Composition Control of Spinel Lithium Manganese Oxide for High Voltage, High Energy Lithium Ion Batteries

Hilary Eikhuemelo
Louisiana State University and Agricultural and Mechanical College, heikhu1@lsu.edu

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COMPOSITION CONTROL OF SPINEL LITHIUM MANGANESE OXIDE FOR HIGH VOLTAGE, HIGH ENERGY LITHIUM ION BATTERIES

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
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in

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by
Hilary A. Eikhuemelo
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To God be the glory
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ABSTRACT

In the quest for renewable source of energy, a remarkable step made was in the introduction of the battery system. The lithium ion battery was revolutionary in this regard particularly for its light weight and high energy density. There has been significant progress in the development of this battery system since the present form was introduced in the 1990s. There is currently a global dependence on the use of lithium ion battery in diverse applications such as in the electronics, communications and automobiles. Unfortunately, the energy obtainable from the lithium ion battery continuously falls behind the energy demand. This setback is mostly noticeable in the operating voltage of the battery. The low operating voltage has limited the use of the battery in high voltage applications such as electric vehicles in the automobile industry, payloads and launch vehicles in aerospace applications. Increasing the available discharge voltage per specific energy density is a key research area required to close this application gap. This thesis work contributes to closing this gap by controlling the composition, microstructure, particle size distribution and morphology of spinel lithium manganese oxide cathode materials. The results reported are such that high discharge voltage greater than traditional 4.7 V vs. Li/Li$^+$ is obtainable. Additionally, suggested routes to improving the voltage are enumerated.
CHAPTER 1: INTRODUCTION

1.1. Overview and Brief Historical Perspective of the Battery System

The global search for renewable source of energy has brought to bear new energy sources comprising primarily of wind, solar, geothermal and biomass. At first glance, it is easy to notice the common indices that connects these energy sources, particularly in the case of wind and solar. Their intermittent and stochastic availability which is dictated mostly by nature, creates a substantial availability gap. Effectively bridging this gap which also exists in traditional energy sources like fossil fuel, although in a different scale of reference, has been the drive for many researchers. An aspect of these research is to provide energy sources which is readily available, can be easily deployed (portable), environmentally benign, and reusable. The most remarkable achievement of these efforts was the introduction of the battery system.

The battery system was invented in 1800 by Alessandro Volta. As a transducer, the battery functions through the conversion of chemical energy to electrical energy. Since its invention, it has metamorphosed into two main types: the primary and secondary batteries. In the primary battery, the electrochemical conversion that occurs is irreversible while the contrast is the case with the secondary battery.

The lead-acid battery became the first rechargeable (secondary) battery developed by Gaston Planté in 1860. Following the development and commercialization of lead-acid battery, the alkaline battery was introduced by replacing the acid electrolyte with a potassium hydroxide (KOH) or sodium hydroxide (NaOH) leading to commercial batteries like nickel-cadmium, nickel-iron and silver-zinc. In 1980, nickel metal hydride battery was introduced to replace the nickel-cadmium battery in order to eliminate the environmentally harmful cadmium.

Further progress in battery development led to the commercial introduction of Lithium-ion battery (LiB) in 1991 by Sony in the form of lithium cobalt oxide (LiCoO₂). This introduction preceded by decades of research, was occasioned by knowledge of the theoretical capacity of lithium = 3,829 mAh/g, together with the realization that some metal compounds can undergo reversible and reductive intercalation electrochemical reaction with lithium. Since its introduction, the LiB has revolutionized the “portable” energy consumption market particularly the electronic industry. The automobile industry with hybrid electric vehicles and electric vehicles is the most recent consumer of the LiB. Stability and performance of these vehicles in terms of available battery power is still below expected range. As such improvement on the LiB is still a major subject in global research interest. The reversible electrochemical process and the primary elements of a typical battery cell will be discussed in the next section.
1.2. Operating Principle and Primary Components of LiB Cell

A typical LiB electrochemical cell is composed of the positive and negative electrodes also described as the cathode and anode material respectively. Between the cathode and anode is the electrolyte and separator, which provide separation between ionic (Li$^+$) and electronic (e$^-$) transport. While the anode is the main source of Li$^+$, the cathode serves as the Li$^+$ sink. The cell reactions of LiB involves intercalation of Li$^+$ in the anode and cathode material during the energy conversion process. This process includes diffusion of solvated Li$^+$ from the host electrode (cathode) and subsequent desolvation and insertion of Li$^+$ into vacant sites in the anode enabled through electrical charge. During the reverse process (discharge), Li$^+$ are intercalated into the host cathode material. The typical reaction scheme is:

$$\text{LiAnode} \rightarrow \text{Anode + e}^- + \text{Li}^+ \text{ (oxidation/charge half-cell)}$$
$$\text{Cathode +e}^- + \text{Li}^+ \rightarrow \text{LiCathode (reduction/discharge half-cell)}$$

The reduction and oxidation processes occurs when the voltage source is equal to or greater than the equilibrium potential difference ($\Delta E$) of half cells or when the Gibbs free energy $\Delta G < 0$. The electronic transport at the cathode during the discharge phase is then available for doing electrical work. This work can be subsequently converted to another form of energy.

To achieve adequate electronic transport, carbon black is typically added to the cathode material in order to enhance its conductivity. Additionally a polymer binder is also included to bind the composite of cathode material and carbon black. Commonly used binder is polyvinylidene fluoride (PVDF).

Selection of appropriate material composition for both cathode and anode is the subject of various LiB battery research efforts, since the intrinsic characteristics of these materials determine the resulting electrochemical performance of the battery. Accordingly certain material parameters are considered for LiB:

- Crystal structures that allow reversible insertion and extraction of Li$^+$, particularly in case of cathode material which is a major determinant of the energy density of the battery.
- Higher average voltage potential versus Li/Li$^+$ for selected insertion cathode material in order to increase the battery energy density: high free energy $\Delta G < 0$
- High Li$^+$ diffusion coefficient resulting in high rate of charge (delithiation) and discharge (lithiation).
- Stable material structure during the delithiation and lithiation process, and stability in high temperature environment.
- Environmentally benign materials.
Therefore, understanding the material properties and subsequently their electrochemical characteristics is a primary focus for battery researchers. Such efforts have generated the need to classify electrode materials.

1.3. **Classification of Lithium ion battery Cathode Materials**

Since the introduction of LiB with LiCoO$_2$ cathode, there have been efforts in enhancing the electrochemical performance of the battery electrode material, especially in terms of the discharge capacity, operating voltage, cyclic (rechargeability) performance, and stability of the crystal structure of electrode materials. In a similar manner, there have been efforts to classify these materials to reflect these electrochemical properties or microstructure.\textsuperscript{5-9} Classification according to molecular structure of electrode materials is briefly discussed:

1.3.1 **Layered Compounds**

Layered compounds contain oxygen anions in a closed-packed lattice with transition metal cations located in the octahedral sites. The general formula for layered cathode material is LiM(O\textsubscript{2}) (M=transition metals). The MO\textsubscript{2} slabs and Li layer are stacked alternatively.\textsuperscript{5-7} The representative crystal structure of LiM(O\textsubscript{2}) is demonstrated in Figure 1.1.

LiCoO\textsubscript{2} is a layered compound, with a theoretical capacity of approximately 140mAh/g.\textsuperscript{2,5-8} The poor capacity of this cathode material is resulted from structural instability during delithiation and has necessitated partial/full substitution of Co with Ni, and Mn leading to increased capacity and voltage range of around 3.6-4.3 V vs. Li/Li$^+$.\textsuperscript{2,5-8} This substitution also serves to limit the presence of Co which was later discovered to be environmentally toxic. General formula for partially substituted LiCoO\textsubscript{2} is LiNi$_{1-x}$Co$_x$O\textsubscript{2}, and LiNi$_y$Mn$_y$Co$_{1-2y}$O\textsubscript{2}.\textsuperscript{4}

![Figure 1.1 Crystal Structure of Layered LiMO\textsubscript{2} showing the alternating MO\textsubscript{2} slab and Li layer.\textsuperscript{7}](image-url)
1.3.2 Olivine Compounds

This group of polyanion materials, with a general formula LiMPO$_4$ (M = typically transition metals), is composed of slightly distorted hexagonal close pack (hcp) anion oxygen arrays as shown in Figure 1.2.$^{5,7}$ Triphylite LiFePO$_4$ is the primary representative of these group of olivine compounds,$^{5,7,24-27}$ with an orthorhombic lattice structure.$^{24}$ LiFePO$_4$ structure consists of corner-shared FeO$_6$ octahedral (4c) and edge-shared LiO$_6$ octahedral (4c) and are linked by the PO$_4$ tetrahedral (4a).$^{7,24,29}$ Half of the octahedral sites are occupied by Fe and one-eighth by Li$^+$. The site sharing causes the LiFePO$_4$ olivine structure to be unstable and converts to spinel structure under pressure.$^5$

Interest in LiFePO$_4$ was generated on realization of its excellent electrochemical performance and thermal stability due to a theoretical capacity of around 170 mAh/g.$^{5-8,12-14,24-27,29}$ Although this material has excellent cyclic performance, there is the drawback of poor Li$^+$ diffusion coefficient leading to poor rate capability in addition to low operating voltage of 3.4V vs. Li/Li$^+$.$^{5,7,12,24-27}$ To improve the energy density due to the low operating voltage, partial and full substitution of Fe with Mn, Ni, Co has been proposed, resulting in a high voltage of 5.1 V vs. Li/Li$^+$ in the case of LiCoPO$_4$.$^{7,10-13,29}$

Figure 1.2 Crystal Structure of LiFePO$_4$, representative member of Olivine compounds.$^{24}$
1.3.3 Spinel Compounds

The spinel compounds are represented by $\text{A}[\text{B}_2]\text{X}_4$ (B = transition metal, X = oxygen anion) with a structure similar to the naturally occurring mineral $\text{MgAl}_2\text{O}_4$. Lithium spinel is represented by $\text{Li}[\text{B}_2]\text{X}_4$. In the lithium spinel structure, $\text{Li}^+$ occupies the tetrahedral (8a) sites, and B refers to the cations which occupies the octahedral (16d) sites in a cubic close packed (ccp) array of oxygen (X) anions. The X anions are located in the 32e sites. In a typical unit cell of lithium spinel, there are 64 tetrahedral (8a) sites of which only 8 sites are occupied by $\text{Li}^+$, and 32 octahedral (16d) sites with only half of them occupied by B cations. Despite the seemingly empty unit cell structure, $\text{Li}^+$ can only be introduced into the spinel chemically and electrochemically at room temperature, as a result of face sharing between the empty tetrahedral and octahedral sites. However the empty sites provide a stable three dimensional (3D) interstitial space for $\text{Li}^+$ transport during lithiation and delithiation. As previously noted, B cations in octahedral sites can be replaced by a variety of transition metal ions, leading to compositional variation and diverse electrochemical performance of lithium spinel. Observing this variety in the electrochemical performance particularly in terms of operating voltage, Thackeray et al. proposed a spinel anode and spinel cathode couple for $\text{LiB}$, such as $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ and $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}/\text{Li}_{7-x}\text{Mn}_5\text{O}_{12}$ which lead to 2.5 V vs. Li/Li$^+$ and 1.5 V vs. Li/Li$^+$ cells respectively.

A notable class of spinel cathode material is Lithium-Manganese-Oxide (LMO) spinel. Several stoichiometric compounds of this spinel type exist with composition between $\text{Mn}_3\text{O}_4$ (hausmannite) and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ in the Li-Mn-O phase diagram in Figure 1.3. The composition of interest for LiB lie on the tie-line between $\text{LiMn}_2\text{O}_4$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}$. This thesis is essentially concerned with the LMO spinel electrode with a composition of $\text{Li}_4\text{Mn}_5\text{O}_{12}$. As such, a further review of LMO spinel is presented in later sections.

1.3.4 Other Insertion Cathode Materials for Lithium Ion Batteries

In recent years, new insertion electrodes materials have been developed including silicates, borates and tavorite.
1.3.4.1 Silicate Compounds

The silicate compounds Li$_2$MSiO$_4$ (M= Fe, Mn or Co) were first introduced in 2005 by Nyten et al with the composition of Li$_2$FeSiO$_4$.$^7,14-15,29$ In contrast to compounds in the preceding section, two Li$^+$ are extracted per unit formula in the case of silicates compounds. Li$_2$MSiO$_4$ forms a layered structure in which the transition metal and silicate tetrahedral share the corner sites. Additionally, this structure has been shown to crystallize in at least three different polymorphs: α-phase, β-phase and Y-phase, dependent on temperature and formation energy.$^{15}$ with at least two phases occurring in many samples of the pristine material.$^{14}$ This instability in the structure causes poor discharge capacity of the material. Although the theoretical capacity is 333 mAh/g upon extracting two Li$^+$ per unit formula, only about 140 mAh/g is achieved practically at voltage range of 2.8-3.1 V vs. Li/Li$^+$, indicating only about one Li$^+$ is extracted per unit formula.$^7$ Varying derivatives and synthesis methods are been investigated to improve the energy density of the material.$^{7,14-15,29}$

1.3.4.2 Tavorite Compounds

Tavorite fluorophosphates LiMPO$_4$F (M= Fe, Mn, Co, Ti etc) is a derivative of the olivine structure, and also possesses characteristics similar to the olivine structure earlier described.$^7,8$ LiVPO$_4$F which represents the typical composition was introduced by Baker et al in 2005.$^{7,16-17,29}$ The crystal structure is similar to the naturally occurring minerals amblygonite (LiAlPO$_4$) and tavorite (LiFePO$_4$OH).$^{7,29}$ Phosphate tetrahedral and vanadium octahedral with oxygen atoms are shared in the corner sites, with lithium existing in two different sites within the structure.$^{7,17,29}$ The discharge capacity of this material is 140 mAh/g (ca = 150 mAh/g), with operating voltage of 4.05 V vs. Li/Li$^+$ and good cyclic performance.$^{7,16-17,29}$ Thermal stability up to 175°C is also reported for this material.$^{7,16}$
1.3.4.3 Borate Compounds

The presence of BO$_3$ in the borate LiMBO$_3$ (M=Mn, Fe, Co) is responsible for the higher theoretical energy density of borate in comparison with other polyanion cathode material.$^7$ The representative of this group is LiFeBO$_3$, with a three dimensional FeBO$_3$ framework consisting of FeO$_5$ bipyramids and BO$_3$ trigonal plane and Li in two tetrahedral sites.$^7$. Discharge capacity of 200 mAh/g (ca = 220 mAh/g) at 4.0 V vs. Li/Li$^+$ was recently obtained for this material by Yamada et al.$^7$.

1.4. The Lithium Manganese Oxide Spinel System

The family of Lithium Manganese Oxide (LMO) spinel of interest in LiB is represented by the general formula Li$_{1+x}$Mn$_{2-x}$O$_4$, where $x$ is defined between 0 and 0.33.$^2$-$^7,^9,^22$. LiMn$_2$O$_4$ and Li$_4$Mn$_5$O$_{12}$ are the respective composition in the boundary limits of $x$. In spinel notation the latter is described as Li[[Mn$_2$]O$_4$ and Li[[Mn$_{1.67}$Li$_{0.33}$]O$_4$ respectively.$^7,^9,^22$.

1.4.1 Lithium Manganese Spinel LiMn$_2$O$_4$ and Derivatives

LiMn$_2$O$_4$ was first introduced by Thackeray et al and it is presently the mostly studied insertion electrode in the LMO spinel family.$^5,^7,^9$. The crystal structure shown in figure 1.4 is typical of the spinel structure. However, a quarter ($1/4$) of B cations (in this case Mn) usually in the octahedral (16d) site are now located in the Li tetrahedral sites (8a).$^7$. The resultant vacancies in the octahedral sites provide a 3D pathway for Li-ion diffusion.

Electrochemical lithium insertion (discharge) into LiMn$_2$O$_4$ takes place at around 2.96 V vs. Li/Li$^+$.$^2$-$^4,^7,^22$

$$\text{Li} + \text{Li}[[\text{Mn}_2]O_4 \rightarrow \text{Li}_2[[\text{Mn}_2]O_4 (\text{rock-salt phase})$$

The irreversible phase transition to rock-salt phase was found to cause up to 16% anisotropic increment in the unit cell of the spinel structure, which consequently introduces a tetragonal symmetry with concomitant decrease in the spinel cubic symmetry caused by the Jahn-Teller distortion of Mn$^{4+}$. As such, the lattice parameter is transformed from $a = 8.248$ Å to $a = 8.007$ Å and $c = 9.274$Å, since smaller Mn$^{4+}$ is replaced by larger Mn$^{3+}$. Additionally, the Li$^+$ insertion to the vacant octahedral sites according to the reaction above also causes a reduction of Mn$^{4+}$ to Mn$^{3+}$ (Mn$^{4+/3+}$), which increases the concentration of Mn$^{3+}$ in the structure and results in a subsequent disproportion reaction and dissolution of Mn$^{2+}$ in the electrolyte by corrosion of H$^+$. $^2,^4,^5,^7,^9,^20,^22$

$$2\text{Mn}^{3+} (\text{solid}) \rightarrow \text{Mn}^{4+} (\text{solid}) + \text{Mn}^{2+} (\text{solution})$$

The disproportion reaction and phase transformation are found to cause a severe capacity degradation which is further accentuated when electrochemical testing is performed at elevated temperature.$^2,^5,^7$. In contrast, when discharge is limited
to 4 V, the spinel structure is preserved resulting in a much more stable capacity but much less than the theoretical capacity of 148 mAh/g.\textsuperscript{2,5,7-8}

Figure 1.4: Crystal structure of LMO spinel LiMn\textsubscript{2}O\textsubscript{4}.\textsuperscript{7}

The drawback of LiMn\textsubscript{2}O\textsubscript{4} is reversed on partial substitution of Mn with other transition metals which leads to varying derivatives of pristine LiMn\textsubscript{2}O\textsubscript{4}. In general, the dopants (transition metals) suppresses the Jahn-Teller distortion of Mn\textsuperscript{3+}, and subsequently enhances the structural stability during cycling with much less capacity degradation.\textsuperscript{2,7-9} Among these derivatives, LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} is reported as the most effective composition for good cycling stability and high energy density at a high operating voltage.

1.4.1.1 LMO Spinel LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}

In LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}, the valence of Ni is 2+, and all Mn is prompted to a valence of 4+.\textsuperscript{7,8,18-19,30-32} The crystal structure is intrinsically similar to the spinel ccp previously described, including the Li diffusion pathway (16c). But it is very sensitive to synthesis condition, particularly temperature.\textsuperscript{7-8,18,31} This sensitivity leads to two distinctive variations in the crystal structure; non-stoichiometric disordered LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4.5} with all face centered space group Fd\textsuperscript{3}m and the stoichiometric ordered LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} with the primitive tetragonal space group P4\textsubscript{3}3\textsubscript{2}\textsuperscript{7,18-19,30-32}, as shown in Figure 5a and 5b. Disordered LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} is reported with a better rate capability when compared to the ordered one,\textsuperscript{7,8,18} while their practical discharge capacity is about 140 mAh/g (ca = 147 mAh/g).\textsuperscript{7} Improvement in the performance of the disordered LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} is attributed to the random occupation of Ni and Mn ions in the 16d octahedral sites, coupled with the quarter vacant octahedral sites. This improves the diffusion pathways for Li located in the 8a tetrahedral sites, resulting in increased Li diffusion coefficient.\textsuperscript{7,8,18-19} Compared with the pristine LiMn\textsubscript{2}O\textsubscript{4}, the most significant improvement in LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} other than its cyclic stability is the new voltage plateau observed around 4.7 V vs. Li/Li\textsuperscript{+}. This voltage peak is attributed to Mn
and Ni redox couple in LiNi$_{0.5}$Mn$_{1.5}$O$_4$, where there is a shift from Mn$^{3+}$/Mn$^{4+}$ to Ni$^{2+}$/Ni$^{4+}$, corresponding to from 4.0 V to 4.7 V.$^{7,8,18-19,30-32}$ This high voltage peak not only increases the energy density of the electrode material, but also increases its application potential particularly in electric vehicles (EVs) and hybrid electric vehicles (HEVs).$^7$ Although Mn is in the tetravalent state in the material, Mn$^{3+}$ results from charge neutrality due to oxygen loss in the disordered LiNi$_{0.5}$Mn$_{1.5}$O$_4$. In other to take advantage of the concentration of Mn$^{3+}$ without incurring the tetragonal Jahn-Teller distortion and the disproportional reaction which oxidizes the electrolyte, the oxygen deficiency is controlled by slow cooling after high temperature calcination of the material.$^{7,8,18}$ Doping of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with transition metal is also reported to decrease the Mn$^{3+}$ concentration, increase the 16d site disorder, and thereby further increase the Li$^+$ diffusion coefficient for better rate capability.$^7,18$ The doping formula is generally represented by LiMn$_{1.5}$Ni$_{0.5-x}$M$_x$O$_4$ (M= Cu, Zn, F, Cr etc).$^{18,19}$ Manthiram et al.$^{16}$ reported on varying doping scenarios and developed LiMn$_{1.5}$Ni$_{0.42}$Zn$_{0.08}$O$_4$, LiMn$_{1.5}$Ni$_{0.42}$Cu$_{0.08}$O$_4$ and LiMn$_{1.5}$Ni$_{0.38}$Cu$_{0.12}$O$_4$.

![Figure 1.5: Lithium ion diffusion paths in LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinel with the space group of (a) Fd$^3$m and (b) P4$_3$32.]

**1.4.2 Lithium Manganese Spinel Li$_4$Mn$_5$O$_{12}$ and Derivatives**

Spinel Li$_4$Mn$_5$O$_{12}$ is the end member of Li$_{1+x}$Mn$_{2-x}$O$_4$ with the spinel notation Li[Mn$_{1.67}$Li$_{0.33}$]O$_4$. It bears similar crystal structure with the Fd$^3$m space group of LiMn$_2$O$_4$ system with slight variation in the octahedral and tetrahedral site occupation.$^{19}$ Chakoumakos et al. reported (Li)$_8$[Li$_{0.33}$Mn$_{1.67}$]$_{16d}$O$_4$ as the site occupation for the Li and Mn cation with the oxygen anion ccp array, which is intrinsically coherent with LiMn$_2$O$_4$ site occupation. However, Li$^+$ occupation of interstitial 16c sites occurs in the LiMn$_2$O$_4$ but not in Li$_4$Mn$_5$O$_{12}$. Also unlike
LiMn$_2$O$_4$ which acts as either a 3 V or 4 V vs. Li/Li$^+$ electrode, Li$_x$Mn$_5$O$_{12}$ operates only as a 3 V because Mn is tetravalent, hence Li$^+$ cannot be extracted from the structure. The tetravalent Mn helps to stabilize the cubic structure during lithiation over a much wider range when compared to LiMn$_2$O$_4$ in the 3 V discharge range. Despite enhanced cyclic performance and a higher theoretical capacity of 163 mAh/g, synthesis of Li$_x$Mn$_5$O$_{12}$ is reported to be very sensitive to temperature, which often leads to the decomposition of the material to spinel Li$_2$Mn$_2$O$_4$ and layered Li$_2$MnO$_3$. Suppressing the decomposition through partial substitution of oxygen anion with fluorine ($\text{Li}_x\text{Mn}_5\text{O}_{12-x}\text{F}_x$) and integrating with a structurally compatible Li$_2$MnO$_3$ have been reported by Manthiram and Zhang et al., respectively, to effectively halt the decomposition.

Due to the significance of the operating voltage to the performance and stability of LMO spinel, these groups of insertion electrodes are also characterized by their voltages primarily as 3 V or 4 V vs. Li/Li$^+$ electrodes. Most recently, particularly resulting from partial substitution of Mn and doping with transition metals including fluorine in some cases, varying voltage plateaus has been reported for LMO derivatives. Table 1 highlights high voltages ($\geq$ 4.5 V) recently reported for LMO spinel derivatives.

Table 1.1: Electrochemical data indicating operating voltage ($\geq$ 4.5 V vs. Li/Li$^+$) of LMO spinel derivatives

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ave. Disch. potential (V vs. Li/Li$^+$)</th>
<th>Redox couple</th>
<th>Discharge capacity (mAh/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.5}$O$_4$</td>
<td>4.7</td>
<td>Ni$^{2+/3+}$/Ni$^{4+/4+}$</td>
<td>147$^a$</td>
<td>8</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.5}$O$<em>{3.9}$F$</em>{0.1}$</td>
<td>4.7</td>
<td>Ni$^{2+/3+}$/Ni$^{4+/4+}$</td>
<td>120</td>
<td>18</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Fe$</em>{0.5}$O$_4$</td>
<td>4.5</td>
<td>Fe$^{2+/3+/4+}$/Mn$^{3+/4+}$</td>
<td>148$^a$</td>
<td>8</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Cu$</em>{0.5}$O$_4$</td>
<td>4.5</td>
<td>Cu$^{2+/3+/4+}$/Mn$^{3+/4+}$</td>
<td>145</td>
<td>8</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.42}$Zn$_{0.08}$O$_4$</td>
<td>4.75</td>
<td>Ni$^{2+/3+/4+}$/Ni$^{4+/4+}$</td>
<td>-120$^b$</td>
<td>18</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.42}$Cu$_{0.08}$O$_4$</td>
<td>4.75</td>
<td>Ni$^{2+/3+/4+}$/Ni$^{4+/4+}$</td>
<td>-120$^b$</td>
<td>18</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.38}$Zn$_{0.12}$O$_4$</td>
<td>4.75</td>
<td>Ni$^{2+/3+/4+}$/Ni$^{4+/4+}$</td>
<td>-120$^b$</td>
<td>18</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.38}$Cu$_{0.12}$O$_4$</td>
<td>4.75</td>
<td>Ni$^{2+/3+/4+}$/Ni$^{4+/4+}$</td>
<td>-120$^b$</td>
<td>18</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.45}$Cr$_{0.05}$O$_4$</td>
<td>4.73/4.81</td>
<td>Ni$^{2+/3+/4+}$/Cr$^{3+/4+}$</td>
<td>141$^b$</td>
<td>19</td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.45}$Cr$<em>{0.05}$O$</em>{3.9}$F$_{0.1}$</td>
<td>4.73/4.81</td>
<td>Ni$^{2+/3+/4+}$/Cr$^{3+/4+}$</td>
<td>130$^b$</td>
<td>19</td>
</tr>
</tbody>
</table>

$^a$ Theoretical capacity
$^b$ Capacity includes high voltage ($\geq$ 4.5 V vs. Li/Li$^+$) and low voltage discharge (< 4.5 V vs. Li/Li$^+$) discharge capacities.

1.5. Scope and objectives of this thesis

This thesis is designed to take advantage of the abundant octahedral and tetrahedral sites in the robust three dimensional crystal structure of the Li$_4$Mn$_5$O$_{12}$ spinel. By partially substituting Mn with divalent and trivalent transition metals, the discharge (operating) voltage will be increased, thereby providing high
energy density insertion electrode material for new-generation lithium ion batteries. The substitution is executed in two fronts: by partial single element substitution of Mn and by partial double elements substitution, resulting in spinel type composition of Li$_{1.33}$Mn$_{1.67-x}$Ma$_x$O$_4$: (Ma= Ni, Fe), (0.25≤x≤2.5) and Li$_{1.33}$Mn$_{1.67-(x+y)}$Ma$_x$Mb$_y$O$_4$: (Ma= Ni, Mb= Zn, Fe), (0.25≤x+y≤1.0) respectively. The operating voltage, cyclic stability and discharge capacity of Li$_{1.33}$Mn$_{1.67-x}$Ma$_x$O$_4$, necessitate the choice of transition metal selections for Li$_{1.33}$Mn$_{1.67-(x+y)}$Ma$_x$Mb$_y$O$_4$ composition

1.6. References

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CHAPTER 2: COMPOSITION CONTROL OF SPINEL LITHIUM MANGANESE OXIDE FOR HIGH-VOLTAGE HIGH-ENERGY INSERTION ELECTRODES FOR LITHIUM ION BATTERIES

2.1 Introduction

Li$_4$Mn$_5$O$_{12}$ in spinel notation Li$_{6z}$[Mn$_{1+2x}$Li$_{0.33}$]$_{3z}$O$_4$ is described as the end member of Li$_{1+x}$Mn$_{2-x}$O$_4$ (0≤x≤0.33) family of Lithium Manganese Oxide (LMO) spinel, with manganese in a tetravalent state, and x = 0.33. In general, Li$_{1+x}$Mn$_{2-x}$O$_4$ spinel is classified as either a 3 V or 4 V vs. Li/Li$^+$ insertion electrodes. This classification reflects the optimized voltage, mostly devoid of Jahn-Teller distortion for Li$^+$ intercalation in the respective spinel member. Thackeray et al. reported a coalition between the value of x, the oxidation state of Mn and the voltage. Such that when x is between 0 and 0.1 (0≤x≤0.1), the spinel offers 4 V vs. Li/Li$^+$ capacity. Whereas as the value of x increases, so does the oxidation state of Mn, resulting in the existence of only a 3 V vs. Li/Li$^+$ capacity, and a tetravalent Mn state. This is the case with Li$_4$Mn$_5$O$_{12}$ spinel. Li$_4$Mn$_5$O$_{12}$ is also widely reported as having excellent cyclic performance and stability of the spinel cubic symmetry in comparison with those with lower values of x.

Li$_4$Mn$_5$O$_{12}$ is an attractive electrode for Lithium battery (LiB) due to its high theoretical capacity of 163 mAh/g, three dimensional Li-ion transport pathway, and environmental friendliness. The 3D diffusion pathway is inherent from the Li occupation of the 8a tetrahedral sites and partially the 16d octahedral sites in the cubic close packed (ccp) crystal structure. Despite these characteristics, the application of Li$_4$Mn$_5$O$_{12}$ is hindered by the low operating voltage, cubic to tetragonal Jahn-Teller distortion which eventually occurs towards the end of discharge corresponding to the transformation of Li$_{4+x}$Mn$_5$O$_{12}$ to Li$_{6.5}$Mn$_5$O$_{12}$ (y=2.5). In addition, Li$_4$Mn$_5$O$_{12}$ is sensitive to the synthesis temperature (T > 500°C), causing it to decompose into layered Li$_2$MnO$_3$ and spinel LiMn$_2$O$_4$. Extensive research have been reported eliminating the decomposition of spinel Li$_4$Mn$_5$O$_{12}$ during synthesis. The methods adopted involve novel synthesis for varying morphology, substitution of O$_2^-$ (anionic substitution) and layered-spinel composite with general formula zLi$_2$MnO$_3$·(1-z)Li$_4$Mn$_5$O$_{12}$. These approaches have not only eliminated the phase decomposition, but also resulted in improved electrochemical performance of the material. However, in the case of increasing the operating voltage, research efforts have been mostly channeled to the LMO spinel with x ranging between 0 and 0.1 (0≤x≤0.1), typically LiMn$_{2}$O$_{4}$ (ca=148 mAh/g, 4.0 vs. Li/Li$^+$).

In this paper, attention is shifted to increasing the operating voltage of Li$_4$Mn$_5$O$_{12}$ spinel, so as to take advantage of its high theoretical capacity. Firstly, by partial substitution of Mn with a transition metal possessing a divalent or trivalent valence state. According to the general formula and composition range Li$_{1.33}$Mn$_{1.67-x}$Ma$_x$O$_{4}$: (Ma=Ni, Fe), (0.25≤x≤2.5). Additionally, by partial Mn substitution using two transition metals according to the general formula Li$_{1.33}$Mn$_{1.67-\{x+y\}}$Ma$_x$Mb$_y$O$_{4}$: (Ma=Ni, Mb=Zn, Fe), (0.25≤x+y≤1.0). Since energy
density of the battery is dependent on the discharge voltage and discharge capacity, increasing the operating voltage gives rise to the enhanced energy density of the battery. As such, Li$_i$Mn$_5$O$_{12}$ can serve as cathode material in high voltage applications such as electric vehicles and hybrid electric vehicles.

2.2 Experimental

2.2.1 Material Preparation

Spinel Li$_{1.33}$Mn$_{1.67-x}$Ma$_x$O$_4$ (Li$_4$Mn$_y$-xMaO$_{12}$) and Li$_{1.33}$Mn$_{1.67-(x+y)}$Ma$_x$Mb$_y$O$_4$ (Li$_4$Mn$_{5-(x+y)}$O$_{12}$), (x, y, Ma and Mb are as previously denoted) powders were synthesized using a solid solution method. In a typical synthesis, stoichiometric Lithium hydroxide (LiOH·H$_2$O) and Manganese (II) acetate tetra-hydrate (Mn(C$_2$H$_3$O$_2$)$_2$·4H$_2$O) were separately dissolved in 40 ml distilled water, until a homogeneous solution was obtained, with the molar ratio of Li : Mn as 4:5. In the first case of partial Mn substitution (Li$_{1.33}$Mn$_{1.67-x}$MaO$_{4}$), the respective transition metal Ma = Ni, Fe was dissolved in 30 ml distilled water and thereafter mixed with the Mn solution. The resulting solution was mixed with the Li solution under continuous stirring. Subsequently, the solution was aged in air at 40°C until the solvent was completely evaporated. To improve the crystallinity of the collected powders, sintering was performed at 900°C for 3 hrs using a heating/cooling rate of 1°C/min. Similar synthesis approach was utilized for partial substitution of Mn with dual components (Ma, Mb). In both cases, the precursors were nickel (II) acetate tetra-hydrate (Ni(C$_2$H$_3$O$_2$)$_2$·4H$_2$O), zinc acetate dehydrate (Zn(C$_2$H$_3$O$_2$)$_2$·2H$_2$O) and Iron (III) nitrate non-anhydride (FeN$_3$ (H$_2$O)$_3$). The substitution concentrations that were prepared are; Ni= 0.25, Ni= 0.5, Ni= 1.0, Ni= 1.5, Ni= 2.0, Ni= 2.5 and Fe= 0.25. For double substitution, Ni, Fe= 0.25, Ni, Fe= 0.5, Ni, Zn= 0.5, Ni, Fe= 0.5, 0.75, and Ni, Fe= 1.0. For comparison purpose, the pristine stoichiometric Li$_i$Mn$_5$O$_{12}$ (as base material) was also synthesized under similar conditions.

2.2.2 Material characterizations and Electrochemical Measurements

Crystal structure of the obtained solid solution (powder) was characterized by x-ray diffraction (XRD) on Empyrean multipurpose diffractometer by PANalytical, equipped with Cu Kα radiation (λ= 1.540598nm). Data was collected in the range of 10°≤2θ≤80° with a step size of 0.0263° at room temperature. Morphology of the powder was observed using field emission scanning electron microscopy (FE-SEM) on a Hitachi S-3600N Variable Pressure SEM.

Electrochemical performance of the samples was evaluated using coin cell LIR2032. Typically, the cathode slurry was prepared by mixing the respective active material powder, with acetylene black (conductive carbon) and polyvinylidene fluoride (PVDF) as binder in an 80:10:10 weight ratio. This solid mixture was then dissolved in 1-methyl, 3-pyrrolidone (NMP) solvent to form the cathode slurry. Subsequently, the slurry was uniformly smeared on aluminum foil substrate as current collector and vacuum-dried at 120°C for 24 h. Cathode disks
were uniformly punched out of this foil. This disk, together with 1 M solution of LiPF$_6$ (dissolved in a 1:1 vol ratio of ethylene carbonate and diethyl carbonate) as electrolyte, Celgard polypropylene micro-porous film as separator and Li metal as anode was assembled in a coin cell (LIR2032) in an argon filled glove box. Galvanostatic charge-discharge performance of the assembled batteries was characterized by a battery analyzer (MIT Corporation) in a voltage range of 3.2 V to 5.0 V vs. Li/Li$^+$, at various charge/discharge rates. 1 C rate was defined as 250 mAh/g since 1.33 Li$^+$ can be extracted from the base material Li$_{1.33}$Mn$_{1.67}$O$_4$ (ca = 163 mAh/g). Cyclic voltammetry (CV) measurement was carried out on a CHI605C electrochemical analyzer at a voltage sweep rate of 0.1 mV/s defined between 3.2 V to 5.0 V vs. Li/Li$^+$. All electrochemical measurements were performed at room temperature.

2.3 Results and Discussion

2.3.1 Phase Composition and Morphology

Figure 2.1: X-ray diffraction patterns for partial substitution of Mn in Li$_4$Mn$_5$O$_{12}$ (Li$_{1.33}$Mn$_{1.67}$O$_{4-\delta}$) with Ni, Fe ratio as indicated.
X-ray diffraction patterns of partially substituted Mn in Li₅MnₓO₁₂ (base material) in various proportion are provided in Fig. 2.1. As can be observed, the diffraction pattern of the base material is also obtained in comparison with the known diffraction data and phase of LMO spinel. It has been widely reported that LMO spinel particularly Li₅Mn₅O₁₂ and LiMn₂O₄ in their pristine state, can exhibit either an ordered 12d octahedral sites or a random 16d octahedral sites in a cubic structure, with space group P4₃32 and Fd3m respectively. The secondary phase, with space group C2/m (monoclinic), is also exhibited in addition to the cubic phase depending on the synthesis condition particularly temperature (> 500°C) X-ray spectrum identification is done using HighScore Plus PANalytical powder analytical tool. From Fig. 2.1, it is clear that all the visible reflections are consistent with the cubic spinel (Li₁₀₆₈Mn₁₃₃₂O₃₉₆₄) Fd3m (PDF 04-009-7766) and the secondary phase (Li₁₃₃₃Mn₆₇₂O₂) C2/m (PDF 04-014-7419). It is also noted that the intensity of the secondary phase reflection increases as the concentration of component partially substituted for Mn increases, as shown in the enlarged view in Fig. 2.1 (a') with θ defined between 32°≤θ≤48°. As the ratio of Mn substitution exceeds 0.2 (z/Mn: z= total substitution, Mn= 5), broadening of the peak at 2θ = ~38° corresponding to plane (222) and a slight peak shift to the right for plane (400) at 2θ = ~44° can be observed in the XRD patterns. Similarly at 2θ = ~19°, broadening of the peak corresponding to plane (111) is noticeable when z/Mn ≥ 0.2. In each case, there is a concomitant reduction in the respective peak intensity. It is also easy to see a relationship between the diffraction peaks shape and the type of component (transition metal) partially substituted for Mn. For Ni= 2.0 (z/Mn = 0.4), the peak differs (larger) from the case of Ni=1.0 and Fe= 1.0 (z/Mn = 0.4). The same conclusion can be made when Ni= 0.25 and Fe =0.25 respectively. This relationship reflects differences in the respective crystal structure, possibly due to the difference in atomic radii between Fe³⁺ (0.064 nm) and Ni²⁺ (0.069 nm). To understand this difference, and also the observable positive peak shift, particularly at large 2θ°, the XRD data is further analyzed using HighScore Plus PANalytical powder analytical tool. The analysis is based on the diffraction peak list without the application of any mathematical curve fitting function and algorithm. Crystallite size (t) calculation is according to the Scherrer equation:

\[ t = \frac{K\lambda}{B \cos(\theta)} \]

\[ B = 2\Delta\theta \] Bragg’s angle, with \( \lambda = 1.540\text{Å} \) according to x-ray type previously defined, \( K = 0.94 \) for cubic crystal structure, and the reference full width at half maximum (FWHM) = 0.02989° for the standard Li₅Mn₅O₁₂ reference.

The average crystallite size for the varying partial substitution of Mn is shown in Fig 2.2. From the line graph, the average crystallite size change across the x-ray spectrum collected (10°≤2θ≤80°) indicates a relation with the substitute component. First, the average crystallite size tends to decrease as Ni ion increases, but this trend changes when Ni=1.0. Also the presence of Fe and Ni ions in the composition tends to reduce the average crystallite size, particularly in the case of Ni= 0.5, Fe= 0.75. The presence of a cubic phase (Fd3m) and the secondary phase (C2/m) can be inferred to create this crystallite behavior. Which
suggest that the peak broadening is not only related to the crystallite size, but also to the crystal shape. This relation is captured in Fig. 2.3 which highlights the changes to the average d-spacing (d) for the different substitution ratio. The d-spacing for cubic crystal was calculated according to;

\[ d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \]

where \((hkl)\) corresponds to the planes identified in the standard cubic and secondary phases. The presence of Fe ion in the composition tends to reduce the average d-spacing across both phases. The trend in Fig. 2.3 also indicates that the component type substituted for Mn also determine the degree of distortion of the crystal lattice. Notably it can be inferred that Fe ion in the composition tends to stabilize the crystal structure. Such that the average d-spacing is \(~1.97 \text{ Å}~\) when \(\text{Ni}= 0.5, \text{Fe}= 0.75\) vs. \(~1.93 \text{ Å}~\) for the standard cubic phase (Fd\(\bar{3}\)m). In the latter case \(\text{Mn}=3.75\), but in the case when \(\text{Mn} = 4.0\) and \(3.5\) with substituted component Ni ion, the average d-spacing is larger; \(~2.10 \text{ Å}~\) and \(~1.97 \text{ Å}~\) respectively. From the above results and analysis of the powdered x-ray diffraction pattern including the crystallite size and d-spacing, there is clearly a characteristic action of the substitute \(\text{Ni}= 0.5, \text{Fe}= 0.75\); (a) a slight secondary phase at \(2\theta = ~38^\circ\) corresponding to plane (200), (b) high peak intensity, (c) a slight deviation in the average d-spacing from the standard cubic structure (Fd\(\bar{3}\)m). This composition indicates that that the Ni ion component can reduce the tetragonal Jahn-Teller distortion of the cubic Fd\(\bar{3}\)m crystal structure during electrochemical reaction, \(^{14-18, 21-22}\) while the presence of Fe ion stabilizes the structure. As widely reported, the presence of Mn\(^{3+}\) resulting from oxygen non-stoichiometry in the crystal structure is responsible for the tetragonal distortion of the cubic structure during Li\(^+\) intercalation. \(^{4,14-18, 21-22,25,28}\)

![Graph showing crystallite size distribution](image)

**Figure 2.2:** Average crystallite size distribution of partial Mn substitution in Li\(_4\)Mn\(_5\)O\(_{12}\).
Figure 2.3: Average d-spacing as a function of partial Mn substitution in Li$_4$Mn$_5$O$_{12}$ with the d-spacing of Fd$_{3m}$ shown as reference.

The surface morphology and particle size can also be characterized by changes in the substitute components. As shown in Fig. 2.4, the particle size decreases as Ni ion substitution increases from Ni= 0.25 to Ni= 1.0. The particle size is apparently uniform within this trend. However, in the case of Fe= 0.25, while it is difficult to interpret a change in the particle size, there is an appreciable change in the surface morphology of the particles. The precipitation of nano-sized particles which are embedded on the surface of micro-sized particles results in a unique composite morphology. These nano-sized particles suggest increase in the available surface area of the cathode for Li$^+$ ionic transport and consequently shorten the Li$^+$ diffusion path. Specifically in Fig. 2.5, the combination of Ni ion and Fe, does not only show a change in the surface morphology, but also a distribution of varying particle sizes: micro/nano-sized. The trend towards a uniform particle size distribution and changes to the surface morphology is more observable in the Ni= 0.5 and Fe= 0.75 composition.
2.3.2 Electrochemical Performance

Electrochemical performance of the electrodes is presented in Fig. 2.6. In Fig. 2.6(a), the initial charge – discharge profiles, at voltage range of 3.2 V – 5.0 V vs. Li/Li⁺, current density 25 mAh/g is shown. In Fig. 2.6(a’), enlarged view of Fig 2.6(a) showing only the discharge profiles between 4.2 V – 4.7 V. Initial charge – discharge of the base material (Li₄Mn₅O₁₂) is also provided. It is noticeable that when Ni= 1.0, the discharge voltage plateau defined around 4.65 V vs. Li/Li⁺ provides the most discharge capacity (~50 mAh/g). Also it is noticeable that as the Ni content increases, there is a slight increase in the discharge voltage, but with a contaminant decrease in the high voltage discharge capacity (Fig 2.6a’). This trend agrees with the increase in the presence of the secondary phase previously observed in the powder x-ray diffraction spectrum Fig. 2.1. According to Zheng et al.,³¹ increasing the secondary phase causes a reduction in the discharge capacity. Another voltage region at ~4.0 V exists in Fig 2.6(a) except in the case of Ni>1.0. This voltage region typical of oxygen non-stoichiometric spinel is attributed to the redox couple Mn³⁺/⁴⁺. Partial substitution of Mn with a transition metal (tm), causes the cation site disorder in the spinel resulting
in the change of valance state of Mn from 4+ in Li$_4$Mn$_5$O$_{12}$ to 3+ in Li$_4$Mn$_{5-x}$Ma$_x$O$_{12}$ (Ma=tm=Ni).\cite{3,11} This change causes the crystal structure to strain (micro-strain) due to the replacement of smaller Mn$^{4+}$ (5.4 nm) with larger Mn$^{3+}$ (6.5 nm).\cite{27,31-32} This strain which also causes increase in the crystal structure d-spacing, peak shift and broadening corresponds to the d-spacing profile in Fig 2.3 and the x-ray diffraction spectrum in Fig. 2.1. Such that at Ni=2.0, the d-spacing is over 20% more than the standard d-spacing of spinel Fd3m (Fig. 2.3). Electrochemically, it is observable in Fig 2.6(a) that when Ni>1.0, there is no presence of Mn$^{3+/4+}$ redox (~4.0 V region), with only slight presence in the case of Ni=1.5. This suggests that all Mn$^{4+}$ is completely replaced by Mn$^{3+}$ at certain concentration of Ni in Li$_4$Mn$_{5-x}$Ni$_x$O$_{12}$. Additionally, this reflects a substantial distortion of the crystal structure at high Ni concentration. In case of the voltage plateau around ~4.7 V, the extraction/insertion of Li$^+$ in the 8a tetrahedral sites causes Ni$^{2+/3+/4+}$ redox couple.\cite{18,29,31}

![Figure 2.5: Scanning electron microscopy (SEM) micrographs (a) – (c) as indicated.](image-url)
Figure 2.6: Charge and discharge profiles for single component partial Mn substitution as shown, at 25 mAh/g (a) Charge and discharge profiles, voltage range of 3.2 V – 5.0 V (a’) Enlarged view of (a) showing corresponding discharge profiles at voltage range 4.2 – 5.0 V

The first charge-discharge profiles in Fig. 2.6(a) also suggest an optimal ratio of partial substitution of Mn in order to obtain a sustainable voltage at ~4.65 V. As noted earlier, this occurs at Ni= 1.0 (implying Mn= 4.0), indicating a composition of Li$_{1.33}$Mn$_{1.33}$NiO$_4$. Taking this as reference state (optimal substitution ratio), further substitution is performed by initial partial substitution of Ni ion by Fe ion and Zn ion. The first charge – discharge profiles of the latter is shown in Fig. 2.7(a), with an enlarged view in Fig 2.7(a’) showing only the discharge profiles within 4.2 V – 4.8 V. Due to the slight increase in the voltage plateau to ~4.7 V vs Li/Li$^+$ when Ni, Fe = 0.5 (Fig 2.6b’), Mn ion is further substituted beyond the defined reference state, to give Ni = 0.5, Fe = 0.75 (Li$_{1.33}$Mn$_{1.25}$Ni$_{0.17}$Fe$_{0.25}$O$_4$). In Fig. 2.7(b) with an enlarged view in Fig. 2.7(b’), the 1st, 3rd, 9th and 15th discharge profiles are shown. In all the cases when the substitutes is Ni, Fe (Ni$^{2+}$ and Fe$^{3+}$), the cathode exhibits a gradual increase in the discharge voltage, as the charge – discharge cycle increases. When Ni= 0.5, Fe= 0.75, the voltage settles at ~4.95 V vs. Li/Li$^+$ at about the 20th cycle as shown in Fig. 2.8. For comparison purpose, it is obvious from Fig. 2.7, that when either Ni ion or Fe ion is used as the only substitute component, the discharge voltage behavior significantly differs from the case when a combination of Ni and Fe ions is used. Indicating the high voltage redox couple is probably a combination of Ni$^{2+}$/Ni$^{3+}$/Ni$^{4+}$ and Mn$^{4+/5+}$ with contribution from Fe$^{2+/3+}$. This high voltage phenomenon can also be related to the microstructure and morphology of the material. It is also important to note that there is a progressive increase in the discharge capacity as the voltage increases.
The reversible voltage occurring between ~4.7 V – 4.95 V indicates Li⁺ intercalation at this voltage range. Also the increase in the discharge capacity, for instance from 101.67 mAh/g to 110.75 mAh/g in the 1st and 3rd discharge respectively, indicates the redox reaction taking place at the high voltage range impacts on the low voltage (<4.7 V) discharge capacity. This trend is continuous as shown in Fig 2.8, suggesting the high voltage redox is not connected to the oxidation of the electrolyte.² Manthiram et al.² suggested that the high voltage redox couple may be related to Mn⁴⁺/⁵⁺ and/or O²⁻/, since Li⁺ extraction in the 4.0 V region already causes Mn³⁺/⁴⁺ oxidation. The presence of a secondary phase (Li₂MnO₃) in pristine Li₄Mn₅O₁₂ is reported to cause extraction of Li⁺ from the 8a sites at high voltage (> 4.7 V) in a reversible manner.²⁷. Ivanova et al. ⁷ noted that only one Li⁺ is re-inserted. Accordingly, the presence of a secondary phase (Li₁.₃₈Mn₀.₆₂O₂) indicates Li⁺ intercalation at high voltage, with each successive Li⁺ extraction/insertion possibly causes the activation of Mn⁴⁺/⁵⁺ redox couple. However, the increasing voltage, for instance, ~4.75 V at the 1st discharge and ~4.9 V at the 3rd discharge, cannot be attributed only to the presence of the
secondary phase and Mn$^{4+/5+}$ redox couple. By observing that the secondary phase also exists when Ni, Fe = 0.25, and Ni, Fe = 0.5 in the x-ray pattern (Fig 2.1). But the high voltage (> ~4.7 V) electrochemical behavior differs in the case of Ni= 0.5 and Fe= 0.75. This suggests that certain crystallographic and morphology changes take place concomitantly with the electrochemical reaction. These changes may also have direct relationship with the presence of Fe$^{3+}$ in the cell. Liu et al.\textsuperscript{19} reported that part of the disorder (Fd$^{3m}$) may experience a transition to the ordered (P4$_332$) which has a higher Mn$^{4+}$ concentration. Additionally from Fig 2.3, increasing the concentration of Fe$^{3+}$ substitutes tends to reduce the d-spacing in the micro-structure for Mn substitution with the same ratio. And since the d-spacing is related to the micro-strain which is mainly due to the presence of larger Mn$^{3+}$, increasing the concentration of Fe$^{3+}$ in the substitution invariably reduces the concentration of Mn$^{3+}$. Hence, Fe$^{3+}$ can be considered to stabilize the crystal structure.\textsuperscript{33} Likely with this micro-structure stabilization in addition to increasing the concentration of Mn$^{4+/5+}$ redox, there is also a possible intermediate Fe$^{3+/4+}$ redox couple. The nano/micro-sized particles embedded on the surface attributed to the presence of Fe, as shown SEM micrographs in Fig 2.4 (a-d) and Fig 2.5(a-c), also suggest an increase in surface area as previously discussed. Since in the presence of Mn$^{3+}$, Jahn-Teller distortion is enabled,\textsuperscript{3,16} there is a chance of particulate stress during the Mn$^{3+/4+}$ redox (cubic to tetragonal distortion). The resulted stress concentration increases more rapidly in the micro-sized particles in contrast to the nano-sized ones.\textsuperscript{7,12,19} As a result, the disintegration of the micro-sized particle creates additional surface area and improves the Li$^+$ intercalation rate.

![Figure 2.8: Charge and discharge profiles Li$_{1.33}$Mn$_{1.5}$Ni$_{0.17}$Fe$_{0.25}$O$_4$ (Ni= 0.5, Fe=0.75) at 25 mAh/g, voltage range 3.2 V – 5.0 V](image)

Although the high voltage plateau obtained is not stable, the discharge capacity obtained at > 4.7 V is around 60 mAh/g as indicated in Fig 2.7(a'). This result also provides basis for optimizing the composition of LMO spinel for higher and constant discharge voltage for LiB cathode material. Using Ni$^{2+}$ and Fe$^{3+}$ as substitute components for partial substitution of Mn ion. Overall the increasing
discharge voltage as cyclic progresses, indicates that in the presence of Ni\(^{2+}\) and Fe\(^{3+}\) in LMO spinel \((\text{Li}_{1.33}\text{Mn}_{1.5}\text{Ni}_{0.17}\text{Fe}_{0.25}\text{O}_4)\) there exist an optimal composition, phase, and morphology combination for obtaining constant high reversible discharge voltage for this cathode material.

![Figure 2.9: (a) Discharge capacity profile Li\(_{1.33}\)Mn\(_{1.5}\)Ni\(_{0.17}\)Fe\(_{0.25}\)O\(_4\) (Ni= 0.5, Fe=0.75), at 25 mAh/g (0.1 C) and 250 mAh/g (1.0 C) (b) Rate performance at specified current densities, voltage range 3.2 V – 5.0 V](image)

The rate performance at various current densities in a voltage range of 3.2 V to 5.0 V vs. Li/Li\(^+\) is provided in Fig 2.9(b). The stability of the composite structure at high current densities particularly at 3C, when Ni= 0.5, Fe= 0.75, can be clearly seen in the rate performance plot. The cycling performance of the cathode at 0.1 C (25 mAh/g) and 1 C (250 mAh/g) is also presented in Fig. 2.9(a). It is clear to see that the discharge capacity increases as the number of cycles increases at the initial cycles. While a fairly stable discharge capacity occurs for subsequent cycles. In both cases (1 C and 0.1 C) the discharge capacity after a 100 cycles is slightly higher than the initial discharge capacity; 113.4 mAh/g vs. 101.7 mAh/g in case of 25 mAh/g and 82.3 mAh/g vs. 81.7 mAh/g (250 mAh/g).

To confirm the redox couple of Ni\(^{2+}/\)Ni\(^{4+}\) and possibly Mn\(^{4+}/\)Mn\(^{5+}\) occurring at high voltage with positive voltage shift, the cyclic voltammetry analysis (Fig. 2.10) is performed for Ni= 0.25, Ni= 1.0, Ni= 0.5,Fe= 0.5 and Ni= 0.5, Fe= 0.75. It can be seen that the increasing cathodic voltage peaks at > 4.6 V occurs only when Fe\(^{3+}\) is present in the material composition as shown in Fig 2.10(c) and Fig 2.10(d). From the CV curves, the anodic and cathodic peaks are reversible for the entire range (4 cycles). The anodic peaks when Fe\(^{3+}\) is present (Fig 2.10c and 2.10d) can be identified as anodic peaks ~4.0 V and ~4.85 V vs. Li/Li\(^+\). In the 1st cycle (when Ni= 0.5, Fe= 0.75), the ~4.85 V anodic peak is missing, but as the cycle progresses, this peak appears. Such phenomenon corresponds to the activation of the secondary phase\(^{34}\), resulting in the high voltage that exists beyond 4.7 V. This result is consistent with the 1st charge curve in Fig 2.7(a) and Fig 2.8, suggesting a stability effect of Fe\(^{3+}\) and the reversible activation of the secondary phase sets in after the 1st charge. It also indicates that there is a possible
crystallographic change after the 1st cycle. These results are consistent with the electrochemical redox couple $\text{Mn}^{4+/5+}$ suggested previously. Therefore, it is likely that $\text{Fe}^{3+/4+}$ redox reactions also occur during $\text{Li}^+$ extraction cation site.

Figure 2.10: Cyclic voltammetry (CV) curves at scan rate of 0.1 mV/s, voltage range 3.2 V – 5.0 V (a) Ni= 0.25 (b) Ni= 1.0 (c) Ni= 0.5, Fe= 0.5, (d) Ni= 0.5, Fe= 0.75

2.4 Conclusion

In summary, by systematic partial substitution of Mn in $\text{Li}_4\text{Mn}_5\text{O}_{12}$ with appropriate transition metals in the right proportion, the discharge voltage of this cathode material can be increased up to 4.95 V vs. Li/Li$^+$. Electrochemical performances of cathodes with various compositions are evaluated and compared. To achieve the high voltage, the substitute elements needs to be a combination of Ni$^{2+}$ and another transition metal such as Fe$^{3+}$. Additionally, the molar ratio of Mn cannot be less than 3.75 after substitution in $\text{Li}_4\text{Mn}_{5-x}\text{O}_{12}$ ($1.0 \leq x \leq 1.25$). It is found that Fe$^{3+}$ does not only help to stabilize the structure, but also contributes to the high voltage during Li$^+$ intercalation process.
2.5 References


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CHAPTER 3: HIGH VOLTAGE IMPROVEMENT OF Li$_4$Mn$_5$O$_{12}$ DERIVATIVES

3.1 Introduction

The experimental results in chapter 2 confirm that high voltage greater than traditional voltage of 4.7 V vs Li/Li$^+$ can be obtained from the derivatives of Li$_{1.33}$Mn$_{1.67-x}$O$_4$ (Li$_4$Mn$_{5-x}$O$_{12}$) spinel. Specifically, the results show that when Mn is partially substituted by Ni= 0.5 and Fe= 0.75 yielding Li$_{1.33}$Mn$_{1.5}$Ni$_{0.17}$Fe$_{0.25}$O$_4$-$\delta$ (Li$_4$Mn$_{3.75}$Ni$_{0.5}$Fe$_{0.75}$O$_{12}$) spinel, the discharge voltage increases from 4.7 V to ~ 4.95 V delivering a discharge capacity of ~65 mAh/g within this voltage range. Electrochemical measurements as well as chemical and physical characterizations suggest a close correlation between the obtained high voltage, the crystallographic changes and morphology of the material. However, the suggested correlation bears certain limitation. For instance, crystallographic transformation of the material, disintegration of micro/nano particles, and surface morphology changes, are not exactly known. Therefore, it would be important to validate the suggested correlation and tune the correlation to optimize the high voltage performance. Regarding validation of the suggested correlation, in-situ analysis of the microstructure during electrochemical cycling is recommended. In this chapter both validation and optimization work are discussed, with emphasis on the experimental validation of the results. Limitation to achieving high voltage is also highlighted. The projected results which is based on the suggested correlation, implies tuning certain features the synthesis method, optimizing the composition of Ni$^{2+}$/Fe$^{3+}$ and varying the synthesis temperature.

3.2 In-situ Validation of Correlated Result

The electrochemical behaviors of the materials in the previous chapter suggest two primary occurrence leading to high voltage (> 4.7 V vs. Li/Li$^+$): (a) the action of Fe$^{3+}$ during electrochemical cycling, and (b) the contribution of the secondary phase. Possible contribution of the secondary phase has been reported for LMO spinel. In contrast, only sparse information exists regarding the role of Fe$^{3+}$ in the high-voltage LMO spinel. In-situ observation of the material’s microstructure during lithiation/delithiation in addition to ex-situ analysis will help to obtain the information.

Several spectroscopic and microscopic techniques exist for in-situ analysis of electrochemical behavior of materials. In the present case, transmission x-ray microscopy (TXM), x-ray diffraction (XRD) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are applicable techniques.

For morphology evolution study, TXM can be used when volume change is expected in the material, such as volume change of the electrode during lithiation and delithiation processes. For instance, cracking has been observed after formation of a core-shell type structure during the first charge of Li$_x$Sn anode material, using the TXM technique. During the later test, it was found
that the cracking phenomenon is dependent on the particle size. In a similar manner using in-situ SEM, Chen et al.\textsuperscript{29} discovered that nano-sized SnO\textsubscript{2} particles form a continuous Li\textsubscript{2}O layer completely encapsulating the nano particles during charging. With in-situ x-ray diffraction technique, Mohanty et al.\textsuperscript{28} found that Li\textsubscript{2}MnO\textsubscript{3} phase was activated in Li\textsubscript{1.2}Co\textsubscript{0.1}Mn\textsubscript{0.55}Ni\textsubscript{0.15}O\textsubscript{2} when charged up to 4.4 V. These experimental results indicate that in-situ techniques are very useful for validating the suggested correlation. Such validation can form the basis for optimizing the material composition, synthesis method and tuning other parameters for maximizing the high discharge voltage.

### 3.3 Experimental Validation

Additional experiments are designed to validate the correlation, wherein the expected electrochemical and microstructural results are based on the suggested correlation. Two main approaches are considered as follows.

#### 3.3.1 Fine Tuning Material Composition – Derivatives of Li\textsubscript{4}Mn\textsubscript{3.75}Ni\textsubscript{0.5}Fe\textsubscript{0.75}O\textsubscript{12}

It has been concluded in the previous chapter that a combination of Ni\textsuperscript{2+} and Fe\textsuperscript{3+} as partial substitutes for Mn is necessary for obtaining high voltage (> 4.7 V vs. Li/Li\textsuperscript{+}). It also suggests that as the concentration of Fe\textsuperscript{3+} is increased in the combination, the discharge voltage increases (Fig. 2.4c and Fig 2.4c'). We can infer the following from the powder x-ray diffraction data (Fig. 2.1) and the SEM micrographs (Fig. 2.2 and Fig. 2.3): (1) Increase in the concentration of Fe\textsuperscript{3+} reduces the secondary phase, i.e., space group Cm/2; (2) The presence of Fe\textsuperscript{3+} causes surface morphology change, and consequently nano-sized particles become embedded on the surface of micro-sized particles.

In the first instance, the presence of Cm/2 (rock salt) secondary phase is reported to downgrade the electrochemical performance of LMO spinel if the phase is of the general formula Li\textsubscript{x}Ni\textsubscript{y}O. This phase is reported as electrochemically active\textsuperscript{1-2,4} and as an impurity phase (Li\textsubscript{2}MnO\textsubscript{3})\textsuperscript{3}. Suggesting a need to validate the action of this phase through controlling the Fe\textsuperscript{3+} concentration. Secondly, increasing Fe\textsuperscript{3+} in the combination (Ni, Fe) indicates a concomitant increase in the nano-sized particles embedded on the surface of the micro-sized. It is known that nano-sized particles provide more surface area for the electrochemical (redox) reaction, as well as shorter Li\textsuperscript{+} diffusion length. It is also reported that increasing surface area would increase the probability of side reaction of the cathode with the electrolyte, particularly at high voltage.\textsuperscript{5-6}.

Considering the above effects of particle size, it can be suggested that an effective distribution of micro/macro sized particles is necessary for optimizing the electrochemical performance of the cathode. Hence, the combination of Ni, Fe as substitutes can be further tuned to optimize the electrochemical performance of the electrode.
Table 3.1 presents the methods of tuning the composition of Li$_4$Mn$_{3.75}$Ni$_{0.5}$Fe$_{0.75}$O$_{12}$ (Li$_{1.33}$Mn$_{1.5}$Ni$_{0.17}$Fe$_{0.25}$O$_{4-\delta}$), for exploring the correlation between composition (Ni, Fe) and the electrochemical performance.

The composition tuning suggested in Table 3.1 can be seen to essentially relate to morphology control, particle size manipulation and minimizing the secondary phase. These features can also be controlled experimentally through changing the synthesis method. 

Table 3.1: Tuning the composition of Fe$^{3+}$ and Ni$^{2+}$ with expected results.

<table>
<thead>
<tr>
<th>Seq.</th>
<th>General formula</th>
<th>Desc.</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li$<em>4$Mn$</em>{3.75}$Ni$<em>{0.5}$Fe$</em>{0.75+x}$O$_{12}$</td>
<td>0.1$\leq x \leq$0.25</td>
<td>Improved discharge voltage performance, since increase in Fe$^{3+}$ correlated with a positive voltage trend</td>
</tr>
<tr>
<td>2</td>
<td>Li$<em>4$Mn$</em>{3.75-x}$Ni$<em>{0.5}$Fe$</em>{0.75+x}$O$_{12}$</td>
<td>0.1$\leq x \leq$0.25</td>
<td>Same as above</td>
</tr>
<tr>
<td>3</td>
<td>Li$<em>4$Mn$</em>{3.75}$Ni$<em>{0.5+y}$Fe$</em>{0.75-x}$O$_{12}$</td>
<td>0.1$\leq x \leq$0.25</td>
<td>Necessarily only as to confirm the projection of either step 1 or 2.</td>
</tr>
</tbody>
</table>

### 3.3.2 Different Synthesis Methods

Electrochemical performance of cathode materials varies with the way they are synthesized. Similarly, structure, particle size, and morphology of these materials change with the synthesis method as well. Therefore the desired material features can be obtained by selecting the appropriate synthesis approach. In the present case, the desired features include enhancing the particle size distribution and improving the surface morphology to support micro/nano-sized particles embedment and control of the secondary phase. Therefore, the following synthesis methods can be considered.

#### 3.3.2.1 Spray Pyrolysis Method

The spray pyrolysis method is a process of preparing multi-functional particles by forming droplets from the precursor solution. Essentially, the process involves three primary steps: atomization of a precursor solution, evaporation in a reactor and formation of solid particles. The particles are formed through drying, decomposition, and crystallization, while the chemical reactants are selected so that the products other than the desired compound are volatile at the decomposition temperature, resulting in multi-functional particles formed at low temperature. Hence, the spray pyrolysis is an attractive synthesis method for improving the high voltage LMO cathode material. The ability to synthesize the spinel material (Li$_4$Mn$_{3.75}$Ni$_{0.5}$Fe$_{0.75}$O$_{12}$) at low temperature while obtaining highly crystalline structure indicates that the secondary phase (space group C2/m) can be easily controlled. Fig. 3.1 shows a schematic of the spray pyrolysis process. In addition to the capability of forming crystalline materials at low temperature,
this method allows for varying solvent, carrier gas and reactor type so that the material morphology and other features can be tuned.\textsuperscript{12}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{design_procedure.png}
\caption{Schematic diagram of the of spray pyrolysis.\textsuperscript{12}}
\end{figure}

3.3.2.2 Sol Gel Method

The sol-gel (Pechini) process also known as chemical deposition involves the generation of nanoparticles by combined methods of gelation, precipitation and hydrothermal treatment.\textsuperscript{11,19} In addition to being able to obtain a homogenous composition at the molecular level, narrow particle size distribution at low crystallization temperature can also be obtained.\textsuperscript{19} Prominent in the sol-gel process is the selection of a chelating agent which serves to extract the metal ions from the solution. It is reported that varying the chelating agent leads to different particle size distribution of the products.\textsuperscript{13,18} Non-chelating agents like polyvinyl alcohol and other surfactants are also been used to tune the material morphology.\textsuperscript{11,17} The ability of this method to form crystalline material at low
temperature crystallization and to tune particle size distribution makes it a suitable choice for synthesizing the LMO cathode materials. Table 3.2 lists sol-gel processing methods to synthesize LMO spinel where chelating, non-chelating and surfactant have been used to tune the material features.

Table 3.2: Synthesis of LMO derivatives using the sol-gel methods.

<table>
<thead>
<tr>
<th>LMO Derivative</th>
<th>Chelating Agent</th>
<th>Max. Synthesis Temp</th>
<th>Secondary Phase</th>
<th>References [ ] / Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$<em>{1.5}$Ni$</em>{0.5}$O$_4$</td>
<td>Urea</td>
<td>800°C</td>
<td>Yes</td>
<td>[13] / slight secondary phase was precipitated.</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>Citric acid</td>
<td>700°C</td>
<td>No</td>
<td>[15] / No secondary phase was precipitated</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>Citric acid</td>
<td>700°C</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>LiMn$<em>{1.5}$Fe$</em>{0.5}$O$_4$</td>
<td>Citric acid</td>
<td>700°C</td>
<td>No</td>
<td>[16]</td>
</tr>
<tr>
<td>Li$<em>{1.4}$Mn$</em>{1.73}$O$_4$</td>
<td>Citric acid</td>
<td>700°C</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Li$<em>{1.27}$Mn$</em>{1.73}$O$_4$</td>
<td>Citric acid</td>
<td>700°C</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>Citric acid</td>
<td>900°C</td>
<td>No</td>
<td>[17] / Polyvinyl alcohol used as non-chelating agent</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>Citric acid</td>
<td>800°C</td>
<td>No</td>
<td>[18]</td>
</tr>
</tbody>
</table>

In each of these cases, the synthesis process adopted has been reported to improve the electrochemical performance by controlling the morphology and microstructure. For instance (as referenced in Table 3.2), Yang et al. synthesized LiMn$_2$O$_4$ using the sol-gel process with P123 tri block copolymer as surfactant and citric acid as the chelating agent, which resulted in a porous morphology and a nano/micro-sized particle distribution. In the work performed by Michalska et al., in addition to citric acid as chelating agent, ethylene glycol as a polymerizing reagent was also added. Particle sizes ranging from 100 to 200 nm composed of much smaller crystallite sizes were obtained. By varying the pH value during the sol-gel processing with citric acid as the chelating agent, Seyedahmadian et al. reported the secondary phase formed at pH < 4 and pH > 6.

3.3.2.3 Modified Solid Solution Method with Temperature Control

Solid state synthesis method is known to cause inhomogeneities, irregular morphology and broad distribution of particle sizes. Specifically for LMO spinel, the high calcination temperature required to obtain crystalline microstructure produces unwanted impurity phases. Despite this setback, this synthesis method is still considered attractive due to its simplified process. Hagh and Amatucci have suggested a modified solid state synthesis method for LMO spinel, including the following two steps: (1) Mixing less reactive NiO and
MnO$_2$ in a conventional milling process, after which the solid solution is annealed at the desired temperature; (2) Mixing the Li precursor with the annealed powder obtained in step (1) in a wet ball milling process, followed by a final annealing process. It was found that the particle size and morphology of the product was a function of the final annealing temperature. At temperature $\leq$ 700°C, second phase was present including non-consistent surface morphology in the as-prepared particles. But at temperature $\geq$ 700°C, there was no second phase and the particle size distribution was tunable at nano/micro scale.

The modified solid state solution described above provides another synthesis route which can easily be tailored to achieve the desired LMO composition. Other synthesis methods which can be tuned to achieve the preferred microstructure and morphology of the present LMO composition are highlighted in the next section.

### 3.3.2.4 Other Novel Synthesis Method

In general, there exist other novel synthesis methods which can be tailored to improve the high voltage performance of Li$_4$Mn$_{3.75}$Ni$_{0.5}$Fe$_{0.75}$O$_{12}$ (Li$_{1.33}$Mn$_{1.5}$Ni$_{0.17}$Fe$_{0.25}$O$_{4-\delta}$). For each method or combination of methods, the focus will be on enhancing the high voltage performance of the material, through control of its micro structure, particle size distribution, and surface morphology. In terms of microstructure, one dimensional (1D), two dimensional (2D) and three dimensional (3D) micro-structure can be synthesized. For instance, Zhan et al. synthesized LiMn$_2$O$_4$ 1D submicro-rods using combined solvothermal and solid state reaction methods. In the solvothermal process, the precursors were dissolved in ethanol/water with various ratios, so that a single phase of cubic structure devoid of any secondary phase was synthesized with high crystallinity at a calcination temperature of 700°C. The diameter of the rod ranges between ~80 – 1000 nm, with lengths of several micrometers. Similarly, Fu et al. synthesized hierarchical porous Li$_4$Mn$_3$O$_{12}$ nano/micro structure using ultrathin nanoflakes as self-templates. In another work, Chen et al. prepared LiMn$_2$O$_4$ using a modified resorcinol–formaldehyde process, with calcination performed up to 850°C. The resultant powdered material was well crystalline, with particle size ranging between 300nm – 900nm and no secondary peaks was detected. In all these approaches, electrochemical performances of the products varied, indicating relationships not only between synthesis method, but also the calcination temperature. Therefore, careful selection and application of a synthesis process can significantly enhance the high voltage performance of the material.

### 3.4 High Voltage Limitation of Li$_4$Mn$_{3.75}$Ni$_{0.5}$Fe$_{0.75}$O$_{12}$ and Its Derivatives

From the experimental data in the previous chapter, the high voltage discharge quasi-plateau exists between ~4.7 V to 4.95 V vs. Li/Li$^+$. It should be noted there are some limitations to improving this voltage through varying the synthesis method and other noted parameters, such as oxidation of the electrolyte,
conductivc carbon black and the binder material polyvinylidenefluoride (PVDF). Oxidations of these materials take places at around 5.0 V. Because of these limitations, the foreseen improvements of high-voltage performance of the cathode include: (i) increasing the discharge capacity at the 4.95 V plateau, (2) increasing the overall discharge capacity at high voltage (> 4.7 V), and (3) increasing the cyclic stability at high discharge voltage.

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4.1 Conclusion

This thesis centered on the provision of high energy density lithium ion batteries by increasing the discharge (operating) voltage shows: (a) on partial substitution of Mn in Lithium Manganese Oxide (LMO) spinel, discharge voltage > 4.7 V vs Li/L+ can be obtained (b) Suggested methods to improve on the voltage reported.

After systematical substitution of Mn in the base material (Li₄Mn₅O₁₂) spinel, the results indicates that double component partial substitution of Mn can successfully deliver voltage > 4.7 V. Specifically, it is shown that the spinel composition Li₄Mn₃.₇₅Ni₀.₅Fe₀.₇₅O₁₂ can operate between 4.7 V - 4.95 V delivering a discharge capacity of ~ 65 mAh/g. Between 3.2 V – 5.0 V, the total discharge capacity is ~ 114 mAh/g. Both at a high current density of 25 mAh/g (ca base material =.163 mAh/g). It also shows that these capacity are consistent for over 100 cycles. In addition, a systematic correlation between the delivered voltage, the substitute components (Ni, Fe), the microstructure and morphology is reported. Pointing a direction that can be explored to improve the discharge voltage and capacity.

The direction suggested for improvement consists in optimizing the material composition and enhancing the synthesis method. For optimizing the composition, the general formula Li₄Mn₃.₇₅Ni₀.₅₋ₓFe₀.₇₅ₓO₁₂ and Li₄Mn₃.₇₅₋ₓNi₀.₅Fe₀.₇₅ₓO₁₂, (0.1≤x≥0.25) is suggested. Synthesis method with ease of tuning particle size distribution, microstructure and morphology is reported as recommended routes to enhancing the material electrochemical performance.

Finally, this thesis highlighted the known constraints with achieving high discharge voltage as it pertains to other components of the battery cell. Such as electrolyte, carbon black and the separator.
VITA

Hilary Eikhuemelo was born in the city of Benin, Edo state Nigeria. In 2004, he earned his Higher National Diploma (HND) in Mechanical Engineering from the Petroleum Training Institute (PTI), in Nigeria. Upon graduation he worked as a design engineer at ILF Consulting Engineers. In the fall of 2012 he completed his Master’s diploma (entry) studies in Management at the University of Wales, United Kingdom. In the spring of 2013, he commenced his Master’s degree in Mechanical Engineering at the Louisiana State University, Baton Rouge.