

Intercalation of Water in P2, T2 and O2 Structure $A_z[Co_xNi_{1/3-x}Mn_{2/3}]O_2$

Zhonghua Lu[†] and J. R. Dahn^{*,†,‡}

Department of Physics and Department of Chemistry, Dalhousie University,
Halifax, N.S. Canada, B3H 3J5

Received September 7, 2000. Revised Manuscript Received January 10, 2001

The intercalation of water into P2- $Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ ($x = 0, 1/6, 1/3$) and T2 or O2 structure $Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ ($x = 0, 1/6, 1/3$) has been investigated by X-ray diffraction and thermogravimetric analysis (TGA). Water can be intercalated into P2- $Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ ($x = 1/6, 1/3$) but not within P2- $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$. This difference may be related to the existence of superlattice ordering of Ni atoms, but not Co atoms, within the transition metal layer which apparently induces a very strong interlayer interaction and inhibits the uptake of water. Two water-containing phases of P2- $Na_{2/3}(H_2O)_y[Co_{1/3}Mn_{2/3}]O_2$ were found and one, with $y \approx 2/3$, could be prepared in pure form. By Rietveld refinement of the X-ray diffraction pattern of P2- $Na_{2/3}(H_2O)_{2/3}[Co_{1/3}Mn_{2/3}]O_2$, it can be concluded that the compound still exists in the ideal P2 structure ($P6_3/mmc$) with the oxygen atoms of the water molecule located on the 2c site. Water cannot be intercalated into the corresponding lithiated phases, $Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ for any value of x that we tested ($x = 0, 1/6, 1/3$).

I. Introduction

Layered alkali transition metal (M) oxides are composed of edge-shared MO_2 sheets with alkali metal atoms sandwiched between them. They can be classified into several groups, according to the site symmetry of the alkali metal and the way that the MO_2 sheets are stacked. On the basis of the nomenclature developed by Delmas and Hagenmueller,^{1–4} the structures P2, P3 (with alkali metals in prismatic sites) and the structures O2, O3, and O6 (with alkali metals in octahedral sites) are commonly found. The numeral in the structural designation gives the number of MO_2 sheets in the conventional unit cell. The structures can be further distinguished into two groups, (P3, O3) and (P2, O2, O6). In the latter group (P2, O2, O6), the orientation of the MO_2 sheets differs from one layer to its neighbor layers, while for the former group (P3, O3), the orientation of the MO_2 sheets is the same and neighboring layers can be obtained simply by translation.

Recently, during the development of new cathode materials for rechargeable lithium-ion batteries, P2 structure $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ and a Co-substituted derivative, P2- $Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ ($0 < x < 1/3$) were found. By ion exchange of Li atoms for Na, the T2 (and/or stacking faulted O2 or O6) structure $Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ phases could be obtained.^{5–11}

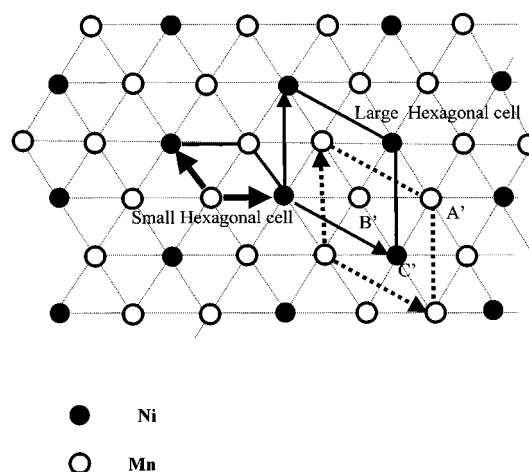


Figure 1. Showing the cation ordering in the Ni–Mn layer of P2- $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$.

The phases have the advantage that they do not convert to the spinel phase, as does O3- $LiMnO_2$, during charge–discharge cycling.

Neutron diffraction experiments showed that there is an ordering of Ni atoms on a $\sqrt{3}a$ by $\sqrt{3}a$ superlattice in the transition metal layers for P2- $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$.^{8,10} Figure 1 gives the transition-metal positions within one transition metal layer. On the basis of

* To whom correspondence should be addressed.

[†] Department of Physics.

[‡] Department of Chemistry.

(1) Delmas, C.; Braconnier, J. J.; Foassier, C.; Hagenmueller, P. *Solid State Ionics* **1981**, *3/4*, 165.

(2) Delmas, C.; Braconnier, J.-J.; Maazaz, A.; Hagenmueller, P. *Rev. Chim. Min.* **1982**, *19*, 343.

(3) Delmas, C.; Braconnier, J. J.; Hagenmueller, P. *Mater. Res. Bull.* **1982**, *17*, 117.

(4) Mendibouire, A.; Delmas, C.; Hagenmueller, P. *Mater. Res. Bull.* **1984**, *19*, 1383.

(5) Paulsen, J. M.; Thomas, C. L.; Dahn, J. R. *J. Electrochem. Soc.* **2000**, *147*, 861.

(6) Paulsen, J. M.; Dahn, J. R. *Solid State Ionics* **1999**, *126*, 3.

(7) Paulsen, J. M.; Dahn, J. R. *J. Electrochem. Soc.* **2000**, *147*, 2478.

(8) Paulsen, J. M.; Donaberger, R. A.; Dahn, J. R. *Chem. Mater.* **2000**, *12*, 2257.

(9) Paulsen, J. M.; Thomas, C. L.; Dahn, J. R. *J. Electrochem. Soc.* **1999**, *146*, 3560.

(10) Lu, Z.; Donaberger, R. A.; Dahn, J. R. *Chem. Mater.* **2000**, *12*, 3583.

(11) Lu, Z.; Dahn, J. R. Submitted to *J. Electrochem. Soc.*

the large hexagonal cell, if Ni atoms occupy C' sites in the first layer along the stacking direction then they occupy B' sites in the next layer and adopt the C'B'C'B' stacking sequence. When Li is ion exchanged for Na, the superlattice ordering in the transition metal layer is preserved. For P2-Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O₂, as Ni is replaced by Co, the superlattice ordering gradually disappears.¹⁰

Water can be intercalated into layered structures to solvate the alkali metals that are sandwiched between the MO₂ layers.¹² During our research on A_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O₂ we studied the effects of moisture on the materials. We find that water can be intercalated for A = Na and $x = 1/6$ and $1/3$, but not for A = Na and $x = 0$. Water could not be intercalated for any x if A = Li. We suspect that the superlattice ordering present for $x = 0$ suppresses the intercalation of water for A = Na. When A = Li, neither large prismatic nor octahedral sites are available for water molecules as they are when A = Na, and this may explain why the Li-containing phases do not intercalate water.

II. Experimental Section

Sample Preparation. The P2-Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O₂ ($x = 0, 1/6, 1/3$) samples were prepared by the "mixed hydroxide" method.⁷ A solution of transition-metal nitrates was slowly dripped into a NaOH solution with rapid stirring. The obtained mixed hydroxide was filtered and was washed and then calcined at 200 °C for 1 day in air. The mixed oxide/hydroxide was then ground with the stoichiometric amount of Na₂CO₃ (nominal composition approximately Na_{0.67}MO_x). Pellets were then pressed, and a solid-state reaction was made. The pellets were heated at 900 °C in air for 1 day and then quenched directly into liquid N₂. The quenched pellets were ground, new pellets were made, and the solid-state reaction was repeated. X-ray diffraction measurements were made after the first heating and after the second heating.

The lithium-containing samples were prepared from the Na-containing phases by ion exchange of sodium for lithium in molten salt. Approximately 2.0 g of precursor were added to 14 g of molten (LiNO₃)_{0.88}(LiCl)_{0.12} eutectic at 280 °C. After about 1.5 h, the melt was poured into water and filtered. The obtained powder was dried at about 100 °C in air.

All powders were ground and passed through a 75 μm sieve.

Water Intercalation Test. The test for water intercalation was performed by two methods. In the first method, a small amount of a powdered sample (about 0.5 g) was placed in a small glass vial. The open vial was then floated inside a wide mouthed bottle that was half-filled with distilled water. The wide mouthed bottle was then closed tightly. After a fixed time, the sample was taken out to check the structure by X-ray diffraction. We call the first method "exposure to humid air". In the second method, powders were directly submerged in distilled water and measured by X-ray diffraction while damp. We call the second method "immersion in water".

To check for the reversibility of water intercalation, if any, the wetted samples were dried in an oven at 100 °C or at 200 °C for a fixed time and then checked by X-ray diffraction. In addition, thermogravimetric analysis (TGA) was used to determine the amount of intercalated water for samples determined to be a pure phase. TGA measurements were performed with a TA instruments TGA using a heating rate of 2 °C/min to a maximum temperature of 500 °C.

XRD Measurement. X-ray diffraction was made using a Siemens D500 diffractometer equipped with a Cu target X-ray tube and a diffracted beam monochromator. Profile refinement

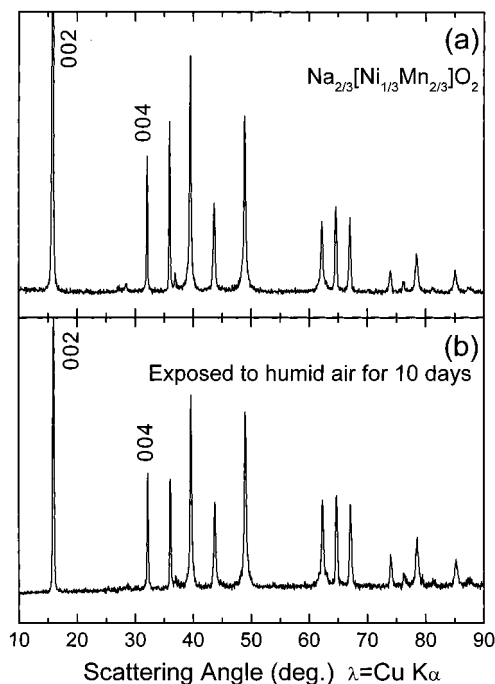


Figure 2. Diffraction patterns of (a) P2-Na_{2/3}[Ni_{1/3}Mn_{2/3}]O₂ and (b) P2-Na_{2/3}[Ni_{1/3}Mn_{2/3}]O₂ exposed to humid air for 10 days.

of the collected data was made using Hill and Howard's version of the Rietveld Program.¹³

III. Results

A. Water Intercalation in P2-Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O₂ as a Function of Co Content. Intercalation of water into the interlayer spaces should enlarge the interlayer distance, which causes the (00*l*) peaks of the X-ray diffraction pattern to shift to lower angles. Figure 2a,b shows the X-ray diffraction patterns of P2-Na_{2/3}[Ni_{1/3}Mn_{2/3}]O₂ before and after exposure to humid air for 10 days. Water is not intercalated into P2-Na_{2/3}[Ni_{1/3}Mn_{2/3}]O₂ under these conditions because the positions of the Bragg peaks do not change.

Figure 3a–d show the X-ray diffraction pattern of P2-Na_{2/3}[Co_{1/6}Ni_{1/6}Mn_{2/3}]O₂ before and after exposure to humid air for 10 days as well as after being dried at 100 and 200 °C for 2 days. Comparing Figure 3, parts a and b, two weak peaks at about 14° and 28° were observed which are indicated by arrows. These two peaks were indexed as (002') and (004') and are due to the shift of the (002) and (004) peaks of the parent phase upon the intercalation of water. The new peaks disappeared when the sample was dried at either 100 or 200 °C for 2 days. It can be concluded that some water can be intercalated taken into the lattice of P2-Na_{2/3}[Co_{1/6}Ni_{1/6}Mn_{2/3}]O₂ and extracted from the lattice upon heating. The small peak in Figure 3b at 17° is thought to be due to an unknown impurity.

Figure 4a–d shows the evolution of X-ray diffraction patterns of P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ during exposure to humid air. As indicated by the arrows, the new peaks gradually form with time. These new peaks are due to a phase with intercalated water. Comparing Figures 2–4 it can be concluded that water can be intercalated

(12) Intercalation Chemistry; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982; Chapter 10.

(13) Hill, R. J.; Howard, C. J. *J. Appl. Crystallogr.* **1985**, *18*, 173. Wiles, D. B.; Young, R. A. *J. Appl. Crystallogr.* **1981**, *14*, 149.

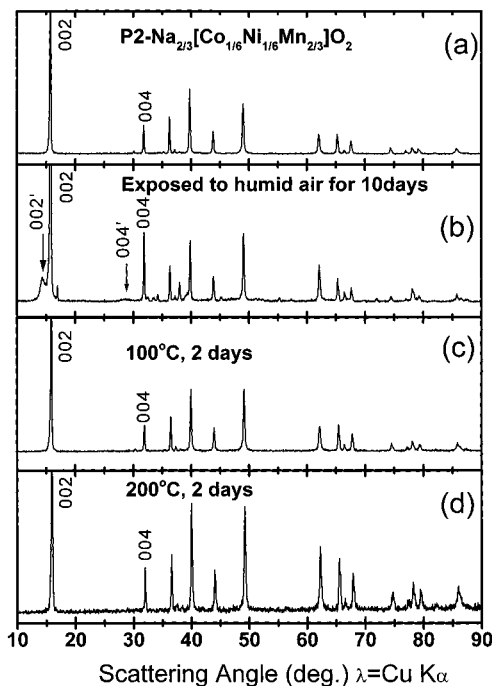


Figure 3. Diffraction patterns of (a) P2-Na_{2/3}[Co_{1/6}Ni_{1/6}Mn_{2/3}]O₂; (b) P2-Na_{2/3}[Co_{1/6}Ni_{1/6}Mn_{2/3}]O₂ exposed to humid air for 10 days showing evidence for the water intercalated phase; (c) P2-Na_{2/3}[Co_{1/6}Ni_{1/6}Mn_{2/3}]O₂ exposed to humid air for 10 days then dried at 100 °C for 2 days; (d) P2-Na_{2/3}[Co_{1/6}Ni_{1/6}Mn_{2/3}]O₂ exposed to humid air for 10 days then dried at 200 °C for 2 days.

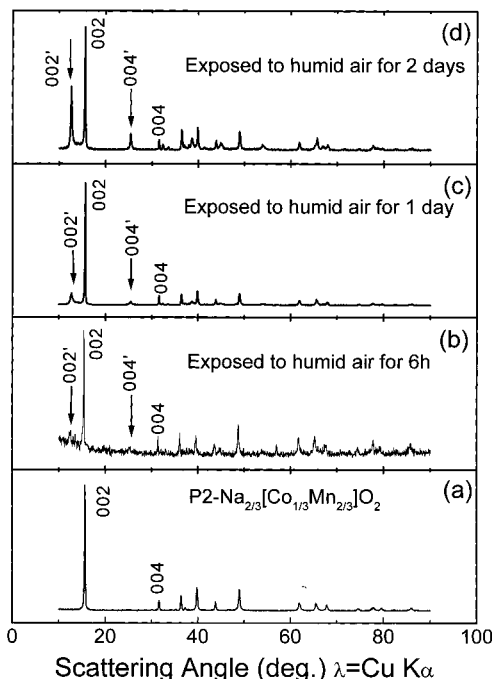


Figure 4. Diffraction patterns of (a) P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂; (b) P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ exposed to humid air for 6 h; (c) P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ exposed to humid air for 1 day; (d) P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ exposed to humid air for 2 days. The peaks belonging to the water intercalated phase are indicated by the primed Miller indices.

into the Co-containing phases but not into the pure Ni phase, at least under the conditions used.

Figure 5a shows that if the P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ sample is immersed in water for 16 days, in addition to

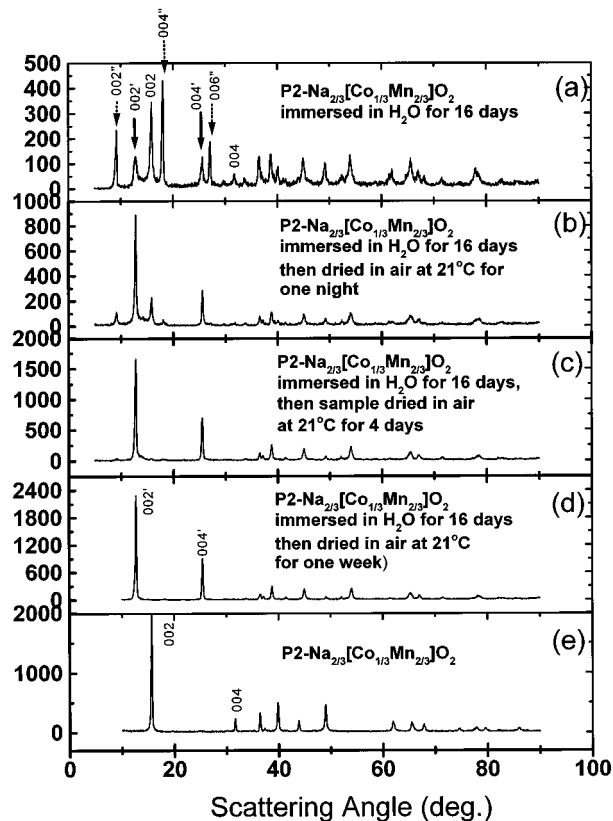


Figure 5. Diffraction patterns of: (a) P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ immersed in water for 16 days (peaks from two water intercalated phases are indicated by primes and double primes); (b) the sample in (a) dried in air for 1 night; (c) the sample in (a) dried in air for 4 days; (d) the sample in (a) dried in air for one week showing pure **phase I**; and (e) the original P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ phase.

the new set of peaks mentioned above (labeled as 002', 004'), a second new set of peaks appear, indicated by dashed arrows (labeled as 002'', 004'', and 006''). This indicates that two types of water-containing phases can be obtained. The sample was then exposed to lab air at room temperature. Figure 5b–d shows that the second new set of peaks and the peaks of the parent phase gradually disappear over a period of 1 week, leaving only the set of peaks from the single prime (') phase. For convenience, we label this set of peaks as originating from phase I and the double primed set of peaks (") as originating from phase II. Phase I appears to be very stable in laboratory air at room temperature.

Figure 6 shows that phase I converts back to the original P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ phase upon drying at 100 or 200 °C for 14 days. The arrow in Figure 6b indicates that the 002 peak of the phase dried at 100 °C is asymmetric and that probably all the water is not yet completely removed. After treatment at 200 °C, the peak is symmetric and the sample most likely contains no water.

B. Water Content and Position of the Water Molecules in Phase I. Figure 7 shows the TGA curve of phase I measured using a heating rate of 2 °C/min. There is rapid weight loss below 100 °C, followed by a region of slower weight loss between 100 and 320 °C. When the temperature exceeds about 340 °C, the water is removed completely. From the weight lost to 400 °C, it can be estimated that Phase I is approximately

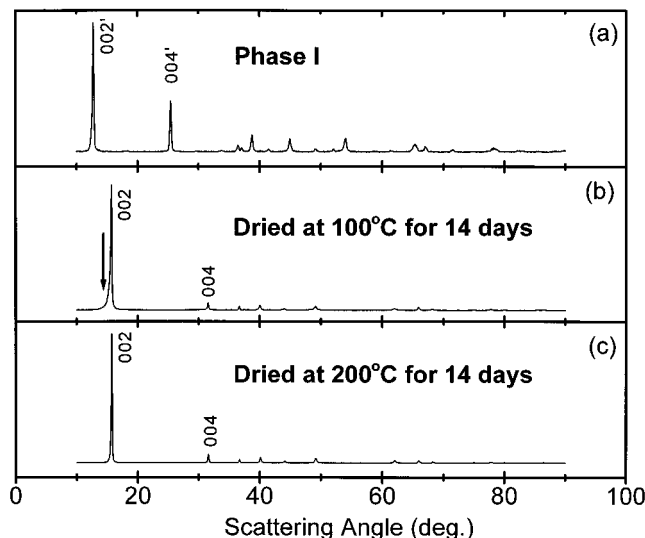


Figure 6. Effect of drying phase I under the indicated conditions. P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ is recovered after drying at 200 °C for 14 days.

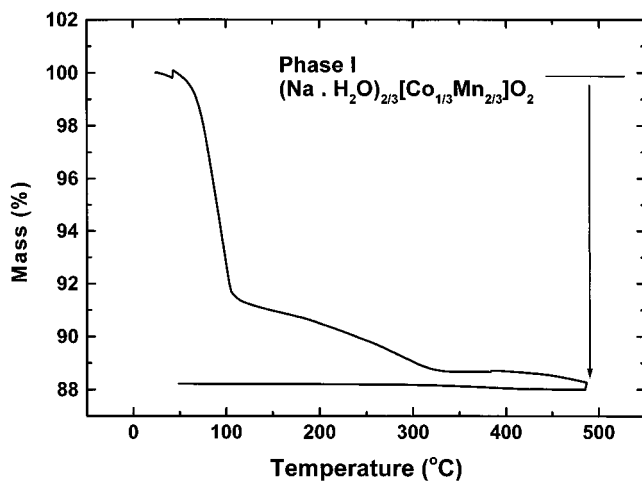


Figure 7. TGA trace of phase I in air.

(Na·H₂O)_{2/3}[Co_{1/3}Mn_{2/3}]O₂. Assuming that the composition of the phase at 340 °C is Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂, then the stoichiometry at the start of the experiment is Na_{2/3}(H₂O)_{0.73}[Co_{1/3}Mn_{2/3}]O₂. This is sufficiently

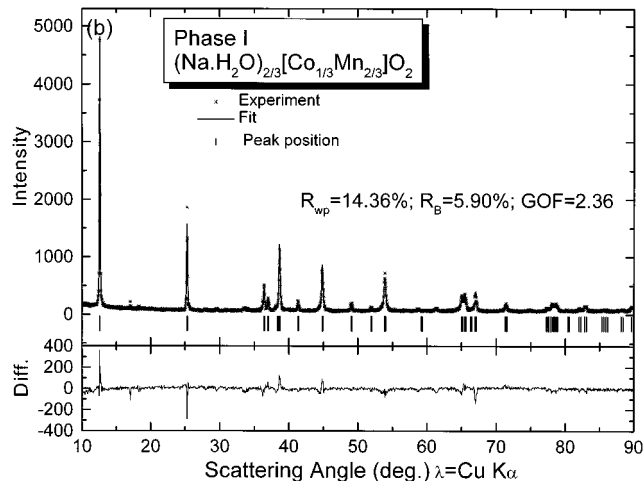


Figure 8. Rietveld profile refinement of phase I. The structural parameters are given in Table 1.

close to one H₂O molecule per sodium that we call phase I, (Na·H₂O)_{2/3}[Co_{1/3}Mn_{2/3}]O₂. It appears that the weight loss occurs in two steps, first in a two phase region between (Na·H₂O)_{2/3}[Co_{1/3}Mn_{2/3}]O₂ and Na_{2/3}(H₂O)_y[Co_{1/3}Mn_{2/3}]O₂ where y is about 0.2, and then in a single phase process as y is smoothly reduced to zero. This would need to be confirmed by in situ XRD studies during heating.

Hydrogen has a small scattering power for X-rays, but oxygen has an appreciable one so X-ray diffraction can be used to locate the oxygen atom of the water molecule intercalated within phase I. From the stoichiometry of phase I determined by TGA, it is natural to assume the oxygen atoms of the water molecule are located in the 2c site in P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂. Figure 8 shows the Rietveld refinement to the X-ray diffraction pattern of Phase I assuming the oxygen atom from water is in the 2c site and that the other atoms are in the same sites they were before water intercalation occurred. The refinement is quite good and the refined structure data is given in Table 1. The refined results indicate that the ratio of water to Na is very close (almost 1:1) to the TGA results. Figure 9 gives a view of the structure. Notice that the water molecules occupy positions at the centers of hexagons statistically ¹/₂-filled by Na.

Table 1. Structures of Phase I, Na_{2/3}(H₂O)_{2/3}[Co_{1/3}Mn_{2/3}]O₂, and P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ Space Group: P6₃/mmc (No. 194)

phase I						
$R_B = 5.90\%$, $R_{wp} = 14.36\%$, $GOF = 2.36$			$a = 2.85040 \pm 0.00014 \text{ \AA}$, $c = 14.0885 \pm 0.0015 \text{ \AA}$			
	Wyckoff position	x	Y	z	B (Å ²)	occ
Mn	2a	0	0	0	0	0.6667
Co	2a	0	0	0	0	0.3333
Na	2b	0	0	1/4	15.0 ± (1.1)	0.399 ± 0.013
Na	2d	1/3	2/3	3/4	15.0 ± (1.1)	0.267 ± 0.013
O	4f	1/3	2/3	0.0724 ± 0.0006	0	1.98 ± 0.03
O* ^a	2c	1/3	2/3	1/4	0	0.719 ± 0.013
original phase						
$R_B = 5.0\%$, $R_{wp} = 21.33\%$, $GOF = 2.0$			$a = 2.8467 \pm 0.0002 \text{ \AA}$, $c = 11.2978 \pm 0.0019 \text{ \AA}$			
	Wyckoff position	x	y	Z	B (Å ²)	occ.
Mn	2a	0	0	0	0	0.6667
Co	2a	0	0	0	0	0.3333
Na	2b	0	0	1/4	13.0 ± 1.0	0.309 ± 0.013
Na	2d	1/3	2/3	3/4	13.0 ± 1.0	0.358 ± 0.013
O	4f	1/3	2/3	0.0769 ± 0.0008	0	2.08 ± 0.03

^a O*: oxygen atom of the water molecule.

Table 2. Comparing Several Refinement Strategies for Phase I^a

trial	Na 2b z	Na 2d z	B (Na) (Å ²)	O 4f occ	O ^{*b} 2c occ	R _B (%)	GOF (%)
1	1/4	3/4	0	2.13	0.786	8.1	3.1
2	0.15 (4e site)	0.85 (4f site)	0	2.00	1.05	16.0	4.5
3	1/4	3/4	15.0	1.98	0.718	5.9	2.4

^a Overall Na occupation constrained to be 0.667, Mn occupation constrained to be 0.667, and Co occupation constrained to be 0.333. The z coordinates of the Na atoms were fixed as indicated. Stable refinements could not be made if the Na z coordinates were allowed to vary freely. ^b O^{*}: oxygen atom derived from the water molecule; occupation should be about 0.7 according to TGA.

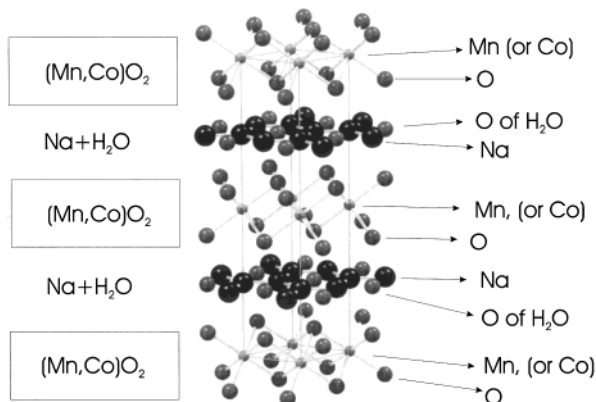


Figure 9. Crystal structure of phase I P2-Na_{2/3}(H₂O)_{2/3}[Co_{1/3}-Mn_{2/3}]O₂. The unit cell is given by the light solid lines. The Na positions are statistically 1/2 filled.

A consideration of interatomic distances in the refined structure for phase I suggests that the Na atoms are closer to the oxygen atoms of the water molecules than they are to the oxygen atoms of the MO₂ slabs. It may be possible, therefore, for the Na atoms to move off the midpoint between MO₂ slabs. We explored this possibility in the refinement by allowing the Na atoms to occupy 4e and 4f sites. Table 2 shows that when the Na thermal factor is fixed at zero (trials 1 and 2), the refinement is much better when the Na z-coordinate is fixed at the midpoint between the MO₂ slabs. Furthermore, as the Na is moved off the midpoint, the occupancy of the oxygen due to water, O^{*}, increases to unreasonable values, based on the TGA results presented earlier. The quality of the refinement improves dramatically when the individual Na isotropic thermal factor is refined (trial 3, same as Table 1). Therefore, we believe that the Na atoms are quite mobile, but on average are found centered between the MO₂ sheets.

As a comparison, a Rietveld refinement of the original P2-Na_{2/3}[Co_{1/3}Mn_{2/3}]O₂ sample was made and the refined structure data are also given in Table 1. Again, including a Na thermal factor improved the fit quality dramatically. The Bragg R factor was reduced from about 9% to about 5%, when the individual Na thermal factor was refined. Table 1 shows that intercalation of water leads to a substantial increase in the c lattice parameter while the change in a is only small. Phase I can be regarded as a monolayer hydrate.¹² The c-axis in the original phase is 11.298 Å, in phase I it is 14.094 Å and in phase II it is 19.530 Å. Because the incremental expansion of phase II is about double that of phase I, we believe that phase II is probably a bilayer hydrate.¹²

C. Lithiated Phase Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O₂ (x = 0, 1/6, 1/3) Exposed to Humid Air. Figure 10 shows the X-ray diffraction patterns of Li_{2/3}[Co_{1/3}Mn_{2/3}]O₂ before and after exposure to humid air for 10 days.

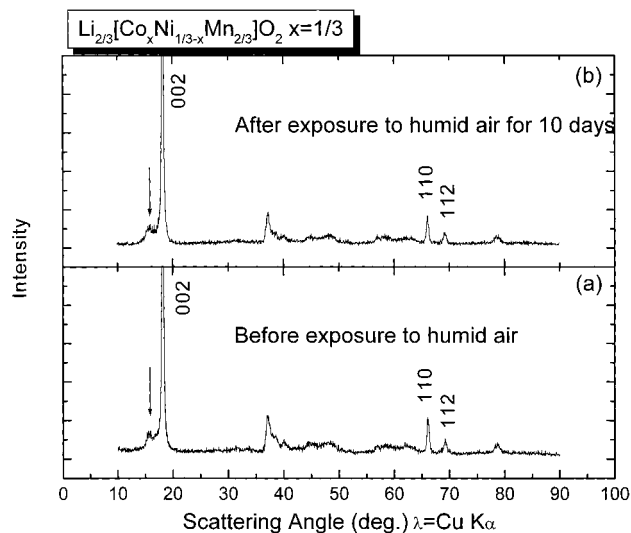


Figure 10. Diffraction patterns of (a) Li_{2/3}[Co_{1/3}Mn_{2/3}]O₂ and (b) Li_{2/3}[Co_{1/3}Mn_{2/3}]O₂ after exposure to humid air for 10 days.

The arrows in Figure 10 indicate the residue of the parent Na-containing phase after Li ion exchange for Na. It is obvious that water was not intercalated into the structure under these conditions. Although not shown, the same results were observed for each of the Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O₂ samples, upon exposure to humid air or upon water immersion.

IV. Discussion

Why is the intercalation of water in P2-Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O₂ easier when the cobalt content increases? The addition of Co suppresses the superlattice ordering in the transition metal layer.¹⁰ We speculate that the superlattice ordering induces a stronger coupling between adjacent MO₂ sheets, which prevents the intercalation of water, at least under the mild conditions used here. It is also possible that the presence of Mn³⁺, that forms as Co is added, also aids the intercalation of water.

Water intercalation was not observed for the lithiated samples. We believe this is because there are no large empty prismatic sites and few empty octahedral sites available for the water molecules in the T2 and stacking faulted O2 structures. By contrast, there are more than enough empty prismatic sites for the water in phase I Na_{2/3}(H₂O)_{2/3}[Co_{1/3}Mn_{2/3}]O₂. However, it is possible that the lithiated phases may intercalate water under more aggressive (higher water pressure) conditions.

V. Summary

It was found that water can be intercalated into P2-Na_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O₂ for x = 1/6 and 1/3 but not for P2-Na_{2/3}[Ni_{1/3}Mn_{2/3}]O₂. It was possible to prepare a pure

phase $\text{P2-Na}_{2/3}(\text{H}_2\text{O})_{2/3}[\text{Co}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ that **appears to have** the ideal P2 structure with the oxygen atoms of the water molecules in 2c sites. Evidence was given for the existence of a bilayer water intercalation phase in $\text{Na}_{2/3}(\text{H}_2\text{O})_y[\text{Co}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ with $y > 2/3$. Finally, it was shown that water cannot be intercalated into the lithated phases $\text{Li}_{2/3}[\text{Co}_x\text{Ni}_{1/3-x}\text{Mn}_{2/3}]\text{O}_2$ ($x = 0, 1/6, 1/3$). The water-intercalated phases may show interesting

magnetic properties due to weaker coupling of the MO_2 slabs.

Acknowledgment. The authors acknowledge the support of 3M Co., 3M Canada Co., NSERC, and NRC for the funding of this work.

CM000721X