6Li NMR Studies of Cation Disorder and Transition Metal Ordering in Li[Li1/3Mn1/3Co1/3]O2 Using Ultrafast Magic Angle Spinning

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Studies of Li[Li1/3Mn1/3Co1/3]O2 prepared under six different conditions are compared using high-resolution solid-state 6Li NMR. Differing degrees of cation disorder are established via integration of the NMR resonances, and this quantification of cation disorder is compared with Rietveld refinements of powder X-ray and neutron diffraction studies. Chemical shift trends to high frequency with decreasing degrees of disorder are established among this family of samples and explained according to the orbital overlap experienced by Li nuclei in the two environments: within the lithium layers and exchanged with nickel into the transition metal layers. Finally, an interesting case of local transition metal charge ordering is observed. Three unique environments are described, which can be accounted for based on electroneutrality arguments, and the known clustering of Ni2+ and Mn4+. This effect has not been detected in these materials by other methods including neutron and X-ray diffraction. Thus, the local ordering, which is observed in the dominant NMR resonance of Li in its own layers is thought to be pervasive (affecting the majority of the NMR nuclei), but very local, so as to be seen only by techniques such as NMR which probe immediate neighborhoods.

Introduction

The success of the layered LiCoO2 cathode coupled with a carbonaceous anode has advanced lithium-ion rechargeable batteries to a new era.$^{1,2}$ However, the high cost of cobalt has driven research to replace it, in whole or in part, with transition metals such as Ni and Mn to meet future demands for large-scale rechargeable batteries. In this paper we explore ordering in Li[Ni1/3Mn1/3Co1/3]O2 which crystallizes in the ordered rock salt R3m isostructural with LiCoO2. This compound has been suggested as a possible cathode material to combine some of the benefits of using Ni (high capacity), Mn (low cost), and Co (stability). Li[Ni1/3Mn1/3Co1/3]O2 has been reported by Ohzuku et al. to have capacities of up to 190 mA h g−1.$^{1,3}$ This material is also promising for battery applications because it has been shown to have better thermal stability than LiCoO2.$^{4}$

Structural properties are related to the electrochemical performance of cathode materials. The understanding of lithium location and transport within the lattice is essential to design concepts that will lead to the development of new materials.$^{5,6}$ Li6 Li solid-state NMR is an effective technique to study these microscopic processes, especially when coupled with X-ray diffraction that gives long-range structural information. Layered cathode materials such as Li[Ni1/2Mn1/2]O2 and, to a lesser extent, Li[Ni1/3Mn1/3Co1/3]O2 undergo mixing of lithium in the lithium layer and nickel from the transition metal layers because of their similar cationic radii (Li+ = 0.76 Å, Ni2+ = 0.69 Å). This cation disorder has been shown to be correlated to irreversible capacity, possibly because it impedes lithium diffusion.$^{5}$ By comparing the area ratios of the (003) and (104) reflections in the X-ray powder diffraction patterns, or by performing quantitative Rietveld analysis, the degree of disorder can be determined experimentally.$^{6}$ Solid-state 6Li NMR has also been used in studies of the Li[Ni1/3Mn1/3Co1/3]O2 and Li[Ni1/2Mn1/2]O2 compounds, for the identification of two lithium environments: Li in the lithium oxide layer and Li exchanged with nickel ions in the transition metal layer.$^{7–10}$ These previous studies identified the two environments according to their chemical shifts. However, no analysis to ascertain the varying degrees of disorder among materials prepared under different conditions was provided. In this paper we demonstrate the use of solid-state NMR to quantify the degree of cation disorder in Li[Ni1/3Mn1/3Co1/3]O2 samples prepared by a variety of methods. We compare the NMR

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data with neutron and X-ray diffraction studies of the same materials. We extend the investigation to include both quantification of cation disorder and comparison of chemical shift trends among samples with differing degrees of disorder. Solid-state NMR is an extremely valuable technique for elucidating local ordering that may not be revealed by other techniques. Evidence for charge ordering of the transition metals within several of the samples is provided and used to develop a local picture of the lithium environment. Here it is useful to point out that two types of order/disorder are discussed in the paper, the first being the disordering among Ni$^{2+}$ and Li$^+$ ions which exchange places with each other in the layered structure, termed cation disorder, and the second is ordering of the transition metal ions within their layers to form locally ordered domains, in accordance with the known Ni$^{2+}$–Mn$^{4+}$ association, predicted in related structures.\(^9,11\) The latter is termed here transition metal ordering, for clarity.

### Experimental Section

Layered Li[Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ compounds were prepared by the mixed hydroxide method. Stoichiometric amounts of Co(NO$_3$)$_2$·6H$_2$O (Fisher), Ni(NO$_3$)$_2$·6H$_2$O (Alfa), and Mn(NO$_3$)$_2$ (Fisher, 50% Solution) were mixed in deionized water and added dropwise into a 1 M LiOH solution. The resultant precipitates were dried at 150 °C overnight prior to mixing with a stoichiometric amount of LiOH·H$_2$O for samples (a) and (b) and 6-Li enriched Li$_2$CO$_3$ to provide Li$^+$ enrichment for (c), (d), (e), and (f). The samples were fired at 1000°C for (a), (b), and (c) 3 h and quenched and (d) 12 h and slow-cooled. Samples (e) and (f) were heated to 1100 °C for 3 h and quenched.

$^6$Li NMR spectra were acquired at a Larmor frequency of 29.7 MHz on a 4.7 T magnet, using a probe fitted to support 1.8 mm diameter rotors, spinning at frequencies up to 50 kHz. The spectra were referenced to 1 M LiCl, at 0 ppm. Spectra were acquired using a Hahn-echo pulse sequence, with a 1.7 μs π/2 pulse, and 3.4 μs π pulse, using an echo delay of two rotor periods, and a recycle delay of 500 ms. For all samples overnight acquisitions of roughly 50k transients were obtained.

$^6$Li spectral decompositions were performed using the xedplot program in the Bruker XwinNMR software. This allows variation of peak position, peak height, line width, and the ratio of Gaussian to Lorentzian functions. 100% Gaussian line shapes were used, as this simplifies the comparison of relative intensities. Error estimates were based on comparisons of multiple deconvolution iterations, which resulted in small variances in peak width and position.

Samples for powder X-ray diffraction (XRD) were measured on a Bruker D8 Advance powder diffractometer using standard Bragg–Brentano geometry with Cu Kα radiation (λ = 1.5406 Å). Data were collected from 10° to 105° in 2θ, using a step size of 0.02° and a count time of 10 s. For powder neutron diffraction (PND) experiments, 2 g of material was loaded in a vanadium can in an Ar-filled glovebox. Patterns were collected over a 16 h period on the C2 constant wavelength (λ = 1.32778 Å) powder diffractometer at Chalk River Laboratories, Canada, in conventional Debye–Scherrer mode. Si powder (NIST 640c) was used as an external calibration standard in a vanadium can and measured in the same configuration as the sample. Measurements were carried out from 5° to 115° in 2θ at 300 K, using a step size of 0.1°. Powder neutron and/or X-ray data sets were both refined by Rietveld methods using the GSAS package with the EXPGUI interface.\(^12\) Background, scale factor, zero point, lattice parameters, atomic positions, and coefficients for the peak shape function were iteratively refined until convergence was achieved.

### Results and Discussion

The X-ray powder diffraction patterns of four Li[Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ samples prepared under different conditions are shown in Figure 1. Samples (a) and (b) were prepared by reacting natural abundance LiOH·H$_2$O with the mixed hydroxides at 1000 °C for 3 h and quenching the oxide. Samples (c) and (d) were prepared similarly but using 6-Li enriched Li$_2$CO$_3$ instead of LiOH·H$_2$O, and sample (d) was slow-cooled rather than being quenched. All patterns were indexed in the space group R$^{3m}$, and refined using the Rietveld method to yield the lattice parameters listed in Table 1 (crystallographic positions for Co, Ni, Mn, Li, and O were typical of those previously described in other publications: see figure caption for details). Refinement in space groups lower than R$^{3m}$ such as P$^3_1$12 did not improve the goodness of fit significantly from a statistical point of view for any of the samples.

### Table 1. Summary of Rietveld Refinements of X-ray Diffraction Data for Li[Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ Samples (a)–(d)

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V ($\text{Å}^3$)</th>
<th>$R_p$ (%)</th>
<th>$R_w$ (%)</th>
<th>$\chi^2$</th>
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</thead>
<tbody>
<tr>
<td>(a)</td>
<td>2.8996(2)</td>
<td>14.2293(2)</td>
<td>100.787(2)</td>
<td>5.32</td>
<td>4.45</td>
<td>2.031</td>
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<tr>
<td>(b)</td>
<td>2.8537(3)</td>
<td>14.2104(3)</td>
<td>100.223(3)</td>
<td>6.3</td>
<td>6.73</td>
<td>2.388</td>
</tr>
<tr>
<td>(c)</td>
<td>2.8672(9)</td>
<td>14.2600(2)</td>
<td>101.530(2)</td>
<td>3.79</td>
<td>2.85</td>
<td>2.178</td>
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<td>(d)</td>
<td>2.8635(4)</td>
<td>14.2492(3)</td>
<td>101.188(4)</td>
<td>6.39</td>
<td>7.13</td>
<td>2.545</td>
</tr>
</tbody>
</table>


LiOH–H₂O, namely, about 3.0%. This was confirmed for (Table 2) was lowest for samples (a) and (b) prepared from it was not for our materials. The degree of Li/Ni exchange unless the difference in the reliability factors is large, which will always produce a slightly better reliability factor. It makes it a poor indicator of the optimum space group. The variability in the reliability factors may depend on the number of d electrons as well as the Li–M bond lengths and bond angles within the lattice. Specific hyperfine shifts have been assigned to specific lithium environments within transition metal oxides as shown in the seminal work of Grey et al. on lithium manganites.

These shifts are based on two possible mechanisms of interaction between the unpaired electrons and the lithium nuclei. The first case is delocalization, which results in the positive transfer of spin density to the lithium nucleus due to the Fermi contact interaction between the lithium nuclei and the unpaired electrons of the Ni²⁺ (high spin t₂g⁶e₈g⁰) and Mn⁴⁺ (high spin t₂g⁷e₅g⁰) both contribute to the observed hyperfine shifts.

When the area of the smaller peak is compared to that of the larger peak (including its sidebands), the amount of cation disorder in these materials can be determined. The degree of cation disorder in these materials is dependent on the number of d electrons as well as the Li–M bond lengths and bond angles within the lattice. Specific hyperfine shifts have been assigned to specific lithium environments within transition metal oxides as shown in the seminal work of Grey et al. on lithium manganites.

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In Li[Ni₁/₃Mn₁/₃Co₁/₃]O₂, Co³⁺ is diamagnetic (low spin t₂g⁶e₈g⁰) so it does not contribute spin density to the hyperfine shift. Ni²⁺ (t₂g⁶e₈g⁰) and Mn⁴⁺ (high spin t₂g⁷e₅g⁰) both contribute to the observed hyperfine shifts.

Probing the Degree of Cation Disorder by NMR. Lithium NMR spectra are strongly affected by the electronic structure of the local environment within the material. They exhibit a wide range of hyperfine chemical shifts because of the Fermi–contact mechanism: the transfer of unpaired electron spin density from the paramagnetic ions to the Li nucleus. The Fermi-contact shift is additive with a magnitude dependent on the number of d electrons as well as the Li–M bond lengths and bond angles within the lattice. Specific hyperfine shifts have been assigned to specific lithium environments within transition metal oxides as shown in the seminal work of Grey et al. on lithium manganites. These shifts are based on two possible mechanisms of interaction between the unpaired electrons and the lithium nuclei. The first case is delocalization, which results in the positive transfer of spin density to the lithium nucleus via the oxygen 2p orbital. The second possible transfer is through spin polarization, which results in negative spin density induced on the lithium 2s orbital. Which of these two mechanisms are active depends on the local geometry of the M–O–Li interaction and the electronic structure of the transition metal ion. In general, delocalization is dominant. In Li[Ni₁/₃Mn₁/₃Co₁/₃]O₂, Co³⁺ is diamagnetic (low spin t₂g⁶e₈g⁰) so it does not contribute spin density to the hyperfine shift. Ni²⁺ (t₂g⁶e₈g⁰) and Mn⁴⁺ (high spin t₂g⁷e₅g⁰) both contribute to the observed hyperfine shifts.

Figure 3a,b shows natural abundance ⁶Li spectra (MAS = 46 kHz) of Li[Ni₁/₃Mn₁/₃Co₁/₃]O₂ samples. Spectra for the ⁶Li-enriched samples are shown in Figure 3c,d. In these materials, the oxidation states of the three transition metals have been previously determined to be Ni²⁺, Co³⁺, and Mn⁴⁺ by density of states calculations and XANES (X-ray absorption near edge spectroscopy) data. In all four spectra, two groups of resonances are evident with large positive shifts due to the Fermi–contact interaction between the lithium nuclear spins and the unpaired electrons of the Ni²⁺/Mn⁴⁺ ions. The set of resonances at lower frequency correspond to the Li present in the Li oxide layers, while those at higher frequency are assigned to Li located in the transition metal layers. The presence of Li in the transition metal layer occurs as a result of mixing with the similar-sized Ni²⁺ ions. The results of spectral decomposition performed to fit the line shapes are shown below the experimental data in Figure 3. When the area of the smaller peak is compared to that of the larger peak (including its sidebands), the amount of cation

<table>
<thead>
<tr>
<th>Sample preparation</th>
<th>Chemical shift (ppm)</th>
<th>Line width (kHz)</th>
<th>% Li/Ni disorder by NMR</th>
<th>% Li/Ni disorder by XRD</th>
<th>% Li/Ni disorder by PND</th>
</tr>
</thead>
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<tr>
<td>(a) heated 3 h, 1000 °C, quenched (Li)</td>
<td>506</td>
<td>20.0</td>
<td>2.5</td>
<td>2.7</td>
<td>3.0</td>
</tr>
<tr>
<td>(b) heated 3 h, 1000 °C, quenched (Li)</td>
<td>1283</td>
<td>7.6</td>
<td>3.6</td>
<td>3.3</td>
<td>3.0</td>
</tr>
<tr>
<td>(c) heated 3 h, 1000 °C, quenched (Li)</td>
<td>483</td>
<td>19.4</td>
<td>4.5</td>
<td>7.3</td>
<td>3.0</td>
</tr>
<tr>
<td>(d) heated 12 h, 1000 °C, slow-cooled (Li)</td>
<td>1259</td>
<td>7.8</td>
<td>2.3</td>
<td>5.5</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* Error estimates are ±10 ppm in the chemical shift and ±0.2 kHz in line width.

Figure 2. Neutron diffraction pattern of sample (a) of LiCo₁/₃Ni₁/₃Mn₁/₃O₂ and Rietveld refinement using the combined X-ray and neutron data. The experimental (+) and calculated (−) data are shown, along with the residual. The positions for the transition metal atoms Co, Ni, and Mn were fixed at the Wyckoff position 3(a) in the unit cell, Li at 3(b), and O at 6(c). Atomic displacement parameters, the fractional coordinate z for O, and the site occupancy exchange of Ni and Li between sites 3a and 3b were refined, the latter giving rise to values of 2.9% for the combined XRD and neutron refinement and 3.0% for the neutron refinement alone. The refinement parameters include a = 2.8597(0) Å, c = 14.227(0) Å, R_root = 4.23%, R_B = 13.89%, χ² = 4.329.

Figure 3a, b shows natural abundance ⁶Li spectra (MAS = 46 kHz) of Li[Ni₁/₃Mn₁/₃Co₁/₃]O₂ samples. Spectra for the ⁶Li-enriched samples are shown in Figure 3c,d. In these materials, the oxidation states of the three transition metals have been previously determined to be Ni²⁺, Co³⁺, and Mn⁴⁺ by density of states calculations and XANES (X-ray absorption near edge spectroscopy) data. In all four spectra, two groups of resonances are evident with large positive shifts due to the Fermi–contact interaction between the lithium nuclear spins and the unpaired electrons of the Ni²⁺/Mn⁴⁺ ions. The set of resonances at lower frequency correspond to the Li present in the Li oxide layers, while those at higher frequency are assigned to Li located in the transition metal layers. The presence of Li in the transition metal layer occurs as a result of mixing with the similar-sized Ni²⁺ ions. The results of spectral decomposition performed to fit the line shapes are shown below the experimental data in Figure 3. When the area of the smaller peak is compared to that of the larger peak (including its sidebands), the amount of cation...
mixing (degree of cation disorder) can be determined. The cation disorder was determined to be 2.5% and 3.6% for the first two samples, which is in good agreement with the values determined by Rietveld analysis of the X-ray powder diffraction patterns for samples (a) and (b), of 2.7% and 3.3%, respectively. Analysis of the neutron diffraction pattern of sample (a) gave essentially identical results (3.0%; Table 2). The cation disorder for samples (c) and (d) were 4.5% and 2.3%, respectively. These cation disorder values are lower than those obtained from diffraction (7.3% and 5%), although the trend is consistent between these two materials. In both measurements, the highest degree of cation disorder is found for sample (c). The anomaly in the trend among the four samples found for sample (d) is attributed to local transition metal charge ordering, an effect which is not observed in the diffraction studies. The error bars for the chemical shift range and the line shapes broadened by paramagnetic interactions are about 10 ppm for the hyperfine shifts and 0.2 kHz for the line widths. This gives an error of about ±0.1% for the degree of disorder. A summary of the chemical shifts and line widths is given in Table 2.

Correlations between Cation Disorder and Chemical Shifts. The results in Table 2 show an important trend. Samples which exhibit lower cation disorder have greater hyperfine shifts for both sets of resonances; this is most apparent in the high-frequency resonance of the lithium ions in the transition metal layer. It can be explained according to the model for the transfer of spin density as described above for Fermi—contact shift interactions and depicted in Figure 4. In the case of the lowest disorder, we expect a strong driving force for the association of Mn$^{4+}$ near the Li$^+$ in the transition metal layer, driven by Coulombic forces. In the first coordination sphere of lithium,
Mn$^{4+}$ will interact with Li via a 90° delocalization of the t$_{2g}$ orbitals with the Li 2s orbital via the oxygen 2p orbital. The delocalization mechanism provides a positive spin transfer; thus, the highest shift is expected for the largest amount of Mn$^{4+}$ in the first coordination sphere. Larger degrees of disorder will interfere with the ordering of Mn$^{4+}$ and Li$^{+}$, allowing cobalt or nickel ions into this first coordination sphere. Ni$^{2+}$ ions cannot interact with lithium in the transition metal layer via delocalization, due to the lack of a 90° orbital overlap, so the contribution to the chemical shift is a negative spin transfer occurring via polarization of the lithium 2s orbital by the Ni$^{2+}$ e$_{g}$ orbital which polarizes the filled t$_{2g}$ orbital. Therefore, the materials with higher degrees of disorder exhibit lower chemical shifts of lithium in the transition metal layer.

Comparing samples (c) and (d), the same trend is observed; chemical shifts of the more disordered sample (c) occur at lower frequency than the less disordered sample (d). The trend suggests a correlation between chemical shift and degree of cation disorder within mixed transition metal oxides, a concept which has not been previously demonstrated.

**Evidence for Transition Metal Charge Ordering.** Analysis of the spectra shows a decreasing degree of cation disorder for sample (d) that was slow-cooled, relative to the other samples that were quenched. This trend is logical, and although there is a small discrepancy with the degree of cation disorder determined by Rietveld analysis, it is self-consistent to detect the presence of transition metal charge ordering in the sample which exhibits the lowest degree of cation disorder according to the NMR line shape and chemical shift results. It is revealed by close examination of the main line shape of the $^{6}$Li NMR spectrum for sample (d). The large hyperfine shifts, compared to the other samples, do support the lower cation disorder in sample (d) established by NMR. Moreover, the spectral decomposition for the central resonance of this spectrum (Figure 5) clearly shows three distinct line shapes. These arise from the ordering of transition metal ions within the lithium local electronic environment. Sample (d) is unique, not only in the complexity of the line shape of $^{6}$Li within the lithium oxide layers but also in that it was slow-cooled. We expect this to result in greater order within the sample.

To confirm this effect, two samples that were heated to 1100 °C were studied, which also show evidence of transition metal ordering in the main resonance. These spectra are shown in Figure 6e,f. Table 3 includes a summary of the decompositions, including chemical shifts and relative areas of the three line shapes that contribute to this main resonance. These two samples exhibit very low cation disorder determined by NMR, as expected due to the higher firing temperatures. Also, the higher chemical shift for the Li environment in the transition metal layer (greater than 1300 ppm in both cases) follows the trend of expecting lower disorder values.

A driving force for ordering in these samples can be understood by considering local charge balance. According to Pauling’s rule of electroneutrality, the sum of the electrovalencies of the nearest neighbor cations should equal...
ordered in Li$_2$MnO$_3$ and the potential cathode material method has been used to understand local short-range 

$\text{Li}_{1.2} \text{Cr}_{0.4} \text{Mn}_{0.4} \text{O}_2.23 \text{Li}_2 \text{MnO}_3$ is the classic example of a 

case Ni$_2^+$ in Table 4 and illustrated in Figure 7. Case (a), where Ni$^2+$

electroneutrality around oxygen. These cases are summarized 

nucleus that satisfy Pauling’s rule by preserving local 

Co$^{3+}$ in ordered rock salt structures. 22 This 

Proposed local charge ordering environments, based on the 

Figure 7. Proposed local charge ordering environments, based on the combination of environments described in Table 4. Case (a) is indicated 

by the blue circle, case (b) by the red circle, and case (c) by the green circle. Solid lines represent the top transition metal layer, and dotted lines represent the bottom transition metal layer. Despite the local ordering around the lithium nuclei, charge balance is maintained in both transition metal layers. The intervening lithium layer is shown as isolated atoms at the centers of the octahedron. Oxygen atoms are left out for simplicity.

the charge of the anion in ordered rock salt structures.22 This method has been used to understand local short-range ordering in Li$_2$MnO$_3$ and the potential cathode material Li$_{1.2}$Co$_{0.4}$Mn$_{0.4}$O$_2$.23 Li$_2$MnO$_3$ is the classic example of a material which long-range orders because of electroneutrality and is identified through X-ray diffraction as a $\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$ superlattice according to Wood’s notation.24

In Li[Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ there are three different ways to distribute the transition metal cations around the lithium nucleus that satisfy Pauling’s rule by preserving local electroneutrality around oxygen. These cases are summarized in Table 4 and illustrated in Figure 7. Case (a), where Ni$^{2+}$, Co$^{3+}$, and Mn$^{4+}$ are evenly arranged around the Li atom, describes a scenario that would result in only one chemical shift in the NMR. If the array were organized to give long-range order, one single narrow line shape would result. Any perturbation of the possible Ni$^{2+}$/Co$^{3+}$/Mn$^{4+}$ arrangements around the Li center would simply result in an equivalent shift but a broader line. Cases (b) and (c), on the other hand, represent uneven distributions that would exhibit different chemical shifts.

These three types of possible environments correspond to the three line shapes present in the decomposition spectrum for the sample which showed the smallest cation disorder by NMR. Ni$^{2+}$ and Mn$^{4+}$ both transfer positive spin density via the delocalization mechanism with the Li 2s orbital, 180$^\circ$ and 90$^\circ$, respectively. Following this model, case (b) is dominated by diamagnetic Co$^{3+}$ and is therefore assigned to the shift at lower frequency while case (c) is attributable to the resonance at highest frequency. The area of these outer peaks is roughly equal, suggesting that there is a similar distribution of each coordination environment throughout the lattice. This assignment is supported by several factors. Considering all three possible arrangements, the total number of ions of each type is the same for all three metals, corresponding to the experimentally determined stoichiometry. As well, strong interactions between Ni$^{2+}$ and Mn$^{4+}$ ions have been shown to be favorable by first-principle calculations which supports the fact that the greater number of Mn$^{4+}$ ions in case (c) is accompanied by a greater number of Ni$^{2+}$ ions.9,11

The “very local” nonrandom distributions of the different transition metal ion environments described above could extend to the formation of clusters or domains. The appearance of domains within mixed transition metal oxides has been observed using solid-state MAS NMR for solid solutions of the form LiNi$_{1-x}$Co$_x$O$_2$ and Li[Li$_{0.6}$Mn$_{0.4}$]O$_2$ and by electron diffraction in Li[Li$_{0.6}$Mn$_{0.4}$]O$_2$.15

A model of the local transition metal ordering in Li[Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ is shown in Figure 7. Hypothetically, if these cation domains reached a critical size, they could become detectable by techniques such as neutron diffraction (PND) that are sensitive to long-range ordering. Our PND experiments on these materials indicate this limit is not reached, however, as no superlattice formation was observed. We noted that the degree of disorder and the existence of short- and long-range ordering are strongly dependent on the synthetic

Table 3. Summary of Decompositions of Samples Exhibiting Transition Metal Ordering

<table>
<thead>
<tr>
<th>sample</th>
<th>chemical shift (ppm)</th>
<th>line width (kHz)</th>
<th>area ratio (highest frequency to lowest frequency)</th>
<th>$%$ LiNi disorder by NMR</th>
<th>$%$ LiNi disorder by XRD</th>
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</thead>
<tbody>
<tr>
<td>(d) heated 3 h, 1000 °C, slow cooled</td>
<td>748</td>
<td>11.5</td>
<td>1:2:1</td>
<td>2.3</td>
<td>5.5</td>
</tr>
<tr>
<td>(e) heated 3 h, 1100 °C, quenched</td>
<td>519</td>
<td>10.3</td>
<td>1:4:1.3</td>
<td>1.4</td>
<td>4.8</td>
</tr>
<tr>
<td>(f) heated 3 h, 1100 °C, quenched</td>
<td>236</td>
<td>10.2</td>
<td>1:4:1.6</td>
<td>2.0</td>
<td>3.5</td>
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</table>

Table 4. Possible Local Coordination Environments for Li$^{+}$ Nuclei, Corresponding to Line Shape Decomposition Given in Figure 7. Based on the Pauling Electroneutrality Principle, and Propensity for Ni$^{2+}$–Mn$^{4+}$ Clustering

<table>
<thead>
<tr>
<th>case</th>
<th>Ni$^{2+}$</th>
<th>Co$^{3+}$</th>
<th>Mn$^{4+}$</th>
<th>chemical shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>intermediate frequency</td>
</tr>
<tr>
<td>(b)</td>
<td>1</td>
<td>4</td>
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<td>low frequency</td>
</tr>
<tr>
<td>(c)</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>high frequency</td>
</tr>
</tbody>
</table>

conditions. In particular, slow cooling and higher firing temperatures seem to minimize disorder and in turn minimize irreversible capacity. In terms of preparation conditions, sample (d), being heated at a high temperature for a long time and slow-cooled, favors the low degree of Li$^+$/Ni$^{2+}$ cation disorder determined by NMR. Similarly, samples (e) and (f), which were heated to 1100 °C, also exhibited lower cation disorder.

It is interesting to note that long-range ordering of the transition metal ions in Li[Li$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ was originally proposed by Ohzuku et al., based on calculations of the formation energy. Their suggested $\sqrt{3}a$$_{\text{hex}} \times \sqrt{3}a$$_{\text{hex}}$ $P$$_3$1$2$ superlattice consists of a single transition metal coordination around the Li nucleus, equally ordered with 2Co$^{3+}$−2Ni$^{2+}$−2Mn$^{4+}$ transition metal neighbors. This corresponds to the long-range ordered extreme of case (a) above. Observation of such a superlattice would likely be highly sample preparation-dependent, and the ordering could range over different domain sizes. The model presented here (Figure 7) differs in that the local ordering we propose is intermediate. It is dominated by a random distribution of two of each of the transition metal ions (case (a)) but includes contributions from the two less random cases ((b) and (c)). Like long-range ordering, the local ordering model maintains charge neutrality, but allows for the preferred association of nickel and manganese ions. It also explains why, to date, X-ray and neutron diffraction have failed to provide clear evidence of the former. Overall, the observation of even the Li$^+$ or Ni$^{2+}$ ordering seen by any experimental technique for the Li[Li$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ compound and should provide further insight into the relationship between structural properties and electrochemical performance in such materials. This local ordering of the transition metal ions is an intermediate scenario, between the full superstructure and a completely random organization of the transition metal layers. This indicates that, in these materials, the observed Ni$^{2+}$−Mn$^{4+}$ association is only a weak thermodynamic driving force and does not result in a complete structural organization, even under carefully controlled synthetic conditions. The evidence for charge ordering within the slow-cooled sample suggests the possibility that this material may form a restricted superstructure and it may display superior electrochemical behavior. These studies of the electrochemical performance of these materials and related materials of differing preparation methods are ongoing.

Furthermore, we have shown a correlation between the degree of cation disorder in a given sample and the magnitude of the NMR chemical shifts. While this effect may be unique to the 1/3 1/3 1/3 class of materials, it will be interesting to see whether it can be established in related materials.

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Conclusions

In summary, solid-state 6 Li NMR has been shown to be a reliable method for determining the degree of cation disorder within cathode materials, when compared to diffraction studies combined with Rietveld refinement. This paper presents the first evidence of local transition metal charge ordering seen by any experimental technique for the Li[Li$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$ compound and should provide further insight into the relationship between structural properties and electrochemical performance in such materials. This local ordering of the transition metal ions is an intermediate scenario, between the full superstructure and a completely random organization of the transition metal layers. This indicates that, in these materials, the observed Ni$^{2+}$−Mn$^{4+}$ association is only a weak thermodynamic driving force and does not result in a complete structural organization, even under carefully controlled synthetic conditions. The evidence for charge ordering within the slow-cooled sample suggests the possibility that this material may form a restricted superstructure and it may display superior electrochemical behavior. These studies of the electrochemical performance of these materials and related materials of differing preparation methods are ongoing.

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