A Study of Stacking Faults and Superlattice Ordering in Some Li-Rich Layered Transition Metal Oxide Positive Electrode Materials

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Li-rich layered transition metal oxides such as Li2(Fe1/3Mn2/3)O2 have in-plane ordering between the excess Li atoms and the transition metal (TM) atoms in the transition metal layer. The √3a × √3a superlattice in the TM layer causes superlattice Bragg peaks in their X-ray diffraction patterns. This article describes the relation between the metal composition of the materials, stacking faults and superlattice ordering. The XRD patterns were fitted with a program called FAULTS, which treats the effect of stacking faults on the superlattice peak shapes. The superlattice peak positions of Li2(Fe1/3Mn2/3)O2 materials changed monotonically with Ni content (x), as did the positions of the main diffraction peaks of the base structure. This proves that the superlattices peaks originate from the Li2(Fe1/3Mn2/3)O2 solid solution and are not caused by any domains of second phase such as Li2MnO3. Fitting the XRD patterns with FAULTS revealed that the stacking fault probability increased monotonically with Ni content.

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Manuscript submitted March 7, 2016; revised manuscript received April 20, 2016. Published April 30, 2016.

Li-rich positive electrode materials (e.g. Li1/2Ni0.5Mn0.5O2, Li1/2MnO2) are potential candidates for high energy density Li-ion batteries.1–3 They are capable of delivering reversible specific capacities up to 250 mAh/g,4 at an average discharge potential of ~3.5 V vs Li metal.5 Understanding the structure of Li-rich materials is essential to improving their properties and performance. Li-rich materials are layered transition metal (TM) oxides comprised of alternating layers of metal atoms (Li or TM) and oxygen atoms.7 Compared to non-Li-rich layered transition metal oxides such as LiCoO2, the Li/TM ratio is greater than 1 for Li-rich layered transition metal oxides and usually Li ions occupy the TM layer in addition to the Li layer.8 Li2MnO3 is a typical example of such a material in which 1/3 of the Li atoms occupy sites in the TM layer.

Li-rich layered transition metal oxides can be defined as O3 structures with A-B-C-A-B-C stacking but the arrangement of the atoms in the TM layer results in superstructure Bragg peaks in the range of √3a × √3a superstructure or superlattice9 and changes the symmetry from R-3m to C2/m. The superlattice ordering in the TM layer results in superstructure Bragg peaks in the range of √3a × √3a space group.10 Overall, any random stacking sequence was better for superstructure reflections characterization techniques such as solid-state NMR11 and EXAFS12 have also been used to study the superlattice ordering.

Stacking disorder of the TM layers along the c axis or “stacking faults” strongly affects the shape of the superlattice peaks in the diffraction patterns. Boulieu et al. have demonstrated the existence of stacking faults in the structure of Li1/2MnO3 using high resolution transmission electron microscopy.13 In their XRD patterns of Li1/2MnO3, the broadening of some selective Bragg peaks was attributed to stacking faults. The extent of superlattice peak broadening increases with increasing probability of stacking faults.

In a separate study, Boulieu et al. have simulated the XRD pattern of Li1/2MnO3 with varying stacking fault probabilities using a program called DiffaX.14 Lu et al. have also used DiffaX to simulate the XRD patterns of Li1/2MnO3 that contained stacking faults.15

In both those studies, the authors compared simulated XRD patterns to experimental ones but did not do fitting to the experimental patterns. Recently, McCalla et al. have used a program called FAULTS, which is similar to DiffaX, allows a complete fit to the experimental diffraction pattern. McCalla et al. studied the stacking faults in Li2FeSiO4.16 There has been no study using FAULTS to fit the XRD data of Li2(Fe1/3Mn2/3)O2 materials to quantify the stacking fault probability. In this work, the XRD patterns of Li2MnO3 as well as Li2(Fe1/3Mn2/3)O2 materials have been fit using FAULTS and the results are shared.

Different stacking sequences of the TM layers along the c axis in Li2MnO3 that generate different space groups have been proposed previously. Breger18 and Meng9 et al. have explained two different ways of stacking – A1-B1-C2 corresponding to C2/m and A1-B1-C2A1-B1 corresponding to P312 space groups. Based on these two stacking sequences, they have simulated the XRD patterns of Li2MnO3 using DiffaX and found that the C2/m stacking scheme was better for estimating the stacking fault probabilities. According to Meng et al., the stacking sequences that generate the P312 space group are due to an abnormality in the C2/m sequence. Riou et al. have proposed an A1-B1-C2A2-B3-C1 stacking sequence to explain the structure of Li2MnO3 in terms of a C2/c space group.19 Overall, any random stacking sequence is possible owing to the negligible energy difference between the sequences. In this work, stacking faults were selected randomly with varying probabilities.

Stacking faults in Li-rich layered transition metal oxides are affected by the synthesis temperature.20 Several researchers have already reported that Li2MnO3 synthesized at low temperature has high probability of stacking faults.21 In particular, Boulineau et al. have suggested that synthesizing an ideal Li2MnO3 with the absence of stacking faults is impossible.15 It would be useful to understand the effect of metal composition on the stacking faults. Here, the composition of the TM layer (presence of ions such as Ni2+) was studied as a factor that affects the probability of stacking faults. The focus of this article is to study the effect of metal composition on the superlattice ordering and stacking faults in Li2(Fe1/3Mn2/3)O2 materials.

Experimental

Mixed transition metal carbonate precursors (example: Ni(II)0.3Mn(II)0.7CO3) were synthesized through co-precipitation. The reaction was started with an aqueous solution of 0.1 M NH4OH to continuously stirred tank reactor (CSTR). NH4OH was used as a source of NH3 ligand for TM coordination to facilitate the formation

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of spherical particles.\textsuperscript{22,23} The temperature of the reaction was held at 60°C and the pH was maintained at 8 by adding appropriate amounts of acid (H\textsubscript{2}SO\textsubscript{4}) or base (NaOH). A 2M aqueous solution of the mixed TM sulfate solutions and an equimolar solution of sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) were pumped at a desired flow rate. After the completion of the reaction, the resulting suspension was collected and washed several (5) times with distilled water. Then it was filtered and the resulting product (Ni\textsubscript{x}Mn\textsubscript{1-x}CO\textsubscript{3}) was dried in an oven at 100–120°C in air for ∼12 h.

The Li[Li\textsubscript{1/3}-2x/3NixMn\textsubscript{2/3-x/3}]O\textsubscript{2} compounds were synthesized by adding stoichiometric amounts of Ni\textsubscript{0.5}Li\textsubscript{0.5}CO\textsubscript{3} precursors and Li\textsubscript{2}CO\textsubscript{3}. A 5 wt% excess of Li\textsubscript{2}CO\textsubscript{3} was added to compensate for Li loss in the high temperature sintering process. The reactants were weighed accurately, mixed, ground well using a mortar and pestle and calcined in air at 900°C to yield the product. The heating and cooling profiles were followed as reported in reference.\textsuperscript{5} The elemental composition of the synthesized materials was obtained using inductively coupled plasma optical emission spectroscopy (ICP-OES).

A powder X-ray diffraction (XRD) pattern for each sample was collected using a Siemens D5000 diffractometer equipped with a copper target X-ray tube and a diffracted beam monochromator. The program “FAULTS” was used for the stacking faults calculation\textsuperscript{25} as well as to fit the XRD data. The program FAULTS considers the layered arrangements of the structure and fits the structure based on a recursive algorithm/method\textsuperscript{25} as explained by Treacy et al. Parameters corresponding to unit cell dimensions, the peak shape, scale factor and the stacking faults probability were refined.

\section*{Results and Discussion}

\textbf{Li\textsubscript{2}MnO\textsubscript{3}.—}Li\textsubscript{2}MnO\textsubscript{3} serves as an ideal model for describing superlattice ordering and stacking faults. Figure 1 shows the structure of Li\textsubscript{2}MnO\textsubscript{3}, in which the boundaries of the monoclinic (C2/m) and hexagonal unit cells (R-3m) have been indicated to highlight the correlation between their atomic arrangements. The unit cells have been slightly tilted and the oxygen atoms are not drawn to scale (smaller) for clear visualization. Equation 1 shows the relation between the monoclinic unit cell and the hexagonal unit cell.

\[
\begin{pmatrix}
\bar{a} & \bar{b} & \bar{c} \\
-2 & 0 & 2/3 \\
-1 & -3 & 1/3 \\
0 & 0 & 1/3
\end{pmatrix}
\]

The stacking faults in Li\textsubscript{2}MnO\textsubscript{3} (as well for Li[Li\textsubscript{1/3}-2x/3NixMn\textsubscript{2/3-x/3}]O\textsubscript{2}) arise from the stacking disorder of the TM layer along the c axis. The top panel of Figure 2 shows a triangular lattice plane, labeled as A1, corresponding to the TM layer of Li\textsubscript{2}MnO\textsubscript{3}. The plane A1 is formed by 1/3 Li (green balls) and 2/3 Mn atoms (pink balls) and it is easy to identify the ordering in the TM layer. The top panel of Figure 2 shows a 2-D hexagonal unit cell of the plane A1.

Referring to the hexagonal 3-D unit cell of Li\textsubscript{2}MnO\textsubscript{3} shown in Figure 1, the very bottom TM layer is considered to be A1 (the starting layer). Since Li\textsubscript{2}MnO\textsubscript{3} can be considered as an O3 structure, the TM layer shifts 3 times within one hexagonal 3-D unit cell. With reference to A1, the stacking of the next TM plane follows a (1/3, 1/3, 1/3) translation in fractional atomic coordinates in accordance with the O3 structure. As a result, the next TM plane, labeled B1, is placed on top of A1. The plane B1 has been constructed by atoms designated by triangles in Figure 2. A subsequent (1/3, 1/3, 1/3) translation from B1 results in a TM layer called C1, in which the atoms are designated as stars in Figure 2. The bottom left and right panels of Figure 2 show the A1 to B1 and B1 to C1 translations, respectively. The A1 to B1 and B1 to C1 translations can be easily understood by following the 2-D hexagonal unit cells in the bottom right panel of Figure 2. If the TM layer stacking perfectly follows the trend A1-B1-C1-A1-B1-C1,..., then there are no stacking faults in the structure. The origin of the stacking faults of these layered Li-rich materials arises only from stacking mistakes in the TM layers whereas the oxygen layers are always in their ideal positions and are not involved in the stacking disorder along the c-axis. In other layered materials, the entire MO\textsubscript{2} slab may be involved in stacking disorder, but that is not the case here.

The XRD pattern of such an ideal structure of Li\textsubscript{2}MnO\textsubscript{3} with zero stacking faults was simulated using FAULTS. The program FAULTS considers the whole structure under investigation as series of layers stacked in a defined sequence and calculates the diffraction pattern based on first principles.\textsuperscript{26} Figure 3 shows the XRD pattern of Li\textsubscript{2}MnO\textsubscript{3} with 0% stacking faults obtained from a FAULTS simulation that considers only the A1-B1-C1-A1-B1-C1 stacking of the TM layers. The simulation was made using the unit cell parameters of Li\textsubscript{2}MnO\textsubscript{3} reported by Boulineau et al.\textsuperscript{14} All the peaks in the simulated XRD patterns can be indexed using a C2/m space group. Figure 3 shows that the superlattice peaks (indicated by the red boxes) are as sharp as the other peaks.

The stacking of TM layers in real samples of Li\textsubscript{2}MnO\textsubscript{3} as well as for Li[Li\textsubscript{1/3}-2x/3NixMn\textsubscript{2/3-x/3}]O\textsubscript{2} involves stacking disorder along the c-axis. In addition to the (1/3, 1/3, 1/3) translation, two other translations are possible: (2/3, 0, 1/3) and (0, 2/3, 1/3), which can create two more triangular lattice planes. For example, the next stacking layer above A1 could be B2 or B3. Figure 4 shows the A1 to B2 and A1 to B3 translations. Thus a total of 9 triangular lattice plane variants, A1, B1, C1, A2, B2, C2, A3, B3 and C3 can be involved in the TM layer stacking sequence. In a structure with stacking faults, the TM layer stacking does not follow the ordered A1-B1-C1... sequence. Instead, a disordered stacking sequence occurs, which involves all the 9 triangular lattice plane variants in various probabilities. For example, a disordered stacking could be A1-B2-C3-A2-B1-C2...

The probabilities of all the 9 triangular lattice variants determine the extent of stacking faults or the stacking fault probability. The transition metal layers always follow the A-B-C-A-B-C... sequence irrespective of the probability of each triangular layer variant. FAULTS simulations were done by including all three translation vectors with appropriate probabilities. Two essential constraints were invoked for the simulations – (i) the sum of the probabilities for all the translations should be one and (ii) the probabilities of the (2/3, 0, 1/3) and (0, 2/3, 1/3) stacking fault translations were constrained to be equal. For a structure with 100% stacking faults, the probabilities of all three translations (1/3, 1/3, 1/3), (2/3, 0, 1/3) and (0, 2/3, 1/3) must be equal to 1/3. In general, the stacking fault probability, s, can be calculated from any set of translation probabilities using Equation 2 below. For example, a set of probabilities of 0.6, 0.2 and 0.2 for the translation vectors (1/3, 1/3, 1/3), (2/3, 0, 1/3) and (0, 2/3, 1/3) respectively would result in 60% stacking faults in the structure. Table 1 shows several sets of probabilities of translation vectors and the expected stacking fault probabilities, s.

\begin{equation}
\text{Stacking fault probability } s = \frac{(1 - P_{11})}{2/3} \times 100\%
\end{equation}

where P_{11} = the probability of the (1/3, 1/3, 1/3) translation.
Figure 2. TM layers of Li$_2$MnO$_3$ made up of pink (Mn) and green (Li) balls (A1), triangles (B1) and stars (C1). Bottom left panel: A1 to B1 translation. Bottom right panel: B1 to C1 translation. The black, red and the blue hexagonal 2-D unit cells correspond to the A1, B1 and C1 TM layers.

Figure S1 shows the simulated XRD patterns of Li$_2$MnO$_3$ with varying stacking fault probabilities. As the stacking fault probability increases from 0% to 100%, the broadening of the superlattice peaks increases simultaneously. At the same time, the increase in stacking fault probability does not have any effect on the other Bragg peaks. Figure S2 shows the simulated XRD patterns of Li$_2$MnO$_3$ with varying stacking fault probabilities but only in the range between 20$^\circ$ to 35$^\circ$. The superlattice peaks of the structure with 0% stacking faults have a clear 3-D peak signature but they gradually change to a 2-D type peak for the structure with 100% stacking faults. Thus the extent of broadening of the superlattice peaks should be taken as a direct measure of the probability of stacking faults.

The occurrence of stacking faults in two samples of Li$_2$MnO$_3$ were analyzed – one made at 1100$^\circ$C (LM1100) and other at 900$^\circ$C (LM900). Figure 5 shows the XRD patterns of both LM1100 and LM900 and the inset shows the comparison of their superlattice peaks.

Figure 3. Simulated XRD patterns of Li$_2$MnO$_3$ with 0% stacking faults.
between 20° and 35°. The superlattice peaks of LM1100 are quite sharp but with very slight broadening observed at the bottom of the (020), (110) and (−111) peaks. On the other hand, obvious SL peak broadening due to the occurrence of stacking faults was observed for Li₂MnO₃ synthesized at 900°C. However, the shape of other peaks (R-3m reflections) are quite similar for both the samples implying the absence of any other broadening effects. To quantify the stacking fault probability in both the samples, FAULTS fitting was done on their XRD patterns. Figures 6a and 6b show the FAULTS fitting results for LM1100 and LM900. The insets show an enlarged view of the superlattice peak region. FAULTS results revealed a ~10% stacking fault probability for LM1100 and a ~30% stacking fault probability for LM900. An increase in the stacking faults for the sample synthesized at low temperature is consistent with the results reported by Breger et al. However, they reported only a 2% stacking faults probability for a sample of Li₂MnO₃ synthesized at 1000°C. It may be that simulation, by contrast to fitting, underestimated the probability of stacking faults in their methods.

**Li[Li₁/₃₋₂x/₃NiₓMn₂/₃₋x/₃]O₂**—The structural and electrochemical properties of materials from the Li[Li₁/₃₋₂x/₃NiₓMn₂/₃₋x/₃]O₂ series were first reported by Lu et al. Table II shows the ICP-OES composition of the studied Li[Li₁/₃₋₂x/₃NiₓMn₂/₃₋x/₃]O₂ samples. The Ni content (x) increased from sample LM900 to LMN3, which has a composition close to LiNi₀.₅Mn₀.₅O₂. Figure S3 shows the XRD patterns of the

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**Figure 4.** TM layers of Li₂MnO₃ showing A1 to B2 translation (Left panel) and A1 to B3 translation (Right panel).

**Figure 5.** XRD patterns of Li₂MnO₃ synthesized at 900°C (LM900) and 1100°C (LM1100). Inset: Enlarged view in the range of 20° to 33°.

**Figure 6.** Experimental (red points), the calculated (black line) XRD patterns of LM900 and LM1100 obtained from Rietveld refinement and their difference (green line).
studied Li[Li\(_{1/3-2x/3}Ni_{x}Mn_{2/3-x/3}\)]O\(_2\) samples. The XRD pattern at the top represents sample LM900 whereas the one at the bottom of the stack represents the sample LNM3. All the samples were O3 structures (α-NaFeO\(_2\)) and most of the diffraction peaks could be indexed using the R-3m space group except for the broad superlattice peaks between 20\(^\circ\) to 30\(^\circ\). Figure S3 (right panel) shows an enlarged view of the (003) peaks (R-3m) that occur around 18.6\(^\circ\). The (003) peak position shifted from higher to lower angle (black dotted line in Figure S3) as x (Ni content) increased from LM900 to LNM3 due to an increase in the fraction of larger Ni\(^{2+}\) ions. The (003) peak shift suggests a solid-solution behavior.

This section discusses aspects of the superlattice peaks of the materials in the Li[Li\(_{1/3-2x/3}Ni_{x}Mn_{2/3-x/3}\)]O\(_2\) series. Some researchers consider the Ni, Mn and Co containing Li-rich layered transition metal oxides compounds as solid solutions between layered Li[Li\(_{1/3}Mn_{2/3}\)]O\(_2\) (or Li\(_2MnO_3\)) and layered LiMO\(_2\) structures such as Li[NI\(_{1.0}Mn_{0.5}\)]O\(_2\). For example, one mole of Li[Li\(_{1.0}Ni_{0.5}Mn_{0.5}\)]O\(_2\) is a solid solution formed by 0.6 moles of Li[Li\(_{1/3}Mn_{2/3}\)]O\(_2\) and 0.4 moles of Li[NI\(_{1.0}Mn_{0.5}\)]O\(_2\). Alternatively, some other researchers consider these materials as composites made up of two separate layered phases. Shukla et al. have recently investigated the microscopic structure of a Ni, Mn and Co containing Li-rich layered transition metal oxides materials and reported that they are pure solid-solutions.

Figure 7 shows the XRD patterns of the studied Li[Li\(_{1/3-2x/3}Ni_{x}Mn_{2/3-x/3}\)]O\(_2\) samples in the range of 20\(^\circ\) to 34\(^\circ\) that represent the superlattice peaks. Only the first superlattice peak (020) that belongs to the C2/m space group and occurs around 20.5\(^\circ\) has been considered for peak position analysis. For samples LNM2 and LNM3, the intensities were scaled up slightly for the purpose of clarity. The (020) peak positions from sample LM900 to LNM3 shift from higher to lower scattering angle as the Ni content increases and has been indicated with a dashed line in Figure 7. The (020) peak position shift with increased Ni content for the materials in the Li[Li\(_{1/3-2x/3}Ni_{x}Mn_{2/3-x/3}\)]O\(_2\) series also suggests the solid solution behavior as expected from the (003) peak shift belonging to the non-superlattice reflections.

The position of the non-superlattice C2/m (33-1) peak (corresponds to the R-3m (110) peak) occurring around 65\(^\circ\) and the superlattice C2/m (020) peak occurring around 20\(^\circ\) were compared from samples LM900 to LNM3. The peak positions (20) were converted into d-spacings using Bragg’s law. Table III shows the 20 (020) and (33-1) peak positions obtained from the XRD patterns (Cu K\(_{\alpha}\)) of the studied samples in the Li[Li\(_{1/3-2x/3}Ni_{x}Mn_{2/3-x/3}\)]O\(_2\) series.

### Table III. (020) and (33-1) peak positions obtained from the XRD patterns (Cu K\(_{\alpha}\)) of the studied samples in the Li[Li\(_{1/3-2x/3}Ni_{x}Mn_{2/3-x/3}\)]O\(_2\) series.

| Sample | 20 (020) | 20 (33-1) |
|--------|----------|-----------|
| LM900  | 20.87\(^\circ\) | 65.62\(^\circ\) |
| LNM1   | 20.85\(^\circ\) | 65.55\(^\circ\) |
| LNM3   | 20.75\(^\circ\) | 65.15\(^\circ\) |
| LNM5   | 20.65\(^\circ\) | 64.73\(^\circ\) |

**Superlattice peak broadening.**—The cause of superlattice peak broadening in the diffraction patterns of Li-rich layered transition metal oxide materials has been a subject of debate. Believers in the composite\(^{32}\) nature of these materials contend that nano-domains of Li\(_2MnO_3\) cause the broadened SL peaks.\(^{33,34}\) On the other hand, believers in the solid solution argue that the SL peak broadening must be attributed to the stacking faults along the c axis.\(^{15,35}\)

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**Figure 7.** XRD patterns showing only the superlattice peaks in the range of 20\(^\circ\) to 25\(^\circ\) of the studied samples in the Li[Li\(_{1/3-2x/3}Ni_{x}Mn_{2/3-x/3}\)]O\(_2\) series. The black dotted line connects the (020) peaks of the shown XRD patterns.

**Figure 8.** d-spacings of C2/m peaks (33-1) vs. (020) of the studied samples in the Li[Li\(_{1/3-2x/3}Ni_{x}Mn_{2/3-x/3}\)]O\(_2\) series.
In the earlier parts of this paper the superlattice peak broadening in Li$_2$MnO$_3$ was attributed to stacking faults. In the same way, Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ materials exhibit stacking faults. The probability of stacking faults in Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ is comparatively high due to the additional presence of Ni$^{2+}$ ions in the TM layers. Boulineau et al. have pointed out that a decrease in the long-range in-plane ordering would lead to sluggish ordered stacking along the $c$-axis. When there are Ni$^{2+}$ ions in the TM layer of Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$, the ratio between the large ions (Li$^+$, Ni$^{2+}$) and the small ions (Mn$^{4+}$) deviates from the ideal value (1:2) in Li$_2$MnO$_3$. The substitution of Ni$^{2+}$ in the TM layer will, therefore, likely affect the 2-D ordering between Li, Ni and Mn ions in the TM layers, which in turn can increase the probability of the stacking disorder along the $c$ axis. Hence it is very likely to observe superlattice peak broadening in Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ materials.

Figure 9 shows the FAULTS fitted XRD patterns of samples LM900 to LNM3 whereas Figure 10 shows only the superlattice region from 20$^\circ$ to 28$^\circ$. The red points and the black solid lines represent the data points and the calculated patterns, respectively. As the concentration of Ni increases, the broadening of the SL peaks increased due to an increase in the stacking fault probability. Figure 11 shows the stacking fault probability plotted versus the Ni content. This plot clearly demonstrates how the presence of Ni$^{2+}$ ions in the TM layer influences the probability of stacking faults. For the sample LNM3, the superlattice peak broadening with change in the stacking faults probability is very subtle due to the very weak superlattice peaks. Hence the uncertainty of the stacking faults probability reported for LNM3 is higher.

**Conclusions**

The superlattice peak broadening in the XRD patterns of layered Li-rich transition metal oxides has been examined. First, by using a fitting program called FAULTS, which can take into account the existence of stacking faults, the XRD patterns of Li$_2$MnO$_3$ were simulated and fitted. The fitting results revealed that the stacking disorder along the $c$ axis (stacking faults) is the underlying reason for the superlattice peak broadening. Similarly, the XRD patterns of Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ materials were also examined. The superlattice peak positions of Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ materials changed monotonically with Ni content, as did the main peaks, demonstrating that the superlattice peaks originate from solid solutions and are not caused by any separate phase such as Li$_2$MnO$_3$ in a composite.

FAULTS results on Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ materials showed that stacking fault probability increased with Ni content. Hence, it is believed that presence of aliovalent ions such as Ni$^{2+}$ in the TM layer can perturb the stacking order along the $c$-axis and thus the broadening of the superlattice peaks of Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ materials. It is

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**Figure 9.** Experimental (red points) and the FAULTS fitted (black line) XRD patterns of the studied samples in the Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ series.

**Figure 10.** Experimental (red points) and the FAULTS fitted (black line) XRD patterns in the superlattice region (20$^\circ$ to 28$^\circ$) of the studied samples in the Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ series.

**Figure 11.** Stacking faults probabilities ($s$) versus Ni content ($x$) of the studied samples in the Li[Li$_{1/3}$-$2x/3$Ni$_x$Mn$_{2/3}$-$x/3$]O$_2$ series.
expected that the presence of Co\textsuperscript{3+} ions in the TM layer can also induce the stacking faults in the same way as Ni\textsuperscript{2+} ions.

Acknowledgments

The authors thank NSERC and 3M Canada for funding this work under the auspices of the Industrial Research Chair program. RS thanks Dr. Eric McCalla for his help and useful discussions on the FAULTS fitting.

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