Investigation of Material Composite Li$_3$V$_2$(PO$_4$)$_3$ with LiMn$_{2-x}$Ni$_x$O$_4$ for Li-ion Batteries

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By

Keeve Gurkin

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Investigation of Material Composite Li$_3$V$_2$(PO$_4$)$_3$ with LiMn$_{2-x}$Ni$_x$O$_4$ for Li-ion Batteries

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ABSTRACT OF THESIS
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ABSTRACT

Today’s mobile devices such as laptop computers, media players, cameras, and even cutting edge automobiles, require a new, more robust grade of Li-ion batteries as a power source. Much research is being done on producing high energy density battery materials, while trying to maintain safety and industrial feasibility.

Currently, most commercial Li-ion batteries use either LiCoO$_2$ based, or LiMnO$_2$ based materials. These materials are industry standard, but display short lifetime, low energy density, and possible safety hazards. Novel materials such as LiMn$_{2-x}$Ni$_x$O$_4$ and Li$_3$V$_2$(PO$_4$)$_3$ have been proposed as possible candidates for a commercialized battery material. LiMn$_{2-x}$Ni$_x$O$_4$ uses manganese, which is of low toxicity and it is abundant as a resource. This material is modified by nickel doping from LiMn$_2$O$_4$, to improve on its electrical conductivity and capacity. Li$_3$V$_2$(PO$_4$)$_3$ is another promising cathode material, contributing very high theoretical capacity of 197 mAh/g. Li$_3$V$_2$(PO$_4$)$_3$ is modified from LiV$_2$O$_5$, which exhibits a low voltage profile and short lifespan. The addition of the phosphate group increases the safety of the material substantially, while still allowing the Li-ions to be highly mobile.

Mechanically mixing two different cathode materials to form a composite, to be used in a battery is explored. Combined Li$_3$V$_2$(PO$_4$)$_3$ and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ has promise as a cathode composite material, demonstrating a capacity of 126 mAh/g, with little capacity fading over time. Cycle profile shows expected Li-ions being extracted and reinserted in a common regime. Further research varying ratios, compositions, and methods can be explored. Composite cathode materials hold promise in that they can offer safe, affordable, high power solutions for consumer demands.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>3</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>4</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>6</td>
</tr>
<tr>
<td>Terms</td>
<td>7</td>
</tr>
<tr>
<td>List of Figures and Tables</td>
<td>8</td>
</tr>
<tr>
<td>Chapter 1</td>
<td></td>
</tr>
<tr>
<td>1.1 - Introduction to Li-ion battery cathode materials</td>
<td>10</td>
</tr>
<tr>
<td>1.2 - Li$_3$V$_2$(PO$_4$)$_3$ Theory</td>
<td>11</td>
</tr>
<tr>
<td>1.3 - LiMn$_{2-x}$Ni$_x$O$_4$ theory</td>
<td>13</td>
</tr>
<tr>
<td>Chapter 2</td>
<td></td>
</tr>
<tr>
<td>2.1 - Experimental</td>
<td>16</td>
</tr>
<tr>
<td>2.2 - Results and Discussion</td>
<td>18</td>
</tr>
<tr>
<td>2.3 - Conclusion</td>
<td>22</td>
</tr>
<tr>
<td>2.4 - Future Work</td>
<td>23</td>
</tr>
<tr>
<td>2.5 - Tables and Figures w/ Captions</td>
<td></td>
</tr>
<tr>
<td>References</td>
<td>48</td>
</tr>
</tbody>
</table>
TERMS

XRD – X-ray Diffractometer

SEM – Scanning Electron Microscope

Li-ion – Lithium ion

mAh/g – Milliamp hour per gram

mV – Millivolt

PEG – Polyethyleneglycol

EC – Ethlyene carbonate

DMC – Dimethyl carbonate

SEI – Solid electrolye interface

NMP – N-Methyl-2-pyrrolidone

EDS – Energy dispersive X-ray Spectroscopy

CV – Cyclcicvoltamogram

NASICON – Sodium super ionic conductor (Na$_3$Zr$_2$Si$_2$PO$_{12}$)

OCP – Open circuit potential

C-rate: example: 1C means that a 1000mAh battery would provide 1000mA for one hour
LIST OF TABLES AND FIGURES

**Figure 2.1:** XRD diffraction patterns for (a) \( x \) 3, starting phase; (b) \( x \) 2.5, deinsertion; (c) \( x \) 2, deinsertion; (d) \( x \) 1, deinsertion; (e) \( x \) 0; (f) \( x \) 1, reinsertion; (g) \( x \) 2, reinsertion; (h) \( x \) 3, reinsertion. Inset: Galvanostatic intermittent titration (GITT) plot, reproduced from ref 13, for Li extraction from Li3V2(PO4)3 illustrating the location of the single phase compositions Li\(_x\)V\(_2\)(PO\(_4\))\(_3\) \((x)\) 3.0 \(\pm\) 0.0, see text), followed by Li insertion. Note the solid solution behavior present between \( x \) 0 and \( x \) 2 even under “equilibrium” conditions.

**Figure 2.2:** (a) Monoclinic Li\(_3\)V\(_2\)(PO\(_4\))\(_3\): (i) crystal structure. V1(V\(_{3+}\))-O and V2(V\(_{3+}\))-O octahedra are shown in gray, and P-O tetrahedra are shown in yellow. Li1, Li2, and Li3 atoms are shown in magenta, green, and orange, respectively. (ii) Li coordination environments.

**Figure 2.3:** Galvanostat cycle profile of synthesized Li\(_3\)V\(_2\)(PO\(_4\))\(_3\). Current set at 1.216x10\(^{-4}\)A, potential window 3.0-4.7V, at C/5. OCP measured at 3.10V

**Figure 2.4:** Differential capacity curves for Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) at C/20 discharge rate.

**Figure 2.5:** Rigaku D-Max 2200 X-ray Diffraction analysis of Li\(_3\)V\(_2\)(PO\(_4\))\(_3\), both lithiated and delithiated.

**Figure 2.6:** 0908#36 Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) Crystal Structure, lithiated.

**Figure 2.7:** 0908#36 Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) Crystal Structure, completely delithiated.

**Figure 2.8:** Galvanostat CV overlay at C/10, showing first, second, and third lithium extractions for Li\(_3\)V\(_2\)(PO\(_4\))\(_3\).

**Figure 2.9:** Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) Cycled at different rates: C/20 C/5 C/

**Figure 2.10:** SEM image of Li\(_3\)V\(_2\)(PO\(_4\))\(_3\).

**Figure 2.11:** SEM image of Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) close up.

**Figure 2.12:** EDS analysis of Li\(_3\)V\(_2\)(PO\(_4\))\(_3\).

**Figure 2.13:** Galvanostat cycle profile of synthesized LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\). Current set at 7.056x10\(^{-5}\)A, potential window 3.0-4.98V, at C/20. OCP measured at 3.20V.

**Figure 2.14:** Differential capacitance of LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\) zoomed in at 4V region.

**Figure 2.15:** XRD spectra of synthesized LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\).

**Figure 2.16:** SEM image of synthesized LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\).
**Figure 2.17**: EDS analysis of LiMn$_{1.5}$Ni$_{0.5}$O$_4$.

**Figure 2.18**: Preliminary testing of composite material using simple primitive cubic type LiMn$_{1.5}$Ni$_{0.5}$O$_4$.

**Figure 2.19**: Galvanostat cycling of composite material. Current set at $8.64 \times 10^{-5}$ A, potential window 3.0-4.98 V, at C/20. OCP measured at 3.06 V.

**Figure 2.20**: Differential capacitance of composite material.

**Figure 2.21**: XRD analysis of composite material.

**Figure 2.22**: SEM image of composite material.

**Figure 2.23**: EDS analysis of composite material.
CHAPTER 1

1.1 Introduction to Li-ion battery cathode materials

With the increased power demands for mobile devices such as cell phones, laptop computers, and media players, along with hybrid and/or full electric cars, lithium ion batteries have become a major concern for consumers around the world. Trying to find novel materials for better batteries is paramount. Conservative and expensive LiCoO$_2$ based materials are being challenged by alternative materials such as LiFePO$_4$, LiNiPO$_4$, LiMnPO$_4$, LiCoPO$_4$, LiFe$_2$(PO$_4$)$_3$, and various other lithium metal phosphates are being used as positive electrode materials. They present highly reversible capacity, operative redox potentials and high safety because of limited O$_2$ liberation due to phosphate scaffolding, although they exhibit poor electrical transport resulting from low ionic and electronic conductivities. Poor electronic conductivity can be combated by alien metal doping.

However, vanadium has been gaining interest because of its tunable oxidation state when included in different compounds. LiV$_2$O$_5$ (lithium vanadium pentoxide) has been studied as a possible cathode material. It has high theoretical capacity of 320mAh/g as reported by Jiang et al.$^4$ One reason this material is not feasible in lower power portable devices that it has a short life span and low voltage limits. Introducing both vanadium and phosphate into a battery electrode material has been beneficial, providing higher electrical conductivity and safety, respectively. Li$_3$V$_2$(PO$_4$)$_3$ (lithium vanadium phosphate) is being explored as an alternative to LiV$_2$O$_5$ due to its high theoretical capacity of 197 mAh/g, high voltage plateaus and phosphate groups acting as a safety mechanism. $^1$ This material has shown to extract and insert, 3 Li-ions per unit cell, upon
discharge and charge, respectively, making it a promising battery cathode material, although 
Li$_3$V$_2$(PO$_4$)$_3$ shows only moderate electrical conductivity.

In addition, studies have been carried out on non-phosphate electrode materials, such as 
the common spinel LiMn$_2$O$_4$. This material shows promise as manganese exhibits low toxicity and is relatively abundant as a viable resource. This spinel offers a good balance of safety and performance, but could be improved because of its poor cycling characteristics at elevated temperatures. Investigations into alien metal doping are being done, adding metals such as Cu, Ni, Zr, Co and so on. LiMn$_{2-x}$Ni$_x$O$_4$ has demonstrated good capacity at 120 mAh/g, good cycling, and robust performance over time.

Until recently, only a single type of material had been used as electrode material in use with batteries. In 2009, Zheng et al combined LiFePO$_4$ with Li$_3$V$_2$(PO$_4$)$_3$ and obtained 139.1 mAh/g at 0.1 C, 135.5 mAh/g at 1 C, and 116 mAh/g at 3C after 30 cycles.$^{13}$ Combining LiMn$_{2-x}$Ni$_x$O$_4$ with Li$_3$V$_2$(PO$_4$)$_3$ as a composite material provides an alternate way to produce the best benefits of both materials in one hybrid material. Since the voltage range for both materials are similar, it can be assumed that there will be no major obstacle to the composite performing admirably. The addition of the LiMn$_{2-x}$Ni$_x$O$_4$ would improve the electrical and ionic conductivity of its vanadium counterpart, and the phosphate groups from the Li$_3$V$_2$(PO$_4$)$_3$ would provide the added safety, as well as the vanadium’s high capacity factor.

1.2 Li$_3$V$_2$(PO$_4$)$_3$ Theory

Monoclinic phase Li$_3$V$_2$(PO$_4$)$_3$ has a first charge between 3.61V and 3.68V which corresponds to an ordered Li phase of intermediate composition. The second step between 3.68V and 4.1V comes from the removal of Li from the tetrahedral sites of the P2$_1$/n space group, with the final step between 4.1V and 4.5V, due to the change of the V$^{3+/4+}$ redox couple to V$^{4+/5+}$. $^5$
This three Li-ion cycling in the vanadium phosphate material, results very high energy density at both slow and fast rates. Li$_3$V$_2$(PO$_4$)$_3$ materials feature theoretical capacities of 197 mAh/g at discharge volumes 500mV higher than that of LiFePO$_4$. Vanadium’s variety of stable oxidation states makes it a unique material for this application. This feature aids in avoiding phase degradation during battery charge/discharge cycling, as lithium transport needs a stable redox couple within the crystal. Also the multiple stable valence states allow for new synthetic routes to be explored.

Two phase transitions display compositional changes during the redox process that denote the electrochemical lithium extraction and insertion in the material. Li$_3$V$_2$(PO$_4$)$_3$ comes in two varieties; a stable monoclinic phase and a rhombohedral or NASICON only accessible through ion-exchange of the corresponding sodium phase. The two phases exhibit different voltage profiles due to their alternate configurations. The NASICON phase displays one plateau ensuing from a two phase transition between Li$_3$V$_2$(PO$_4$)$_3$ and Li$_1$V$_2$(PO$_4$)$_3$. Two Li are being extracted from a single tetrahedrally coordinated site, shifting the remaining Li to another site. However, in the monoclinic phase, all three Li are mobile and show a complex series of two-phase transitions while being extracted, succeeded by a solid solution phase upon Li insertion. Solid solution behavior is analogous to a solute in a liquid solvent, although in this case, the solvent is the crystal lattice of the Li$_3$V$_2$(PO$_4$)$_3$ material and the solute is the lithium. Changes in the Li$_3$V$_2$(PO$_4$)$_3$ hysteresis occurs during extraction and insertion of Li, because of the disruption of vanadium charge ordering in the fully delithiated phase.

Monoclinic phase Li$_3$V$_2$(PO$_4$)$_3$ is slightly more dense than its fast ion-conducting NASICON counterpart, and it is reasonable to assume that this property remains the same when cycled. Electronic transport is limited, as with most metal phosphate materials due to the
(PO₄)³⁻ groups. These groups raise the redox potentials to practical values but at the detrimental outcome of localizing d-bands. Comparing the conductivity of Li₃V₂(PO₄)₃ at 2 x 10⁻⁸ S/cm, to that of other metal phosphates such as LiFePO₄ at the same order of magnitude, shows no great deviation in typical conductivity for materials of the sort. However, fully reversible extraction of Li can occur at fast rates by nucleation and restricted growth of small Li₃V₂(PO₄)₃ crystallites in a conductive carbon matrix.¹²

The third Li that is extracted is also the most kinetically hindered. Once all the Li-ions are extracted, there is a slight loss of crystallinity, as seen in Figure 2.¹² Figure 2.2 shows the structure of V₂(PO₄)₃ framework with the three Li-ions configured in quasi-tetrahedral interstitial sites within the crystal lattice. Two vanadium sites, V(1) and V(2) represent almost identical slightly distorted VO₆ octahedra with average V-O bond lengths of 2.003 and 2.006 Å. Li NMR data from Yin, S.-C. et al, give good evidence that V³+/V⁴⁺ ordering, and the existence of monoclinic symmetry.¹²

Ordered valance states in Li₃V₂(PO₄)₃ demonstrates that the electrons are pinned on both long and short time scales. “Each plateau in the V versus x curve corresponds to a two-phase transition involving the reorganization of electrons and Li ions within the lattice.”¹² Yin et al suggests that li-site ordering and electron ordering are inextricably coupled, resulting in paired electron/ion transport in the deinsertion regime.¹²

1.3 LiMn₂ₓNiₓO₄ theory

Sony Corporation had commercialized LiCoO₂ as a cathodic material for the first generation of lithium rechargeable batteries for their devices.² Due to its high cost, it is not feasible to use in large scale devices such as battery operated vehicles. Materials have been investigated to compete with Sony’s flagship battery material, while trying to maintain safety,
capacity and strong power density. LiMn$_2$O$_4$ has been investigated as a secondary battery cathodic material, because of Mn’s low cost, low toxicity, structural stability, and facile synthesis. However, LiMn$_2$O$_4$ alone has limited performance exhibiting capacity loss during electrochemical charge-discharge at temperatures around 50-80°C. Recently, research groups have been doping this LiMn$_2$O$_4$ spinel with metals in an effort to improve its usability in large scale devices. Along with Cr, Zr, Cu, and Co, Ni has been looked at as a possible doping agent to improve the stand alone spinel. One composition of main interest is the LiMn$_{2-x}$Ni$_x$O$_4$ spinel. This material has a high discharge capacity and a dominant plateau at 4.7V. It has shown to have a capacity of around 120mAh/g, but shows limited stability upon cycling. In the charge-discharge process, lithium ions are reversibly inserted and extracted from the Li$_x$Mn$_{0.5}$Ni$_{1.5}$O$_4$ in two composition ranges of $0 \leq x \leq 1$, $1 \leq x \leq 2$ over two potential plateaus near 4.7V and 2.7V respectively. Around 4.7V, a lithium ion is extracted from and inserted into 8$a$ tetrahedral sites and the electrode cycles well with Ni$^{2+}$/Ni$^{4+}$ redox couples. At around 2.7V, lithium ions are inserted into the 16$c$ octahedral sites in a two-phase reaction resulting in the reduction state from Mn$^{4+}$ to Mn$^{3+}$. Important to note, is S.H. Park et al’ s work on distinguishing via in situ XRD analysis that the primitive simple cubic phase structure of the LiMn$_{0.5}$Ni$_{1.5}$O$_4$ material performed slightly better than the cubic face centered structure. Upon discharge, both structures changed to a tetragonal phase, but only the primitive simple cubic was able to form back upon subsequent charge. This indicates that the primitive simple cubic structured material is better suited for reversible charge-discharge uses over the cubic face centered phase. In addition, the primitive simple cubic phase material exhibited a slightly higher voltage plateau and its voltage gap was narrower. S.H. Park et al speculate that the Ni separated from the Mn site so that Ni-O
surroundings could be independent from the Mn$^{4+}$/Mn$^{3+}$ redox pair for primitive simple cubic symmetry.\textsuperscript{9}

Nickel content in the spinel has a direct effect on performance of the spinel material, and therefor must be carefully tuned to obtain optimal usability. Heavily Ni-substituted spinels have shown to have poor performance, specifically around 3V. X-ray data has shown that the oxidation state of the Ni ions depend on the overall Ni concentration in the material. More specifically in the LiMn$_{2-x}$Ni$_x$O$_4$ type spinel, the replacement of the Mn with Ni contributes to shrinkage of the unit cell volume.\textsuperscript{7} A lattice contraction on Ni substitution such as this suggests that the lattice parameter of the spinel lithium manganate is mainly reliant on the average oxidation state of manganese, which is improved by the Ni substitution. In their study, Dae Hoon Park et al, conclude that that the poor performance attributed to heavy Ni doping in the 3V region is due to low structural stability of the NiO$_6$ octahedra upon lithium intercalation.\textsuperscript{7}
CHAPTER 2

2.1 Experimental

2.1.1 Materials and preparation

2.1.1.1 Li$_3$V$_2$(PO$_4$)$_3$ synthesis

Using rheological phase reaction to synthesize Li$_3$V$_2$(PO$_4$)$_3$, adapted from Chang, et al., Li$_2$CO$_3$, V$_2$O$_5$(99.6%), and NH$_4$H$_2$PO$_4$ were ground and ball milled in the Spex 8000 mill for 12 hours with 5ml acetone to achieve stoichiometric Li$_3$V$_2$(PO$_4$)$_3$ (accounting for 0.3g loss in mill). PEG(300) and water were added to obtain rheological consistency. The mixture was transferred to a Teflon coated vessel to sit at 100°C under vacuum for 12 hours. The substance was then pelletized using a press with stainless steel cast. Pellets were cast at 5000psi to give dimensions approximately 0.95cm in diameter and 0.16cm thick. The pellets were then sintered at 350°C for 5 hours, and then ramped up to 900°C for 12 hours under H$_2$/argon flow conditions. After cool down, the pellets were ground to a fine powder for analysis.

2.1.1.2 LiMn$_{2-x}$Ni$_x$O$_4$ synthesis

Ni(CH$_3$COO)$_2$·4H$_2$O, Li(CH$_3$COO)$_2$·4H$_2$O, and Mn(CH$_3$COO)$_2$·4H$_2$O were mixed drop wise to achieve stoichiometric LiMn$_{1.5}$Ni$_{0.5}$O$_4$. Ammonium hydroxide was added to maintain basic conditions until precipitate/gel formed. The solution was heated at 80°C until the solvents had evaporated and left a yellow solid. The material was ground down and pelletized using a press and a stainless steel vessel and cast at 5000psi to give dimensions approximately 0.95cm in
diameter and 0.16cm thick. The material was sintered at 500°C in air for 12 hours, and then 850°C in air for 12 hours. The resulting material was then ground and prepared for analysis.

2.1.2 Characterization and Electrochemical measurements

2.1.2.1 Electrochemical Preparation

Both LiMn$_{1.5}$Ni$_{0.5}$O$_4$ and Li$_3$V$_2$(PO$_4$)$_3$, separately, were prepared by mixing 77% active material with 20% Super-P conductive carbon (TimCal Carbon and Graphite, Belgium), and 3% PVDF. The mixture was ground in the Spex 8000 mill for 3 hours. Next, 7 drops of NMP were added to achieve ink consistency. Ink was painted evenly over a 1 x 1 cm square a piece of heavy duty Reynolds Wrap aluminum foil. The painted foil was placed in a vacuum oven overnight at 80°C to dry. Coin size holes were punched out to fit into the T-cell.

Composite was milled with 77% active ingredient as comprised of 1:3, Li$_3$V$_2$(PO$_4$)$_3$ to LiMn$_{1.5}$Ni$_{0.5}$O$_4$.

2.1.2.2 T-cell

Polypropylene Swagelok Li-half cells (T-cells) with stainless steel current collectors were used with Whatman glass microfiber paper separator and 1M LiPF$_6$ in 1:1.2 EC/DMC in testing. Ethylene carbonate (Sigma) and Purolyte® dimethyl carbonate (Ferro) were mixed in 1:1.2 ratio. Sigma high purity lithium foil was used as a reference.

2.1.2.3 Electrochemical Analysis

Arbin Instruments cycler Galvanostatic was used for charge/discharge experiments for the following materials:
For Li₃V₂(PO₄)₃, the active mass of the sample was calculated at 0.00304g. The current was set at 1.216x10⁻⁴A, with a potential window from 3.0V to 4.7V, at a rate of C/5. OCP was measured at 3.10V.

For LiMn₁.₅Ni₀.₅O₄, the active mass of the sample was calculated at 0.01176g. The current was set at 7.056x10⁻⁵A, with a potential window from 3.0V to 4.98V, at a rate of C/20. OCP was measured at 3.20V.

For the composite, the active mass of the sample was calculated at 0.00864g. The current was set at 8.64x10⁻⁵A, with a potential window from 3.0V to 4.98V, at a rate of C/20. OCP was measured at 3.06V.

2.1.2.4 XRD

X-ray powder diffraction measurements were performed on crystalline sample powders. A Rigaku D-Max 2200 (Cu Kα₁,₂ radiation) was used.

2.1.2.5 SEM

Images were taken on a Hitachi Field Emission Scanning Electron Microscope S-4800. Scans were taken at 5.0kV, for 90 seconds. For EDS, 20.0kV at 15mm sample distance was used. Peaks for carbon and aluminum appear as result of the aluminum tray and carbon mounting pad.

2.2 Results and discussion

2.2.1 Li₃V₂(PO₄)₃

Figure 2.3 represents a charge/discharge experiment carried out on Li₃V₂(PO₄)₃ material using the experimental parameters described in section 2.1.1.1. Upon first charge, a capacity of 171 mAh/g was achieved. The first discharge capacity obtained was 131 mAh/g. After two more subsequent charges and discharges, there was only a minor loss of capacity at around 5 mAh/g.
This was most likely due to uneven casting of the cathode ink on the aluminum substrate. Figure 2.4 demonstrates the voltages at where the Li-ions are being extracted from the material, and then reinserted into the lattice. At 3.5-3.6V and 3.6-3.7V, Li-ions from competing areas in the lattice are extracted. It important to note that this only represents one full Li-ion extraction, happening at two different locations, simultaneously. This is seen by the two close peaks at 3.5-3.6V and 3.6-3.7V. This reveals that in the monoclinic lattice structure of Li$_3$V$_2$(PO$_4$)$_3$, there are two sites that are very structurally similar, that release Li at voltages slightly offset from each other. Next is the extraction of a Li-ion at 4.0-4.1V, and the final Li-ion extraction at 4.4-4.6V. It is reasonable to assume that the reason for kinetic difficulty of removing the final lithium, lie in the reduced ionic/electronic conductivity of the fully extracted phase. The lithium extraction process occurs in a more ordered fashion than the re-insertion process. All lithium extractions and insertions occur in the two-phase scheme, except for the reinsertion of the two Li-ions at 4.3-3.7V, which is single phase. This single phase is seen in Figure 2.4 as a broadened peak. The two Li-ions reinserted into the lattice at this point are disordered, giving a single phase scheme. Because of the crystal lattice contraction after extraction, the kinetics of the reinsertion is hindered, and the voltage profile at 4.3V to 3.7V reflects observation. Upon re-insertion of the last Li-ion, the two-phase form returns, as seen by the typical peaks comparable to two-phase extraction. These results are expected and comparable to results listed in literature.

Figure 2.5 shows XRD analysis of Li$_3$V$_2$(PO$_4$)$_3$ shows comparable structure to literature results, with no major anomalies to be reported. XRD analysis of the delithiated material shows some loss in crystallinity upon full lithium extraction, which is expected. XRD measurements were only taken before and after to confirm the process of delithiation, as crystallinity changes over all phases have been reported accurately by Yin et al. There are three peaks at 38, 44, and
identified as aluminum. These peaks appeared as a result of the aluminum substrate being mixed in because it had been accidentally scratched off when the material was removed from the foil for XRD analysis.

As shown by Figure 2.6 and Figure 2.7, the crystal structure of Li$_3$V$_2$(PO$_4$)$_3$ suffers in a reduction of cell volume by about 10Å. The loss of lithium in the crystal lattice contributes to its formation of a single-phase structure.

Figure 2.8 confirms the notion of order and disorder in extraction and insertion of Li-ion into the crystal lattice. Cycling only one Li-ion, order can be seen to be fairly apparent, as indicated by sharp peaks at the typical voltage range for one Li-ion extraction and insertion at 3.5-3.6V and 3.6-3.7V. When cycling two Li-ion, order is still maintained as indicated by the sharp peaks at the typical voltage range at 4.0-4.1V. However, after the second Li-ion has been extracted, there is a shift to the single phase, and the final Li-ion is extracted, as seen by a broad peak compared to the previous peaks. Upon insertion of the first two Li-ions following the extraction of the third, the crystal lattice is in single phase, contributing to the disorder in the reinsertion scheme.

Figure 2.9 shows a trend demonstrating performance at different discharge rates. At C/20, the discharge capacity is 131 mAh/g. Discharging faster, at C/5 and C/1, there is a capacity loss of about 20 mAh/g. This is most likely due to the carbon in the electrode material. SEI film can crack in high temperature situations resulting from high rate discharging, and cause detrimental effects, including capacity loss.

Figure 2.10 shows an SEM image of the Li$_3$V$_2$(PO$_4$)$_3$ synthesized in rheological phase. Material forms in varying shapes and sizes 1 to 10μm. Upon close inspection in Figure 2.11, it appears that there are crystals or dendrites of some type that has formed on the bulk material.
These dendrites could possibly be lithium, but it is unclear, and further analysis is required. This could be a byproduct of the rheological phase synthesis, in where crystal growth occurred after water was added to the mixture and left to sit under vacuum. Figure 2.12, EDS analysis of the sample verifies that the elemental composition is that of typical $\text{Li}_3\text{V}_2\text{(PO}_4\text{)}_3$ with no impurities. Most prominent is the phosphate group in the material, which is expected.

### 2.2.2 LiMn$_{1.5}$Ni$_{0.5}$O$_4$

Figure 2.13 shows high very high first charge capacity of synthesized LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinel at 222 mAh/g. The charging capacity fades to 181 mAh/g upon second charge, then to 170 mAh/g on the third charge. First discharge capacity is measured at 135 mAh/g and subsequent discharge capacities remain in that area without major deviation. For this particular sample, 30mAh/g increase in capacity was observed after pressing the electrode to 5000psi for 15 minutes. LiMn$_{1.5}$Ni$_{0.5}$O$_4$ has on plateau at 2.7V (not shown) and has two plateaus at 4.7V based on the redox couple of Ni$^{2+/4+}$. In the analysis of this sample, it was found that there is a minor plateau at 4.0V due to Mn$^{3+/4+}$ redox couples, shown in Figure 2.14. Based on the report by Park, S. H., et al, this indicates that the sample is of face centered symmetry.

Figure 2.15, X-ray diffraction results indicate that the synthesized LiMn$_{1.5}$Ni$_{0.5}$O$_4$ is in fact of face centered symmetry comparable to XRD spectra reported by Park, S. H., et al. The lattice contracts upon Ni insertion, even though Ni has a larger radius, dependent on the oxidation of Mn. When the Ni count increases, the averages oxidation state of Mn also increases, the reinforcing the Mn-O bonds.

SEM imaging of the spinel, Figure 2.16, shows particle size ranging from 50 to 200nm, usually presented in a geometric spherical shape. Texture of the particle is relatively smooth, with clusters forming regularly. Typical topography given the nature of the material. Figure 2.17
shows EDS profile of LiMn$_{1.5}$Ni$_{0.5}$O$_4$, confirming low levels of Ni and higher levels of Mn in the spinel.

2.2.3 Composite

It has been proposed that mechanically mixing two different types of cathode materials into one electrode, might produce beneficial effects, taking into account each materials voltage plateaus, kinetics, etc. As seen in **Error! Reference source not found.**, the addition of a high-voltage LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinel material to the Li$_3$V$_2$(PO$_4$)$_3$ cathode has extended the voltage range of the original phosphate material. The Li$_3$V$_2$(PO$_4$)$_3$ cathode material in Figure 2.18 was of primitive simple cubic symmetry and performed typically and moderately. However, Figure 2.19, the Li$_3$V$_2$(PO$_4$)$_3$ cathode material used in the composite was of face centered symmetry. In this case, the composite with the more undesirable face centered symmetry had higher charge/discharge capacity than the composite with the more desirable primitive simple cubic symmetry. Initial charge capacity upon first charge was 175 mAh/g, with a first discharge capacity of 126 mAh/g. Subsequent charging capacities faded by 30 and then 10 mAh/g, respectively. However, discharge capacity only faded by 10 mAh/g over three charges.

Figure 2.20 shows differential capacitance to more clearly see where the Li-ions are being extracted. Seen at 3.60 and 3.67V is the typical first Li-ion extraction from the Li$_3$V$_2$(PO$_4$)$_3$ material. At 4.08V there is the second Li-ion extraction from Li$_3$V$_2$(PO$_4$)$_3$. There is evidence of the LiMn$_{1.5}$Ni$_{0.5}$O$_4$ face centered symmetry by the broadening near the base of the peak at 4.0V. At 4.54V there is the third Li-ion extraction peak in Li$_3$V$_2$(PO$_4$)$_3$, and at 4.73V, the Li-ion extraction peak of LiMn$_{1.5}$Ni$_{0.5}$O$_4$. Upon reinsertion, there is peak seen at 4.61V, denoting a Li-ion being reinserted into LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinel. Following that reinsertion, there is a peak seen at 3.91V, and a pair of peaks at 3.57V and 3.50V. These are not as sharp and clean as
typically seen in pure Li$_3$V$_2$(PO$_4$)$_3$. It can be assumed that the addition of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ to the composite hinders the return to single phase at this point, normally seen in pure Li$_3$V$_2$(PO$_4$)$_3$.

Figure 2.21 X-ray diffraction analysis shows good crystallinity and evidence of the composite being mixed well to give good uniform distribution throughout the powder. XRD shows an expected overlay of similar peaks from both LiMn$_{1.5}$Ni$_{0.5}$O$_4$ and Li$_3$V$_2$(PO$_4$)$_3$.

A SEM image of the composite, Figure 2.22, shows bulk material. It appears that the small spherical pieces of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ were deposited on the larger Li$_3$V$_2$(PO$_4$)$_3$ material. There is no evidence of the dendrites in the composite material, however, the LiMn$_{1.5}$Ni$_{0.5}$O$_4$ could be on top of these dendrites, but this is unlikely to be the case throughout the entire bulk of the composite. Figure 2.23, EDS analysis confirms the presence of elements from both Li$_3$V$_2$(PO$_4$)$_3$ and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ in the quantities expected.

2.3 Conclusion

Composite battery Li-ion cathode materials are only now being explored as viable options, and show much promise in producing high capacity with safety. Mechanically mixing Li$_3$V$_2$(PO$_4$)$_3$ with LiMn$_{1.5}$Ni$_{0.5}$O$_4$ to form a composite, produced a cathode material with a discharge of 126 mAh/g, which is modest. The composite material showed promise, performing slightly better than stand alone Li$_3$V$_2$(PO$_4$)$_3$ and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ with the capacity fading being less pronounced. There was no major defect in the operation of the composite cathode operation under normal conditions, proving that composite materials such as these, are viable options for industry. Interesting to note, the less desirable face centered symmetry LiMn$_{1.5}$Ni$_{0.5}$O$_4$ enhanced the performance of the composite, compared to the more favored primitive cubic symmetry analog. This could be due to many things, including the effects of many redox couples interacting at once, such as Ni$^{2+/3+}$, Mn$^{3+/4+}$, V$^{2+/3+}$, interaction between the phosphate scaffold
and the Ni-O, Mn-O bonds, etc. More crystallographic structure studies need to be performed. In addition, there were no ill effects of having two cathode materials with different lithium extraction and insertion sites operating in conjunction with each other. Exploring composites further would be prudent at this point, considering the increasing variety of Li-ion cathode materials being researched and produced. Perhaps tunable capabilities will be a product of composite mixing, allowing for easily specialized materials custom tailored for customers.

2.4 Future work

Optimization of the materials and processing is needed to try to reach the highest possible specific capacity available. Large batch LiMn$_{2-x}$Ni$_x$O$_4$ should be prepared in both face centered and primitive cubic symmetries. Li$_3$V$_2$(PO$_4$)$_3$ should be prepared and mixed mechanically with the two types of LiMn$_{2-x}$Ni$_x$O$_4$. Comparative analysis, via galvanostat and XRD should be carried out on different stoichiometric mixtures of composites. XAFS could be used to more closely examine the crystallographic structure variations between all the composites. Closer studies such as Electrochemical Impedance Spectroscopy or other internal resistance and impedance measuring techniques could be employed to see to what extent the LiMn$_{2-x}$Ni$_x$O$_4$ enhances the conductivity of the Li$_3$V$_2$(PO$_4$)$_3$. Also long term cycling tests can be run to determine if the phosphate scaffold groups contribute their safety enhancement to the overall composite like they do to the native Li$_3$V$_2$(PO$_4$)$_3$.

Other composites could be explored using the previously mentioned phosphate based cathode materials such as LiFePO$_4$, LiNiPO$_4$, LiMnP0$_4$, LiCoPO$_4$, LiFe$_2$(PO$_4$)$_3$ mixed with non-phosphate cathode materials.
2.5 Tables and Figures w/ Captions

Figure 2.1: XRD diffraction patterns for (a) $x = 3$, starting phase; (b) $x = 2.5$, deinsertion; (c) $x = 2$, deinsertion; (d) $x = 1$, deinsertion; (e) $x = 0$; (f) $x = 1$, reinsertion; (g) $x = 2$, reinsertion; (h) $x = 3$, reinsertion. Inset: Galvanostatic intermittent titration (GITT) plot, reproduced from ref 13, for Li extraction from Li$_3$V$_2$(PO$_4$)$_3$ illustrating the location of the single phase compositions Li$_x$V$_2$(PO$_4$)$_3$ ($x = 3.0$ f $0.0$, see text), followed by Li insertion. Note the solid solution behavior present between $x = 0$ and $x = 2$ even under “equilibrium” conditions.
**Figure 2.2:** (a) Monoclinic Li$_3$V$_2$(PO$_4$)$_3$: (i) crystal structure. V1(V$^{3+}$)-O and V2(V$^{3+}$)-O octahedra are shown in gray, and P-O tetrahedra are shown in yellow. Li1, Li2, and Li3 atoms are shown in magenta, green, and orange, respectively. (ii) Li coordination environments.
Figure 2.3: Galvanostat cycle profile of synthesized Li₃V₂(PO₄)₃. Current set at 1.216x10⁻⁴A, potential window 3.0-4.7V, at C/5. OCP measured at 3.10V
Figure 2.4: Differential capacity curves for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at C/20 discharge rate.
Figure 2.5: Rigaku D-Max 2200 X-ray Diffraction analysis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, both lithiated and delithiated.
Monoclinic Structure

**Space group:** P 21/n

**Cell volume:** 839.79 Å³

**Cell parameters:**

- **a:** 8.4094 Å
- **b:** 8.5432 Å
- **c:** 11.690 Å

**Angles:**

- **α:** 90.000°
- **β:** 90.900°
- **γ:** 90.000°

**Figure 2.6:** 0908#36 Li₃V₂(PO₄)₃ Crystal Structure, Lithiated.
Monoclinic Structure

Space group: P 21/n

Cell volume: 827.1 Å³

Cell parameters:

a: 8.4603 Å
b: 8.5153 Å
c: 11.482 Å

Angles:

α: 90.000°
β: 89.296°
γ: 90.000°

Figure 2.7: 0908#36 Li₃V₂(PO₄)₃ Crystal Structure, Completely Delithiated.
Figure 2.8: Galvanostat CV overlay at C/10, showing first, second, and third lithium extractions for Li$_3$V$_2$(PO$_4$)$_3$. 
Figure 2.9: $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Cycled at different rates: C/20 C/5 C/1
Figure 2.10: SEM image of Li$_3$V$_2$(PO$_4$)$_3$. 
Figure 2.11: SEM image of \( \text{Li}_3\text{V}_2(\text{PO}_4)_3 \) close up.
Figure 2.12: EDS analysis of Li$_3$V$_2$(PO$_4$)$_3$. 
Figure 2.13: Galvanostat cycle profile of synthesized LiMn$_{1.5}$Ni$_{0.5}$O$_4$. Current set at 7.056x10$^{-5}$ A, potential window 3.0-4.98V, at C/20. OCP measured at 3.20V.
Figure 2.14: Differential capacitance of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ zoomed in at 4V region.
Figure 2.15: XRD spectra of synthesized LiMn_{1.5}Ni_{0.5}O_{4}.
**Figure 2.16:** SEM image of synthesized LiMn$_{1.5}$Ni$_{0.5}$O$_4$. 
Figure 2.17: EDS analysis of LiMn$_{1.5}$Ni$_{0.5}$O$_4$
Figure 2.18: Preliminary testing of composite material using simple primitive cubic type LiMn$_{1.5}$Ni$_{0.5}$O$_4$. 
Figure 2.19: Galvanostat cycling of composite material. Current set at $8.64 \times 10^{-5}$ A, potential window 3.0-4.98 V, at C/20. OCP measured at 3.06 V.
**Figure 2.20:** Differential capacitance of composite material.
Figure 2.21: XRD analysis of composite material.
Figure 2.22: SEM image of composite material.
Figure 2.23: EDS analysis of composite material.
References


9. Park, S. H.; Oh, S. W.; Kang, S. H.; Belharouak, I.; Amine, K.; Sun, Y. K., Comparative study of different crystallographic structure of LiNi0.5Mn1.5O4-delta cathodes with wide operation voltage (2.0-5.0 V). *Electrochim Acta* **2007**, *52* (25), 7226-7230.

