Synthesis and Electrochemical Performance of a Homogenously Dispersed $\text{Li}_a\text{Mn}_{2-x-y-z}\text{Fe}_x\text{Co}_y\text{Ni}_z\text{O}_{4-d}\text{Cl}_d$ Lithium Ion Battery Cathode Material

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Abstract

Lithium manganese oxide spinels are attractive materials for lithium-ion battery cathodes due to their capability for high voltage application paired with a three-dimensional conductive pathway that can allow for improved lithium insertion and deinsertion kinetics. However, this material suffers from limited cyclability as a result of the energy barriers for removing lithium from the octahedral sites and capacity fading as a result of manganese dissociation. This work incorporates a multiple doping strategy for selecting capacity distribution across various voltage regimes. The resulting electrochemical cells are able to produce useful capacity at 5.2 V, 4.7 V, 4.1 V, and 2.75 V. Additionally, materials synthesized in a laboratory setting and via large scale production via licensing with no cobalt content has resulted in capacities exceeding 200 mAh/g. These materials achieve 75% capacity retention at 3C vs. C/10 discharge down to 2.75 V.

1.1 Introduction:

Lithium manganese spinel AB_2O_4 with B and O-site substitution of the general formula $\text{Li}_a\text{Mn}_{2-x-y-z}\text{Fe}_x\text{Co}_y\text{Ni}_z\text{O}_{4-d}\text{Cl}_d$ were synthesized via laboratory synthesis and large batch manufacturing via licensing and evaluated as a cathode for lithium ion batteries. The multiple-doping strategy introduces voltage control to allow for facile state-of-charge monitoring with enhanced capacity due to optimized interfacial interactions. The material properties were verified with x-ray diffraction, x-ray fluorescence, thermogravimetric analysis, and scanning electron microscopy. Button cells were fabricated to evaluate the performance of the $\text{Li}_a\text{Mn}_{2-x-y-z}\text{Fe}_x\text{Co}_y\text{Ni}_z\text{O}_{4-d}\text{Cl}_d$ cathode.

Background:

Lithium manganese oxide (LMO) spinel is a strong candidate for lithium-ion battery cathodes due to its high operational voltage, three-dimensional network of lithium pathways within the structure, low toxicity, reasonable capacity, and low cost of raw materials (1-3). However, LMO spinel suffers from diminished cycle life due to loss of crystallinity or fracturing of the structure either through the alternative phase formation or Jahn-Teller distortion (4-7). Historically, cycle life enhancements are achieved through stabilization of the spinel structure via

transition metal doping on the B-site of the lattice; creating disorder necessary to stabilize the lattice structure during cycling (7-15). Previously, we have demonstrated a stabilization of this structure can also be achieved with a chlorine dopant on the oxygen site that results in enhanced performance at voltages below 3.0V when homogeneously dispersed throughout the crystal, giving a desirable added capacity in a robust chemistry protected by this low voltage plateau (16-18). Additionally, when pairing single B-site dopants with the chlorine substitution on the O-site others have demonstrated enhanced rate capability and capacity (19-20).

Raw material's monetary and environmental cost must be taken into consideration when designing a novel cathode. An ideal cathode would limit scarce or unethically sourced materials like cobalt, and instead focus on considering inexpensive and available materials like iron. This effort focuses on the manganese substitution of up to three metals, iron, cobalt, and nickel, in order to stabilize the structure for further cycling while minimizing the need for cobalt incorporation. Several variations for $\text{Li}_a\text{Mn}_{2-x-y-z}\text{Fe}_x\text{Co}_y\text{Ni}_z\text{O}_{4-d}\text{Cl}_d$ will be presented that exhibit opportunities for 5.0+ V operation.

Experimental:

A wet chemical gel combustion method was used to synthesize metal-doped chlorinated lithium manganese oxide spinel. Stoichiometric amounts of $\text{Li}(\text{NO}_3)$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, a metal-chloride salt appropriate for each metal, $(\text{Fe}, \text{Co}, \text{and/or Ni})(\text{NO}_3)_n$, and a chelating agent (glycine or citric acid with ethylene glycol, Alfa Aesar/Sigma Aldrich) were dissolved into either an aqueous or ethanol solution. The solution was heated to evaporate the water and form a gel, which was heated further to 250 °C when auto ignition occurs. The resultant ash was fired between 600 – 700°C for 2 to 12 hours to achieve the desired lithium spinel phase. Alternatively, an acetate-based synthesis is performed with metal acetate salts less a chlorine or lithium additive dissolved in distilled water. NH_4OH is added to form a gel and is heated to evaporate the water. The gel is ignited above 200 °C and calcined at 400 °C in air. The resultant oxide is mixed with LiClO_4 and LiOH and ground in solid state prior to a final calcination at 600 °C for 4 hours. Alternatively, an optimized material of proprietary nature was prepared through a licensing partner available through NEI. Material characterization was performed using X-ray diffraction (Bruker D8 Advance, $\text{Cu-K}\alpha$) for structural verification, X-ray fluorescence (Bruker S2 Ranger) for chlorine content, thermogravimetric analysis and differential scanning calorimetry (Perkin Elmer STA 8000) was performed from 30 °C to 650 °C at a rate of 10°C per minute in argon on the precursor ash material, and scanning electron microscopy (JEOL JSM-IT100).

Experimental button cells were assembled using a lithium anode separated from the cathode by a nonwoven glass separator. Prepared active cathode materials were mixed with carbon black and polytetrafluoroethylene in a weight ratio of 85:10:5 of active to carbon to Teflon binder and calendared to 0.04 cm, punched into disks and pressed onto aluminum mesh opposite a Li metal anode cut from 0.075 cm thick lithium foil. CR2025 button cells were filled with glass fiber separators soaked with 1 M LiPF_6 in a proportional mixture of diethyl carbonate, dimethyl carbonate, and ethylene carbonate. Electrochemical characterization was performed on an ARBIN MSTAT4 battery cycler system controlled by MITS Pro software. The cells were charged and discharged from several voltages within 5.25 to 2.0 V to capture various oxidation/reduction

plateaus at high voltages (5.25 to 4.5 V), middle voltages (4.5 to 3.5 V), and low voltages (3.5 to 2.0 V). The charge/discharge rates varied from at 0.2 – 6.4 mA/cm² (C/10 – 3C rate). A rest period of 15 minutes between charge and discharge cycles was used to allow for cells to achieve equilibrium on all experiments.

Results and Discussion

Calcined lithium spinel powder will have different chemical compositions measured in x-ray fluorescence depending on our desired composition. For the various chlorination methods and independent of transition metal dopants, it is critical to determine if chlorine remains after structural formation as well as the amount of chlorine in the powder. Chlorinating the oxygen site has been shown to improve capacity retention, increase operational temperature range, increase capacity, and increase voltage range (21). The amount of Mn⁴⁺ in the lattice increases with increased chlorine content which limits Jahn Teller effects (20). Figure 1 shows an example of the XRF of a nickel, cobalt, iron, and chlorine doped powder and confirms chlorine is included after calcination using the citric acid method. In order to optimize the capacity achieved below 3V, it is important to have the optimized amount of chlorine in the lattice structure. We have previously shown when d=0.05, the capacity can be increased by 120 mAh g⁻¹ (16-18, 22). Optimizing the chlorine and transition metal amounts will be explored in the electrochemical performance.

Figure 1: X-ray fluorescence of a calcined chlorinated spinel with Ni, Co, and Fe as transition metal dopants. Silicon and phosphorous are included as system components measured during the experiment.

Figure 2: X-ray diffraction of a calcined chlorinated spinel with Ni, Co, and Fe transition metal dopants. LiMn_2O_4 00-035-0782 XRD peaks are included in the bottom of the Figure.

Calcination times and temperatures used during experimental procedures varied depending on the method used to make chlorinated spinel. Eliminating nonconductive impurities such as Li_2MnO_3 is critical to making a cathode material with high capacity. Figure 2 shows an example of the same chlorinated spinel powder seen in Figure 1. There are no secondary phases detected and is standard for all the experimental processes described herein.

The precursor material for the citric acid method was thermally characterized using TGA and DSC. Figure 3 displays the results where several stages of weight loss are seen which is typical of citric acid method (23). The peaks at 200°C are excess ethylene glycol breaking down and releasing while the peaks at 400°C are the polymeric chains decomposing, releasing the carbon and oxygen species. At 500°C, the spinel phase appears to begin stabilizing but at 610°C, LiCl appears to be melting. Breakdown of LiCl must take place for chlorination of the spinel lattice.

Figure 3: Thermogravimetric analysis (red) and dynamic scanning calorimetry (blue) results for the chlorinated spinel with Ni, Fe, and Co transition metal dopants.

Figure 4: A) Scanning electron microscope image of chlorinated spinel with transition metal dopants (Ni, Co, and Fe) and B) back scattered electron image of the same sample.

The Pechini method and glycine nitrate methods can form sub-micron powder after calcination (24). The SEM image in Figure 4a and the back scattered electron image in Figure 4b displays an example of the submicron powder formed during both processes. Surface morphology of sub-micron, single phase cathode material enhances the electrochemical performance, specifically the rate capability (25). The back scattered image confirms the XRD results in there are no secondary phases which will allow for high rate and long cycle life.

Figure 5A: Differential capacity from 3.5 to 5.25 V of $\text{LiMn}_{1.90}\text{Co}_{0.05}\text{Fe}_{0.05}\text{O}_{4-b}\text{Cl}_b$ and 5B) Discharge capacity for extended cycling from 4.5 to 3.5 V at 1 mA for 3 separate samples of varying weights of $\text{LiMn}_{1.72}\text{Co}_{0.22}\text{Fe}_{0.06}\text{O}_{4-b}\text{Cl}_b$.

Half-cell cycling between 5.25V and 3.5V with the stoichiometry of $\text{LiMn}_{1.90}\text{Co}_{0.05}\text{Fe}_{0.05}\text{O}_{4-b}\text{Cl}_b$ activates the transition metals within the lattice. Figure 5A displays the differential capacity vs. voltage plot where stability of the upper voltages (5.25V to 3.5V) is confirmed over 10 cycles. There are no horizontal shifts in peaks or decrease in magnitude of the peaks, both of which would signal an increase in cell resistance or lattice degradation.

Extended cycling data was performed for $\text{LiMn}_{1.72}\text{Co}_{0.22}\text{Fe}_{0.06}\text{O}_{4-b}\text{Cl}_b$ across a moderate voltage regime from 4.5 to 3.5V due to the known vulnerability of electrolyte above 4.5 V as a result of oxidation at the electrode surface (27-28). Figure 5B demonstrates the ability of the material to maintain performance at a cycle life that is relevant for military application. It is worth noting that the capacity is low due to the amount of remaining capacity above 4.5 V that is not captured. Due to the limitations of the knowledge gained from this data, electrolytes with higher voltage stability are incredibly important for advancing this research and demonstrating endurance of the material across the full voltage regime. Studies are ongoing for finding an appropriate electrolyte that would enable this research and performance.

Figure 6: Charge capacity (dashed) and delivered discharge capacity (dotted) for cycles 1-20 of coin cell containing $\text{Li}_a\text{Mn}_{1.89}\text{Fe}_{0.1}\text{Co}_{0.11}\text{O}_{4-d}\text{Cl}_d$ Cathode.

One aspect of particular interest is the accessibility of enhanced capacity at various voltages. This is useful for being able to tailor the chemistry to a desired plateau length for accurate state of charge measurements. In a military environment, precision in this regard is of paramount importance. In Figure 6, electrochemical cycling data at 1 mA charge and discharge rates (approximately C/10) is presented where $\text{Li}_a\text{Mn}_{1.89}\text{Fe}_{0.1}\text{Co}_{0.11}\text{O}_{4-d}\text{Cl}_d$ is the active cathode material and lithium is the active anode material. For this example, the cell was initially cycled between 4.5 V and 3.5 V for ten cycles. For the next three cycles, the cell was cycled between 5.25 V and 3.5 V. The next three cycles included a deep discharge between 5.25 V and 2.25 V before returning to cycling between 5.25 V and 3.5 V. The cycle plots indicate a minimal loss of capacity when cycling between the aforementioned voltages. When discharging deep, there is a 50% increase in capacity and the return to high voltage charging without the deep discharge indicates the material is reversible and does not undergo permanent structural deformation. Importantly, a two-fold

increase in capacity is shown when cycling to 4.5V (cycles 1-10) vs. 5.25V (cycles 11-13). Furthermore, on cycle 14 the cell delivers 246 mAh/g when the voltage regime deepens further to 2.25V on discharge. The benefit here is two-fold; the cell has access to added capacity in emergent environments and the cell is protected from over discharge conditions allowing for recovery when operating at the traditional 3.7 V nominal voltage.

Figures 7A and 8A show the charge/discharge curves, and Figures 7B and 8B show the subsequent differential capacity curves for two cobalt free variants of the spinel cathode material discussed in this paper. The charge and discharge current was maintained at 1 mA: this corresponds to $\sim 500\mu\text{A}/\text{cm}^2$, $\sim 15\text{ mA/g}$ active or $\sim \text{C}/20$. The formulas for the example spinel materials are $\text{LiMn}_{1.54}\text{Fe}_{0.12}\text{Ni}_{0.34}\text{O}_{4-d}\text{Cl}_d$ and $\text{LiMn}_{1.34}\text{Fe}_{0.08}\text{Ni}_{0.58}\text{O}_{4-d}\text{Cl}_d$, respectively. Figures 7A and 8A show three thermodynamic plateaus during charge and discharge. These plateaus are at approximately 4.5-5.0 V, 3.5-4.5 V, and 2.5-3.5 V. When the data is displayed as a differential capacity trace Figures 7B and 8B, it reveals that the 4.5-5.0 V thermodynamic region can also be divided further to allow for the resolution of two regions within the 4.5-5.0 V plateau. Comparing the data from the two formulations, the 3.5-4.5 V thermodynamic region is enhanced at the expense of the 4.5-5.0 V region, as the nickel content is reduced from a 0.58 to a 0.34 stoichiometry. This electrochemical behavior allows for the formulation of a cathode that has built-in state of charge calibration points.

Through the Capability Needs Analysis (CNA) process, the U.S. Army derives a list of specific Warfighter requirements that are not currently being met. These requirements are known as CNA gaps. Two power- and energy-related CNA gaps require accurate monitoring to increase awareness and management of power (26). The development of an effective battery diagnostic/prognostic device directly addresses both of these gaps. Tables 1 and 2 demonstrate example state of charge calculations using the built-in calibration points for electrochemical cells with $\text{LiMn}_{1.54}\text{Fe}_{0.12}\text{Ni}_{0.34}\text{O}_{4-d}\text{Cl}_d$ and, $\text{LiMn}_{1.34}\text{Fe}_{0.08}\text{Ni}_{0.58}\text{O}_{4-d}\text{Cl}_d$ respectively. Indexing lines to aid in the visualization of this property are included in Figures 7 and 8. The bold values in the tables represent the shift in the state of charge as a result of tailoring the cathode composition. The ability to adjust state of charge indicators to meet specific applications needs is of great value to the user.

There is a trend in research to reduce the amount of cobalt present in lithium-ion batteries due to potential global shortages, high costs, and unethical sourcing (29-30). With the prevalence of LiCoO_2 in traditional lithium-ion batteries, the impact of a supply shortage of cobalt would be detrimental. Additionally, from a national defense standpoint, any offshore supply chain is cause for concern. The data presented in Figures 7 and 8 represent suitable solutions that do not contain cobalt. These two cobalt-free chemistries exhibit greater than 200 mAh/g capacity, achieving >85% of the capacity for the cobalt-containing variant.

Table 1 Remaining capacity of cells with C5ISR $\text{LiMn}_{1.54}\text{Fe}_{0.12}\text{Ni}_{0.34}\text{O}_{4-d}\text{Cl}_d$. Charged and Discharged at 1 mA: $\sim 500\mu\text{A}/\text{cm}^2$, $\sim 11\text{mA}/\text{g}$ active

Cell Potential (V)	Capacity Remaining (Ah/g active cathode)	State of Charge (%)
5.0	0.210	100
4.7	0.184	87.6
4.4	0.137	65.2
3.5	0.089	42.4
2.25	0	0

Figure 7A: Charge and discharge curves from cycles 12-15 of $\text{LiMn}_{1.54}\text{Fe}_{0.12}\text{Ni}_{0.34}\text{O}_{4-d}\text{Cl}_d$ and 7B) Differential capacity curves from the same data set.

Table 2. Remaining capacity data of cells with C5ISR $\text{LiMn}_{1.34}\text{Fe}_{0.08}\text{Ni}_{0.58}\text{O}_{4-d}\text{Cl}_d$. Charged and Discharged at 1 mA ~ 500uA/cm², ~14mA/g active

Cell Potential (V)	Capacity Remaining (Ah/g active cathode)	State of Charge (%)
5.0	0.205	100
4.7	0.170	82.9
4.4	0.110	53.7
3.5	0.099	48.3
2.25	0	0

Figure 8A: Charge and discharge curves from cycles 12-15 of $\text{LiMn}_{1.34}\text{Fe}_{0.08}\text{Ni}_{0.58}\text{O}_{4-d}\text{Cl}_d$ and 8B) Differential capacity curves from the same data set.

Figure 9 shows data comparing two C5ISR cathode formulations with cathode material of proprietary nature that was prepared through a licensing partner and available through NextGen Battery Technologies, LLC and their affiliate NEI Corporation under the name LMOX. The data presented is normalized to approximant stoichiometry for the active material. Stoichiometry (X in $\text{Li}_x(\text{MnFeNi})_2\text{O}_{4-d}\text{Cl}_d$ cathode material was determined using the following assumptions. The theoretical capacity of the material was set at 280 mAh/g and X=1 for Li_x in $\text{Li}_x(\text{MnFeNi})_2\text{O}_{4-d}\text{Cl}_d$ at a cell potential of 3.0V. The figure shows the customization of the electrochemical couple as well as the robustness of the manufacturing process. Data displayed in this graph are representative of material made via laboratory scale wet chemical gel combustion method and acetate-based

hydrothermal solid-state synthesis method formulated at the C5ISR laboratory; and via manufacturing scale methods through NextGen Battery Technologies, LLC and their affiliate NEI Corporation. One noticeable variation in the data is a reduction of capacity for the LMOX100. This is likely due to an excess of one of the dopants contained within the material interfering with further reaction. Adjustments to the dopant concentration will be made in future work.

Figure 9: Comparison of two different stoichiometries of C5ISR Data and similar LMOX Capacity Data at a C/10 rate. The curves are shifted to align at the 3.5 V knee representing lithium stoichiometry of unity.

Figure 10: Electrochemical performance of LMOX100 when varied from 0.2 to 6.4 mA discharge displayed as A) discharge curves and B) differential capacity.

Figure 11: Electrochemical performance of LMOX101 when varied from 0.2 to 6.4 mA discharge displayed as A) discharge curves and B) differential capacity.

Figures 10A and 11A display the charge/discharge curves, and Figures 10B and 11B display the subsequent differential capacity curves for two cobalt free variants of the spinel cathode material of proprietary nature that was prepared through a licensing partner and available through NextGen Battery Technologies, LLC and their affiliate NEI Corporation under the name LMOX. For these performance traces the charging current was maintained at 200 μA , this corresponds to $\sim \text{C}/10$ and the discharge current ranged from 200 μA to 6400 μA . Two formulations LMOX100 and LMOX101 are represented in Figures 10 and 11, respectively. Each possessing unique retention of capacity at varying rates where LMOX 101 has less capacity retention (90mAh g^{-1} at $\sim 3\text{C}$) during discharging but achieves 180mAh g^{-1} at $\text{C}/10$ discharges. However, LMOX 100 retains slightly more capacity at high discharge rates (100mAh g^{-1} at $\sim 3\text{C}$) but achieves less capacity (160mAh g^{-1}) during $\text{C}/10$ discharges.

Half-cell cycling demonstrates the rate capability of the LMOX material. The data presented in Figures 10A and 11A determine the rate capability and the high capacity achieved when the cells is charged to 5.0 Volts. Particular attention should be placed on the charge portion of the differential capacity traces for the material. This data collected during the 200 μA charge shows the stability of the LMOX crystal structure as the traces are comparable during the entire 30 cycle test regime. This stability is maintained during high discharge and charge rates at voltages to 5.0V.

The LMOX material and the laboratory made chlorinate spinel have similar properties but LMOX has rate capabilities confirmed experimentally. Additionally, the ability of the licensing partner to manufacturer material in larger quantities. Allowing us to package these materials into pouch cells for more representative data with production-ready separators rather than the glass mat used in these samples. We anticipate further research and analysis in order to present that work in the future.

Conclusion:

Electrochemical data is presented for B-site dopants with two or more of the metals iron, cobalt and/or nickel. The results demonstrate an enhanced high voltage operation above 5.0 V coupled with a deep discharge capability below 3.0 V. This material ($\text{Li}_{1.89}\text{Mn}_{1.89}\text{Fe}_{0.1}\text{Co}_{0.11}\text{O}_{4-\text{d}}\text{Cl}_{\text{d}}$) demonstrates a very high capacity of 246mAh/g . In the case of $\text{Li}_{1.54}\text{Mn}_{1.54}\text{Fe}_{0.12}\text{Ni}_{0.34}\text{O}_{4-\text{d}}\text{Cl}_{\text{d}}$, a cobalt-free cathode material exhibits a capacity of 210mAh/g from 5.0V to 2.25V. This is among the highest reported for cobalt-free and low cobalt cathodes including layered cathodes like $\text{Li}[\text{Ni}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}]\text{O}_2$ and $\text{Li}[\text{Ni}_{0.9}\text{Mn}_{0.1}]\text{O}_2$ recently reported at 236mAh/g at increased temperature $30\text{ }^{\circ}\text{C}$ and 208mAh/g for the cobalt free variant with $\text{C}/2$ cycling at $30\text{ }^{\circ}\text{C}$ (31).

The material introduces the ability to select voltage regimes for built-in calibration of state of charge. This is critical in a tactical environment where remaining battery life must be accurate for mission planning and reliable execution. Additionally, the lower voltage plateau below 3.0V offers protection for the chemistry from over-discharge without detrimental impact to the cell as demonstrated by repeated cycling down to 2.25 and 2.0 V. This material is capable of large scale manufacturing and demonstrates high capacity and maintenance of the distinct voltage regimes for future application in state of charge monitoring.

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