} exchange process were determined by fitting the experimental results in CIFIT. For this exchange process a forward and backward rate coefficient exists, \((k\textsubscript{15} \text{ and } k\textsubscript{51}, \text{ respectively})\). Because the Li\textsubscript{1A}:Li\textsubscript{5F} occupancy is 0.5:1.0, under a steady-state approximation, \(k\textsubscript{15} = 2k\textsubscript{51}\). In this study, the CIFIT parameters were set such that the faster coefficient, \(k\textsubscript{15}\), was found while the reverse coefficient, \(k\textsubscript{51}\), was predicted based on the site-populations (Table 8.3). Detail on the treatment of unequal populations in CIFIT is outlined in greater detail elsewhere.\textsuperscript{13}
The forward rate coefficients for Li$_{1A}$-Li$_{5F}$ ranged from 14 ± 4 s$^{-1}$ at 326 K up to 49 ± 6 s$^{-1}$ at 348 K (Table 8.3). Data collected at temperatures below 326 K, had timescales that could not be accurately fit using CIFIT and were therefore excluded from the analysis of the energy barriers.

**Table 8.3** – Summary of CIFIT results over a variable temperature range of $^6$Li SI measurements where Li$_{1A}$ was the site chosen for inversion. The forward rate coefficients (k$_{15}$) are reported from CIFIT while the backward coefficients (k$_{51}$) are predicted from the site-populations.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>k$_{15}$ (s$^{-1}$)</th>
<th>k$_{51}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$<em>{1A}$-Li$</em>{5F}$</td>
<td>Li$<em>{1A}$-Li$</em>{5F}$</td>
</tr>
<tr>
<td>312 K</td>
<td>Not Determined</td>
<td>Not Determined</td>
</tr>
<tr>
<td>319 K</td>
<td>Not Determined</td>
<td>Not Determined</td>
</tr>
<tr>
<td>326 K</td>
<td>14 ± 4</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>333 K</td>
<td>18 ± 5</td>
<td>9 ± 3</td>
</tr>
<tr>
<td>340 K</td>
<td>40 ± 5</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>345 K</td>
<td>45 ± 5</td>
<td>23 ± 3</td>
</tr>
<tr>
<td>348 K</td>
<td>49 ± 6</td>
<td>25 ± 3</td>
</tr>
</tbody>
</table>

Energy Barrier (eV) 0.6 ± 0.1 0.6 ± 0.1

The activation energy of Li$_{1A}$-Li$_{5F}$ hopping was calculated from the slope of the natural log of (k/T) plotted against the inverse temperature in an Eyring analysis (Figure 8.7). An energy barrier value of 0.6 ± 0.1 eV was calculated with the error determined from the standard error of the slope from the regression analysis. The large error on the energy barriers is attributed to the large relative error for the ion hopping rates determined at 326 K and 333 K (Table 8.3). It is noteworthy that the overall timescales measured for this exchange pair in Li$_5$V(PO$_4$)$_2$F$_2$ are considerably slower than those measured for Li ion hops between corner-shared polyhedra of Li$_3$Fe$_2$(PO$_4$)$_3$ (from $^6$Li 2D
EXSY measurements, Chapter 5) and Li$_3$V$_2$(PO$_4$)$_3$ (from $^7$Li 2D EXSY study of Cahill et al.$^{14}$). This difference is discussed in greater detail in 8.3.2.

![Eyring plot of the natural log of the Li$_1$A-Li$_5$F ion hopping rate (k) over temperature plotted against 1000/T.](image)

**Figure 8.7** – Eyring plot of the natural log of the Li$_1$A-Li$_5$F ion hopping rate (k) over temperature plotted against 1000/T.

8.3.1.2 $^6$Li Selective Inversion Results for Inversion of Li$_4$C

Results from the inversion of Li$_4$C over a variable temperature range are given in Figure 6.7. Here, both Li$_5$F and Li$_6$D show well-developed transients attributed to ion exchange with Li$_4$C. This is supported by the previous reports of Li$_4$C-Li$_5$F, and Li$_4$C-Li$_6$D exchange observed in the $^6$Li 2D EXSY studies.$^1$
Figure 8.8 – Results of the $^6$Li 1D selective inversion of Li4C over a variable temperature range. Clockwise from the top left, magnetization curves of Li1A, Li2B, Li3E, Li4C, Li5F and Li6D. The points represent measured values and the lines are the best fit to the data from the CIFIT program. For the non-inverted resonances, the depth of the transient well increases with increasing temperature, as expected for ion exchange processes.

Slight transient features also appear in the magnetization curves of Li3E. This transient is not attributed to Li4C-Li3E exchange but more to Li3E-Li6D exchange. Due to the proximity of the Li6D resonance ($\delta = 16$ ppm at 312 K, Figure 8.2) to the Li4C inversion site ($\delta = 11$ ppm, at 312 K), slight inversion (~ 5 %) of the Li6D site is observed (Figure 8.9). As the temperature is raised, the paramagnetic resonances migrate towards 0 ppm, (due to Curie-Weiss changes in the magnetic susceptibility) creating a less resolved spectrum. The attenuation of the neighbouring Li6O magnetization has now increased to ~ 30% relative to the signal observed at a mixing time where all spins are at equilibrium.
Therefore, the determined timescales of ion hopping for Li4C-Li5F and Li4C-Li6D are treated with some caution. This is not only due to the slight inversion of the neighbouring Li6D resonance, but also due to the unknown influence that the unmeasureable Li3E-Li6D, Li3E-Li5F, and Li5F-Li6D exchange pairs has on the hopping rates of the measureable exchange pairs, Li4C-Li5F, Li4C-Li6D, and Li1A-Li5F. As stated previously, the CIFIT model includes the ion hopping rate matrices from all six exchange pairs. However, because the Li3E-Li6D, Li3E-Li5F, and Li5F-Li6D hopping rates cannot be measured experimentally, the influence that they have on the measureable Li4C-Li5F, Li4C-Li6D, and Li1A-Li5F rates is difficult to determine. A more detailed presentation of this latter strategy is given in section 8.3.1.3.
Rates of Li$_4$C-Li$_5$F extend from $9 \pm 2$ s$^{-1}$ at 326 K up to $58 \pm 7$ s$^{-1}$ at 348 K. Slightly faster kinetics were observed for the Li$_4$C-Li$_6$D exchange with timescales ranging from $12 \pm 4$ s$^{-1}$ at 326 K up to $71 \pm 11$ s$^{-1}$ at 348 K (Table 8.4). In both exchange pairs, data collected at 312 K had dynamics too slow to be accurately determined. This temperature was therefore excluded from the Eyring analysis of the energy barriers. Plots of the natural log of the rate constant over temperature as a function of inverse temperature in an Eyring analysis yielded energy barriers of $0.79 \pm 0.04$ eV for Li$_4$C-Li$_5$F and $0.76 \pm 0.04$ eV for Li$_4$C-Li$_6$D (Figure 8.10). These energy barriers are equivalent within error and reflect the similarity in bottleneck dimensions and internuclear distances (Table 8.2) as well as bond valence density maps (Figure 8.4), for these two hopping pairs.
Here the timescales and energy barriers of ion hopping in the face-shared polyhedra, \( \text{Li}_{4c}-\text{Li}_{5f} \) and \( \text{Li}_{4c}-\text{Li}_{6d} \), are compared to that of the edge-shared polyhedral pair \( \text{Li}_{1A}-\text{Li}_{5f} \). This comparison is made more complex by the unequal populations of the \( \text{Li}_{1A} \) and \( \text{Li}_{1f} \) sites of this pair as compared to the equal population of the face-shared pairs. Comparing the backward (\( k_{51} \)) and forward rate (\( k_{15} \)) coefficients for the \( \text{Li}_{1A}-\text{Li}_{5f} \)
(where $k_{15} = 2k_{51}$), $k_{15}$ is higher due to the lower concentration of the Li$_1$A site, while $k_{51}$ is lower due to the higher population of the Li$_5$F site. If the Li$_1$A and Li$_5$F populations were equal, the rate coefficients would both sit at the lower, $k_{51}$, value, as there would no longer be an overcompensation of the coefficient for the low population. Therefore, the reverse rate coefficients of the Li$_1$A-Li$_5$F (which are of half-value to those solved for in CIFIT) are more suitable for comparison to the rate coefficients of the Li$_4$C-Li$_5$F, Li$_4$C-Li$_6$D exchange pairs where occupancy is 1:1. Therefore, comparing timescales found at 348 K, the edge-shared rate coefficient ($25 \pm 3$ s$^{-1}$) is considerably slower than the timescales found for the either of face-share ion-hopping pairs ($71 \pm 11$ s$^{-1}$ and $58 \pm 7$ s$^{-1}$ for Li$_4$C-Li$_6$D and Li$_4$C-Li$_5$F, respectively). Furthermore, ion pairs having face-shared polyhedral geometries have significantly higher energy barriers to the site hop than the edge-shared Li$_1$A-Li$_5$F pair. Returning to the BSV maps of these three exchange pairs in Figure 8.4, the face-shared geometries have a more confined pathway for diffusion resulting in a more direct and therefore faster exchange rate. A higher energy threshold however, accompanies this tighter, but more direct pathway. The edge-shared interaction, while having a more open bottleneck for diffusion, results in a less direct pathway for the ion to diffuse giving longer correlation times.
Table 8.4 – Summary of exchange rates and activation energies of Li ion hopping as determined from $^6$Li selective inversion studies of Li$_3$V(PO$_4$)$_2$F$_2$.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_{51}$ (=0.5 $k_{51}$) (s$^{-1}$)</th>
<th>$k_{46}$ (=$k_{64}$) (s$^{-1}$)</th>
<th>$k_{45}$ = ($k_{54}$) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>312 K</td>
<td>Not Determined</td>
<td>Not Determined</td>
<td>Not Determined</td>
</tr>
<tr>
<td>319 K</td>
<td>Not Determined</td>
<td>3 (± 3)</td>
<td>4 (± 2)</td>
</tr>
<tr>
<td>326 K</td>
<td>7 (± 2)</td>
<td>12 (± 4)</td>
<td>9 (± 2)</td>
</tr>
<tr>
<td>333 K</td>
<td>9 (± 3)</td>
<td>20 (± 3)</td>
<td>15 (± 2)</td>
</tr>
<tr>
<td>340 K</td>
<td>20 (± 3)</td>
<td>38 (± 4)</td>
<td>26 (± 3)</td>
</tr>
<tr>
<td>345 K</td>
<td>23 (± 3)</td>
<td>51 (± 7)</td>
<td>41 (± 5)</td>
</tr>
<tr>
<td>348 K</td>
<td>25 (± 3)</td>
<td>71 (± 11)</td>
<td>58 (± 7)</td>
</tr>
<tr>
<td>Energy Barrier (eV)</td>
<td>0.6 ± 0.1</td>
<td>0.76 ± 0.04</td>
<td>0.79 ± 0.04</td>
</tr>
</tbody>
</table>

8.3.1.3 CIFIT Results for Unresolved Exchange Pairs

The results presented in Table 8.4 of the previous section, are the $k_{45}$, $k_{46}$ and $k_{15}$ values determined from CIFIT where the rates of exchange between the unresolved sites, Li$_3$E-Li$_5$F, Li$_3$E-Li$_6$D, and Li$_5$F-Li$_6$D ($k_{35}$, $k_{36}$, and $k_{56}$, respectively) were set to zero. Here, the effect that non-zero values for $k_{35}$, $k_{36}$, and $k_{56}$ has on the fit of the measurable data ion hopping rates ($k_{45}$, $k_{46}$) is investigated. Table 8.5 summarizes the values of $k_{45}$ and $k_{46}$ given from a series of fit procedures (labeled LD1 through LD12) where the values of $k_{35}$, $k_{36}$, $k_{56}$ values were varied from 0 s$^{-1}$ to 300 s$^{-1}$, in different combinations.
An initial set of fits (LD2, LD3, and LD4) have only one of $k_{35}$, $k_{36}$, or $k_{56}$ set to 50 s$^{-1}$, while the others were held at 0 s$^{-1}$. These were compared to the fits from LD1 where $k_{35}$, $k_{36}$, or $k_{56}$ are all at set to zero and LD5 where $k_{35}$, $k_{36}$, and $k_{56}$ are all set to 50 s$^{-1}$. A value of 50 s$^{-1}$ was chosen for the rates of the unresolved sites as it is of the same magnitude of values determined from the initial fits of $k_{45}$, $k_{46}$ and $k_{15}$ and is comparable to other fluorophosphate frameworks studied in this thesis (Li$_2$VPO$_4$F, Chapter 6). It is evident that having only one of $k_{35}$, $k_{36}$, and $k_{56}$ rates set to a non-zero value does not alter $k_{45}$ and $k_{46}$ beyond the error bounds given from LD1. The fits of the transient wells of the Li$_5$F and Li$_6$D magnetization under these different fitting conditions (Figure 8.11), maintain a $\chi^2$ value close to, or better than, the one given for LD1 (Table 8.5).
Figure 8.11 - Fit of Li₆D (left) and Li₅F (right) transient wells at 348 K as the values of $k_{36}$, $k_{35}$ and $k_{56}$ are varied in the fitting regimes of LD1, LD2, LD3, LD4, and LD5. Parameters for each fit are summarized in Table 8.5

When two out of the three rates are set to 50 s⁻¹, the values of $k_{45}$ and $k_{46}$ are impacted to a greater extent (outlined in fits LD6, LD7, and LD8). When $k_{36}$ and $k_{56}$ are both set to 50 s⁻¹ while $k_{35}$ is left at 0 s⁻¹ (LD6), the fitted values for $k_{45}$ and $k_{46}$ are pushed further away from the LD1 results, than the rates given in the LD2, LD3, and LD4 fits. However, these values are still equivalent within error to the LD1 results with fits of the transient wells of the Li₅F and Li₆D magnetization (Figure 8.12) under the different fitting conditions giving $\chi^2$ values close to, or better than, those for LD1 (Table 8.5).
Figure 8.12 - Fit of Li$_6^D$ (left) and Li$_5^F$ (right) transient wells at 348 K as the values of $k_{36}$, $k_{35}$ and $k_{56}$ are varied in the fitting regimes of LD1, LD6, LD7, and LD8. Parameters for each fit are summarized in Table 8.5.

When all three rates, $k_{35}$, $k_{36}$, and $k_{56}$ are set to 50 s$^{-1}$ (LD5), there is minimal change to the values of $k_{45}$ and $k_{46}$ than those determined from LD1. When the $k_{35}$, $k_{36}$, and $k_{56}$ are set to values slightly lower (25 s$^{-1}$ (LD9)) there is still no movement of the fit values of $k_{45}$ and $k_{46}$ outside the error limits of the LD1 results. Only when much higher values of $k_{35}$, $k_{36}$, and $k_{56}$ are selected, do the fit values of $k_{45}$ and $k_{46}$ begin to move outside the error limits of the LD1 results (Table 8.5). This was the case when $k_{35}$, $k_{36}$, and $k_{56}$ were set to 100 s$^{-1}$ (LD10), 200 s$^{-1}$ (LD11) and 300 s$^{-1}$ (LD12). For this set of conditions, the transient wells of the Li$_5^F$ and Li$_6^D$ magnetization for fits LD1, LD5, and LD9-12 are given in Figure 8.13. The $\chi^2$ values for this last group of fits also does not deviate from the goodness of fit given in the LD1 calculations (Table 8.5)
Figure 8.13 – Fit of Li6D (left) and Li5F (right) transient wells at 348 K as the values of $k_{36}$, $k_{35}$ and $k_{56}$ are varied in the fitting regimes of LD1, LD9, LD10, LD11, and LD12. Parameters for each fit are summarized in Table 8.5.

Figure 8.14 - Left: Plot of the fit values of $k_{45}$ and $k_{46}$ at 348 K against the held values of $k_{35}$, $k_{36}$ and $k_{56}$ (from fitting regimes LD1, LD5, LD9-12). Right: Fit of Li4C over all fitting regimes (LD1-12). Parameters for each fit are summarized in Table 8.5.

It is noteworthy that in this last fitting procedure, the $k_{45}$ and $k_{46}$ values diverge away from one another with a linear dependence on the held value of $k_{35}$, $k_{36}$, and $k_{56}$ (Figure 8.14, left). Moreover, the sum of the $k_{45}$ and $k_{46}$ rates remains consistent (within error) over all possible fitting regimes. This shows that although the distribution of the $k_{45}$ and
k_{46} values may change, the total contribution of the ion mobility to the relaxation of Li_{4C} is unchanged. This is more clearly demonstrated when the fits of Li_{4C} are shown over the entire set of fitting parameters (LD1-LD12) (Figure 8.14, right).

Overall, the results from this series of fitting procedures (LD1-LD12) show that the values of k_{45} and k_{46} are accurately determined when the values of, k_{35}, k_{36}, and k_{56}, are set to 0 s^{-1} in the CIFIT rate matrices. For the ion hopping rates of the unresolved exchange processes k_{35}, k_{36}, and k_{56}, little information regarding the magnitude of these values can be extracted from this set of initial conditions.

8.3.2 Comparison to Materials Studied in this Thesis and Other Works

Here we compare the timescales and energy barriers of ion hopping within the set of materials studied in this thesis and other works. Table 8.6 summarizes the timescales, energy barriers, and key parameters that influence ion mobility in Li₃M₂(PO₄)₃ (M = Fe and V), Li₂VPO₄F, Li₅V(PO₄)₂F₂ and Li₃VF₆.
Table 8.6 – Summary of Li ion hopping rates, energy barriers, internuclear distances, bottleneck area, bond sum valence (BSV) values and bond sum value distribution ($\Delta$BSV) for ion hopping pairs in a series of Li intercalation compounds.

<table>
<thead>
<tr>
<th>Material and Hopping Pairs</th>
<th>$k$ Range (s$^{-1}$)</th>
<th>$E_a$ (eV)</th>
<th>Li-Li distance (Å)</th>
<th>Bottleneck Area (Å$^2$)</th>
<th>BSV Lix-Liy</th>
<th>$\Delta$BSV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$Fe$_2$(PO$_4$)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li1-Li2</td>
<td>108 – 760</td>
<td>0.59 ± 0.05</td>
<td>3.139</td>
<td>1.054-0.952</td>
<td>0.102</td>
<td></td>
</tr>
<tr>
<td>Li1-Li3</td>
<td>112–1025</td>
<td>0.63 ± 0.03</td>
<td>3.417</td>
<td>1.054-0.898</td>
<td>0.065</td>
<td></td>
</tr>
<tr>
<td>Li2-Li3</td>
<td>8 –990</td>
<td>0.81 ± 0.04</td>
<td>3.110</td>
<td>0.952-0.989</td>
<td>0.037</td>
<td></td>
</tr>
<tr>
<td>Li$_3$V$_2$(PO$_4$)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li1-Li2</td>
<td>142 (± 7)</td>
<td>0.83 ± 0.01</td>
<td>3.4</td>
<td>1.057-0.909</td>
<td>0.148</td>
<td></td>
</tr>
<tr>
<td>Li1-Li3</td>
<td>155 (± 10)</td>
<td>0.73 ± 0.01</td>
<td>3.08</td>
<td>1.057-1.064</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Li2-Li3</td>
<td>130 (± 10)</td>
<td>0.79 ± 0.01</td>
<td>3.28</td>
<td>0.909-1.064</td>
<td>0.155</td>
<td></td>
</tr>
<tr>
<td>Li$_5$V(PO$_4$)$_2$F$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li1-Li2</td>
<td>49</td>
<td>N/A</td>
<td>2.72</td>
<td>1.045 – 0.959</td>
<td>0.086</td>
<td></td>
</tr>
<tr>
<td>Li1-Li3</td>
<td>225</td>
<td>N/A</td>
<td>2.72</td>
<td>1.045 – 0.901</td>
<td>0.144</td>
<td></td>
</tr>
<tr>
<td>Li2-Li3</td>
<td>31</td>
<td>N/A</td>
<td>3.51</td>
<td>Edge</td>
<td>0.959 – 0.901</td>
<td>0.058</td>
</tr>
</tbody>
</table>

First, the results from the fluorophosphates, Li$_5$V(PO$_4$)$_2$F$_2$ and Li$_2$VPO$_4$F$_2$ are compared. In Chapter 6, two ion exchange pathways with face-shared polyhedral geometries were identified as the most probable pathways for ion exchange in Li$_2$VPO$_4$F and labeled as the $\alpha$- and $\beta$-pathways, respectively. The range of ion hopping rates of these pathways is similar to those found for the Li$_4$C-Li$_5$F and Li$_5$F-Li$_6$D partners, of Li$_3$V(PO$_4$)$_2$F$_2$, which also have face-shared polyhedra. However, a lower energy barrier of exchange was found in Li$_2$VPO$_4$F which we attribute to the more open diffusion bottlenecks (~ 4 Å$^2$) whereas in Li$_5$V(PO$_4$)$_2$F$_2$ the Li$_4$C-Li$_5$F and Li$_5$F-Li$_6$D bottlenecks are smaller at 3.59 Å$^2$ and 3.43 Å$^2$, respectively. The energy barrier of the face-shared
Li$_2$VPO$_4$F pathways is closer to that of the Li$_{1A}$-Li$_{5F}$ pair in Li$_5$V(PO$_4$)F$_2$ which is an edge-shared polyhedral exchange pair. This is consistent with the similar appearance of the bond valence maps of the two exchange pathways (Figure 8.15) and the bottleneck dimensions of the two being much closer. The $\alpha$- and $\beta$-pathways of Li$_2$VPO$_4$F have areas of 3.92 Å$^2$ and 4.22 Å$^2$ respectively, while the Li$_{1A}$-Li$_{5F}$ exchange pair in Li$_5$V(PO$_4$)F$_2$ has a pseudo-face sharing geometry bottleneck area of 4.17 Å$^2$.

![Figure 8.15](image)

**Figure 8.15** – Comparison of bond valence density maps of the Li$_1$-Li$_2$ $\alpha$-pathway in Li$_2$VPO$_4$F (left) and the Li$_{1A}$-Li$_{5F}$ exchange pathway in Li$_5$V(PO$_4$)$_2$F$_2$. Each map shown has a viewing radius of 2 Å and contour increment of 0.485.

Comparing the fluorophosphates to other fluorinated polyanion frameworks, we turn to the recently published report on the ion hopping rates in Li$_3$VF$_6$ from a $^6$Li 2D EXSY study by Wilkening et al.$^{16}$ Between the three crystallographic sites, three exchange pairs were identified with ion hopping rates for Li$_1$-Li$_2$, Li$_2$-Li$_3$, and Li$_2$-Li$_3$ as 49 s$^{-1}$, 225 s$^{-1}$ and 35 s$^{-1}$, respectively, at 340 K. Results from only a single
temperature were presented, meaning a comparison of the energy barriers of this system to other frameworks is not possible. In terms of ion hopping rates, within Li$_3$VF$_6$, the authors attributed the slow (31 s$^{-1}$) Li$_2$-Li$_3$ ion hop to the Li ion possibly occupying an intermediate tetrahedral interstitial site. This is more simply referred to in our work as an edge-shared polyhedral geometry, where a less direct pathway and subsequent longer ion diffusion time is expected. The more quickly exchanging, Li$_1$-Li$_2$ and Li$_1$-Li$_3$ pairs have face-shared polyhedra with similar internuclear distances and bottleneck areas, giving more direct pathways for ion hopping and faster ion hopping rates of 41 s$^{-1}$ and 225 s$^{-2}$, respectively. We attribute the very fast hopping rate of the Li$_1$-Li$_3$ to a region of low bond valence density observed in its BV density map, that is not observed in the Li$_1$-Li$_2$ pair (Figure 8.16).

**Figure 8.16** – Bond valence density maps of the Li$_1$-Li$_2$ (left) and Li$_1$-Li$_3$ (right) exchange pathways in Li$_3$VF$_6$. Contour increment is 0.485 with a 2 Å radius shown.
Comparing the fluorophosphates to Li$_3$VF$_6$, the timescales of the Li$_4$C-Li$_5$F and Li$_4$C-Li$_6$D pairs (with face-shared polyhedra) in Li$_5$V(PO$_4$)$_2$F$_2$ (at $26 \pm 3 \text{ s}^{-1}$ and $38 \pm 4 \text{ s}^{-1}$, respectively at 340 K) are quite close to the Li1-Li2 pair of Li$_3$VF$_6$ (41 s$^{-1}$ at 340 K). Returning to the Li$_4$C-Li$_5$F and Li$_4$C-Li$_6$D bond valence maps for Li$_5$V(PO$_4$)$_2$F$_2$ of Figure 8.4, these maps closely resemble the map belonging to the Li1-Li2 pair of Li$_3$VF$_6$ (Figure 8.16). This again illustrates the usefulness of bond valence density maps in interpreting measured timescales of ion mobility in Li intercalation compounds.

Li ion hopping in the fluorophosphates and metal fluoride (Li$_3$VF$_6$) frameworks are much slower relative to those in the phosphates, Li$_3$Fe$_2$(PO$_4$)$_3$ and Li$_3$V$_2$(PO$_4$)$_3$. Not only are the measured rates of ion hopping in the phosphates ~ 10 times faster than the fluorophosphates and Li$_3$VF$_6$, but this is observed within a much lower temperature range. This fast exchange is not explained by the geometry of the exchange pairs as the phosphates host only corner- and edge-shared geometries of ion hopping pathways, which are less favourable for fast ion mobility than the face-shared geometries found in Li$_3$VF$_6$ and fluorophosphates. It is evident that the introduction of fluorine atoms to the anion within the framework contributes to the slow ion exchange in Li$_3$VF$_6$, Li$_2$VPO$_4$F and Li$_5$V(PO$_4$)$_2$F$_2$. It is proposed that the ion dynamics in a larger set of materials having different phosphate, fluorophosphates, and fluorosulfate anion compositions be studied in order to further investigate the role that the anion composition plays on the Li ion mobility properties. This study should include the tavorite based Li$_2$FePO$_4$F$^{17}$ as its structure and dynamics are easily compared to the isostructural Li$_2$VPO$_4$F as well as Li$_3$Fe$_2$(PO$_4$)$_3$. 
8.4 Conclusions

This chapter highlights the influence of bond valence density on the probability of ion hopping in fluorophosphates. $^6$Li Selective Inversion measurements revealed the timescales and energy barriers of ion hopping between Li1$_A$-Li4$_C$, Li4$_C$-Li5$_F$, and Li4$_C$-Li6$_D$ in Li$_5$V(PO$_4$)$_2$F$_2$. Faster ion hopping with a higher energy barrier was observed in the face-shared Li4$_C$-Li5$_F$ and Li4$_C$-Li6$_D$ pairs, where more direct bottlenecks were revealed in the bond valence density maps. The more open bottleneck of the Li1$_A$-Li5$_F$ pathway gives a lower energy barrier but a less direct pathway giving a longer correlation time for exchange. These results were compared to frameworks having different anion structures including phosphates (Li$_3$Fe$_2$(PO$_4$)$_3$ and Li$_3$V$_2$(PO$_4$)$_3$) and the metal fluoride (Li$_3$VF$_6$). The fluorinated structures have restricted ion mobility relative to the phosphates, indicating that the introduction of fluorine atoms influences the Li ions significantly.
8.5 References


Chapter 9: Summary and Outlook

9.1 Summary

This thesis presented multinuclear solid-state NMR results that elucidated the structural and Li ion mobility properties in a series of phosphate and fluorophosphate Li intercalation compounds used as cathode materials for Li ion batteries. NMR of these materials is made non-trivial by the strong through-bond and through-space coupling between the nuclei being measured and the unpaired electron spin density sitting on the transition metal center. While this coupling can lead to complications in the NMR spectra, it also allows for subtle changes in the electronic structure of the redox active center to be easily identified through changes in the paramagnetic shift, isotropic lineshapes, and span of the sideband manifolds. This thesis also sought to expand the number of NMR tools available to study ion dynamics in this class of materials. Previous studies of Li ion mobility have used $^6,^7$Li 2D EXSY measurements over a variable temperature range to quantify ion hopping rates and energy barriers in paramagnetic Li intercalation compounds including Li$_3$Fe$_2$(PO$_4$)$_3$ studied in Chapter 5.$^{14}$ Analysis of this data is most accurate when the longest mixing time extends well beyond the correlation time of the exchange process(es). However, in strongly paramagnetic systems such as those studied here, short spin-lattice relaxation of the Li nuclei limits the range of mixing times available leading to a more complicated data analysis. This thesis showed that $^6$Li Selective Inversion (SI) experiments are an excellent alternative means to measure ion dynamics in solid-state paramagnetic materials, especially in systems where the ion
hopping rates are slow relative to the spin-lattice time of the Li nuclei. As a result, a combination of $^6\text{Li} \, 2\text{D EXSY}$ and $^6\text{Li} \, 1\text{D SI}$ measurements led to quantification of the ion hopping timescales in Li$_3$Fe$_2$(PO$_4$)$_3$, Li$_2$VPO$_4$F, Li$_2$VOPO$_4$ and Li$_5$V(PO$_4$)$_2$F$_2$. This gave a more detailed picture of the structural factors that enhance or inhibit ion mobility in a framework including Li-Li internuclear distance, atomic bottlenecks for diffusion and bond valence density along the ion hopping pathway. Here, a chapter-by-chapter breakdown of the key results from each section is given with suggestions for future work included.

In Chapter 4, the influence of the paramagnetic centers on the appearance of both the $^7\text{Li}$ and $^{31}\text{P}$ MAS NMR spectra of LiMnPO$_4$ and LiFePO$_4$ was investigated. Significant differences in paramagnetic shift, span of the sideband manifold, and full-width half-maximum (FWHM) of the isotropic peak of these isostructural frameworks was observed and attributed to the different electron configuration at the transition metal center where, Mn$^{2+}$ is a d$^5$ t$_{2g}^3$ e$_g^2$ configuration and Fe$^{2+}$ is a d$^6$ t$_{2g}^4$ e$_g^2$ configurations. This sensitivity to electronic changes at the transition metal center was used to monitor the high-temperature phase transformation in Li$_m$FePO$_4$ from biphasic 0.5LiFePO$_4$:0.5FePO$_4$ to the solid solution Li$_{0.5}$FePO$_4$. Here the large difference in the $^{31}\text{P}$ paramagnetic shift of the Fe$^{3+}$PO$_4$ and LiFe$^{2+}$PO$_4$ domains allowed the coalescence of these two domains to be monitored as a function of temperature. This was the first in-situ NMR study of the high-temperature phase transformation in this electrochemically important material. Moreover, this chapter also showed the presence of phase-interface Li regions in 0.5LiFePO$_4$:0.5FePO$_4$, using solid-state $^7\text{Li}$ MAS measurements. Lack of site mixing in
the phase boundary regions are often attributed to poor cycling rates in the phosphate family of cathode materials. Our identification of distinct Li environments at these regions confirms that the Li ions are not hopping between the lithiated and delithiated regions on a timescale faster than that of the NMR acquisition.

The focus of ongoing work is the quantification of Li ion mobility timescales in the olivine phases. Only a single crystallographic Li site is found within these frameworks meaning exchange measurements, which rely on the movement of Li ions from one crystallographic environment to another, cannot be used effectively. Similarly, measurements which rely on changes to the $^{6,7}\text{Li}$ NMR lineshape over a variable temperature, also cannot be used to quantify ion dynamics. This is due to temperature-dependent changes to the magnetic susceptibility having a larger influence on the appearance on the NMR spectra than any changes to the average homo- or heteronuclear dipolar couplings brought on by Li ion mobility. In this thesis, an attempt to probe heteronuclear dipolar couplings was made by using $^6\text{Li} \{ ^{31}\text{P} \}$ REDOR measurements. However, the incomplete excitation of the broad $^{31}\text{P}$ resonance introduces a large number of variables that makes accurate interpretation of the resulting REDOR buildup curves non-trivial. Therefore, it is proposed that future studies focus on REDOR measurements that investigate changes in $^6\text{Li}$-$^7\text{Li}$ dipolar couplings as both $^6\text{Li}$ and $^7\text{Li}$ resonances are narrow relative to the $^{31}\text{P}$ meaning fewer complications from incomplete excitation are encountered.
In Chapter 5, the timescales and energy barriers of ion hopping in α-Li$_3$Fe$_2$(PO$_4$)$_3$ were quantified using $^6$Li 2D EXSY measurements. Unlike previous reports on the $^7$Li 2D EXSY measurements of isostructural Li$_3$V$_2$(PO$_4$)$_3$, the measured timescales and energy barriers did not correlate to trends in internuclear distances and atomic bottlenecks for diffusion. Rather, for Li$_3$Fe$_2$(PO$_4$)$_3$, bond valence density maps revealed a significant obstruction of valence density from an Fe atom along the diffusion pathway leading to the highest energy barrier for the Li2-Li3 pair despite it having an open bottleneck and short internuclear distance. This highlighted the importance of considering the three-dimensional bond valence density along the Li-Li exchange route when discussing possible pathways for Li ion diffusion.

Chapter 5 also demonstrated how the ion dynamics are changed in samples of as-prepared Li$_x$V$_2$(PO$_4$)$_3$ ($x = 3$) as it first cast as a cathode slurry and then as it is cycled to a composition of $x = 1.2$. Preliminary results show that coalescence of the three isotropic peaks (A, B, and C) takes place at lower temperature in the cycled materials than in either the cast material or the as-prepared compound. Similar to the case for 0.5LiFePO$_4$:0.5FePO$_4$, the presence of phase interface regions may be hindering the ion mobility in this phase as well. Quantification of these timescales using $^6$Li Selective Inversion (SI) measurements are proposed as a continuation of this project, as the low signal to noise of the cycled samples makes $^6,^7$Li 2D EXSY measurements impractical from the standpoint of spectrometer time.
Proposed future work for Li$_3$Fe$_2$(PO$_4$)$_3$, is based on the recent work of Cabana et al. where insertion of a fourth and fifth Li ion was characterized using $^6$Li MAS measurements. Here, the isotropic peaks were broadened significantly which the authors attribute to enhanced mobility and/or Li ion disorder of the newly prepared phases Li$_{3+x}$Fe$_2$(PO)$_3$ ($1 \leq x \leq 2$). It is possible however, that this broadening is due to changes in T$_{1e}$ at the paramagnetic center brought on by the change in Fe oxidation state. A lengthened T$_{1e}$ could greatly increase the FWHM of the isotropic Li lineshapes, as was shown in our study of the FWHM of Li near a Fe$^{3+}$ site versus a Fe$^{2+}$ site in biphasic 0.5LiFePO$_4$:0.5FePO$_4$ (Chapter 4). Therefore, it is proposed that quantification of the ion dynamics in the electrochemically intercalated phases be made either through $^6$Li SI or $^6$Li 2D EXSY measurements. This will allow for the source of the line broadening to be properly identified as arising either from the changes in ion dynamics brought on by Li insertion, or because of electronic changes at the paramagnetic center leading to different electron spin relaxation properties. This differentiation is critical as faster ion mobility at higher lithiation levels would make Li$_{3+x}$Fe$_2$(PO$_4$)$_3$ a very high-capacity material for Li ion battery applications.

Chapter 6 detailed the characterization of the structure and ion mobility properties of the fluorophosphate phase Li$_x$VPO$_4$F ($x = 0.0, 1.5, 2.0$) using $^{19}$F, $^{31}$P and $^6$,$^7$Li NMR measurements. Collaborators from the University of Waterloo provided samples of Li$_x$VPO$_4$F allowing for $^6$,$^7$Li MAS NMR measurements to map an *ex-situ* lithiation of the host framework from $x = 0.0$ to 1.5 to 2.0. The two new environments in the Li$_2$VPO$_4$F phase were assigned initially based on the Fermi-contact interaction with the
paramagnetic V center, and then through analysis of the sideband manifolds where CSA parameters were extracted and correlated to the symmetry of each site. $^6\text{Li}\{^{19}\text{F}\}$REDOR measurements further confirmed the assignment where the Li site having shortest Li-F contact (as given from the crystallographic data) gave rise to the strongest REDOR buildup. $^6\text{Li}$ 1D EXSY measurements were applied to Li$_2$VPO$_4$F in order to determine the ion hopping rates over a variable temperature range. This was the first application of selective inversion NMR methods to quantify ion mobility timescales in paramagnetic solid-state materials. It has subsequently expanded the NMR tools available to study ion mobility timescales in this class of materials. The timescales measured were correlated to one of two possible pathways for ion hopping. However, due to similarities in internuclear distance, bottleneck area, and bond valence density, distinguishing between the equally favourable pathways was not possible.

While the $^6\text{Li}$ 1D EXSY method used in Chapter 6, was an excellent selective inversion method for determining the timescales and energy barriers in Li$_2$VPO$_4$F, it is limited to systems having only a single exchange process. This is due to the delay period ($\tau_1$) in the $90^\circ - \tau_1 - 90^\circ$ inversion step being dependent on the frequency difference between the two sites observed to exchange. In Chapter 7, the use of selective inversion methods was expanded from a two-site, single exchange system to the three-site, three exchange system by replacing the $90^\circ - \tau_1 - 90^\circ$ step of 1D EXSY with a selective shaped pulse. In the three-site material, Li$_2$VOPO$_4$, the A, B, and C resonances were observed to participate in AB, BC, and AC exchange first from $^7\text{Li}$ 2D EXSY measurements. $^6\text{Li}$ selective inversion measurements using shaped pulses ($^6\text{Li}$ 1D SP)
were used to quantify the hopping rates through a series of experiments over a variable temperature range. The exchange rate for each hopping pair was determined twice, where each site in an exchange pair was selectively inverted in separate experiments. For example, the rate of AB exchange was first determined from the inversion of A and then again from the inversion of B where the timescales were found to be within error of one another from each experiment over a variable temperature range. It was concluded that selective inversion measurements using shaped pulses is an accurate method for determining ion exchange rates in solid-state paramagnetic materials. This method therefore, becomes a powerful tool for elucidating the timescales and structural constrains for high capacity battery materials, which more than likely, have multiple crystallographic Li sites.

$^6$Li SP methods were then applied to quantify the ion hopping rates in the novel layered cathode material, Li$_3$V(PO$_4$)$_2$F$_2$. Here, six crystallographic sites were observed to participate in six different exchange processes from $^6$Li 2D EXSY measurements in previous studies$^3$ and this work. $^6$Li selective inversion of the A and C resonances (Li1 and Li4, respectively) gave ion hopping rates for three out of the six exchange pairs, over a variable temperature range. The CIFIT rate matrix used to fit the experimental data included variables for all six exchange processes, meaning the effect of the exchange rates arising from the unresolved pairs on the resolved exchange processes need to be considered. A series of fits were performed where the rates of ion hopping between unresolved pairs were held anywhere from 0 s$^{-1}$ to 300 s$^{-1}$ and the rates of the resolved pairs determined. It was shown that the ion hopping rates of the resolved pairs were not
altered outside the errors bounds given when the hopping rates of unresolved pairs were held at zero. The ion hopping rates in Li$_5$V(PO$_4$)$_2$F$_2$ were found to be on a similar timescale to those determined for Li$_2$VPO$_4$F, where bond valence density maps of the diffusion pathways correlated well to the measured ion dynamics. Our results show that the fluorophosphates have considerably slower timescales of ion mobility than the phosphates Li$_3$Fe$_2$(PO$_4$)$_3$, Li$_3$V$_2$(PO$_4$)$_3$\textsuperscript{2,4} The fluorophosphates have been introduced as a class of positive electrode materials that have higher redox potentials over their phosphate counterparts. This thesis has shown that the gains in redox potential come at the expense of fast ion mobility, meaning that any improvements to the power output of the battery through higher voltage may be lost due to slow charge/discharge rates.

These results showed that the anion plays a significant role the ion mobility timescales, and subsequently opens an avenue for future studies. Measurement of the ion mobility timescales in a larger number of Li intercalation materials using solid-state NMR methods will better reveal trends in ion mobility as they correlate to the properties of anion species. This includes study of the tavorite-based materials, LiFePO$_4$F and Li$_2$FePO$_4$F recently reported by Ramesh \textit{et al.}\textsuperscript{6} LiFePO$_4$F is isostructural with LiVPO$_4$F, meaning any information gained from NMR studies would compare well to those already studied in our group. Study of the ion mobility timescales in the silicate family of cathode materials, including Li$_2$FeSiO$_4$\textsuperscript{7} and Li$_2$MnSiO$_4$,\textsuperscript{8} would reveal whether a change in polyanion has a significant effect on the ion dynamics relative to those observed in the phosphates. Both $^6^7$Li 2D EXSY and $^6^7$Li 1D selective inversion methods over a variable temperature range are proposed for investigating the ion dynamics in these
frameworks. As this thesis and other works have shown, these methods prove to be very reliable for studying Li ion exchange processes between different crystallographic sites. However, for materials having only a single crystallographic site, methods to quantify the ion hopping timescales in are still needed. As stated previously, $^6\text{Li}$-$^7\text{Li}$ REDOR measurements should be investigated as a possible method for studying ion mobility in single site materials. These experiments will initially be carried out on systems where the ion mobility timescales are known. Materials such as Li$_2$VPO$_4$F or Li$_3$V$_2$(PO$_4$)$_3$, are proposed as they are well characterized from this thesis and previous works. Overall, development of this experimental method will allow for mobility timescales of single-site materials including favorite LiVPO$_4$F and olivine LiFePO$_4$, to be probed.

Despite the challenges posed by the strong paramagnetic influences of the transition metal centers, multinuclear NMR methods continue to be an effective tool for characterizing both the structural and ion mobility properties of solid-state Li intercalation compounds. This thesis focused on unraveling the structural details that give fast charge-discharge rates in Li ion cathode materials with either phosphate or fluorophosphate anion compositions, by measuring the ion mobility timescales in using solid state NMR methods. Information of this type will assist materials development in bringing cost-effective and environmentally benign cathode materials to battery applications.
9.2 References


