

Formation and Structural Properties of Layered LiMnO_2 Cathode Materials

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$\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ compounds ($x \leq 0.10$) with an α - NaFeO_2 layer-type crystal structure have been prepared by a high temperature solid-state route. The compounds are well ordered with Al or Cr sharing the Mn sites and no detectable cation mixing between Mn and Li layers. Both Al- and Cr-substituted materials cycled between 4.4 and 2.0 V in Li cells at 55°C show high stability of capacity. However the Al-substituted materials undergo a structural transformation to a spinel-type phase, accompanied by evolution of the discharge voltage curve to a two-plateau profile. Materials modified with small amounts of Cr show a different evolution of the discharge voltage. X-ray diffraction data for cycled $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ cathodes show that these compounds do not undergo significant transformation to spinel on cycling, but retain a hexagonal structure established on first charge.

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LiMnO_2 with the α - NaFeO_2 layer-type crystal structure (similar to layer-type LiCoO_2 and LiNiO_2) is an attractive alternative to spinel-type lithium manganese oxides as a cathode active material in lithium-ion batteries. The LiMnO_2 stoichiometry offers a lithium source twice that of spinel compounds on charge and has a theoretical discharge capacity of 285 mAh/g based on a $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple.

Under equilibrium conditions, pure LiMnO_2 crystallizes in an orthorhombic structure (space group $Pmmn$). The reasons for the crystallization of LiMnO_2 in this structure, rather than in the layered α - NaFeO_2 rock-salt structure adopted by LiCoO_2 and LiNiO_2 , have been discussed by Ceder and Mishra.¹ Layered α - NaFeO_2 -type LiMnO_2 has been successfully prepared by soft chemistry methods,²⁻⁴ however, the compounds so prepared seem to be metastable with respect to orthorhombic and spinel-type phases.⁵ Spinel phase nucleates in the material on first charge (delithiation), and transformation to spinel is usually complete within a few charge-discharge cycles.⁵

LiMnO_2 may be stabilized in the layer structure by a number of possible substituent elements, if appropriate synthetic routes can be developed.¹ Preparation of layered α - NaFeO_2 -type LiMnO_2 at high temperature (>950°C) has been reported by substituting a small fraction (as little as 5%) of the Mn with Al⁶ and with Cr.^{7,8} These $\text{LiM}_x\text{Mn}_{1-x}\text{O}_2$ materials with $M = \text{Al}$ or Cr form under reaction conditions which produce orthorhombic o - LiMnO_2 in the absence of the structure modifier. It may be expected that substitution could also stabilize the layer structure against transformation to a spinel-type structure when employed as the cathode active material in a lithium cell. However, both $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ ⁹ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ ^{7,8} have been reported to transform to spinel on cycling, except for materials with high levels of Cr (>50%).

We have recently developed a high temperature solid-state synthesis for $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ which allows well-ordered layered phases to be obtained that have electrochemical properties equivalent to those shown by materials previously prepared by a coprecipitation, freeze-drying route.¹⁰ In this paper, we compare structural and electrochemical data for $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ materials prepared by the same solid-state route. Contrary to expectations from previous reports, here materials modified by Cr show different cycling characteristics than materials containing Al.

Experimental

$\text{LiM}_x\text{Mn}_{1-x}\text{O}_2$ ($0.03 \leq x \leq 0.10$) materials with $M = \text{Al}$ or Cr were prepared by reacting stoichiometric amounts of MnO_2 (99.0% purity), Li_2CO_3 (99.9% purity), and Al_2O_3 (99.9%) or Cr_2O_3

(99.0%) at 1000 to 1050°C under flowing nitrogen. Powders were mixed and ground before reaction using a vibratory rod mill. All samples were prepared in a single heating cycle, using reaction times of 5-10 h, and cooled slowly to ambient temperature.

X-ray diffraction (XRD) data were recorded on a Philips 1729 diffractometer using $\text{Co K}\alpha$ radiation and analyzed using the Rietveld refinement program FULLPROF.¹¹ XRD data for cycled cathodes were recorded *ex situ* on the cathode films stripped from the aluminum backing and mounted on a silicon sample holder using double-sided tape.

X-ray absorption spectra were recorded at the Cr and Mn K-edges in transmission mode on the EXAFS 13 spectrometer at the French synchrotron facility DCI at the Laboratoire pour l'Utilisation de Rayonnement ElectroMagnétique (LURE). Samples were diluted in boron nitride powder, prepared as Nujol mulls pressed between the parafilm windows of steel holders, and maintained at 77 K in a cold finger cryostat. Analyses of the extended X-ray absorption fine structure (EXAFS) to determine nearest M-O and M-M distances, where M is Cr or Mn, were carried out using the programs of Michalowicz¹² as described in previous work.¹³

For electrochemical evaluation, samples were tested in 2032 button cells. Cathodes comprised the $\text{LiM}_x\text{Mn}_{1-x}\text{O}_2$ powder + carbon black + poly(vinylidene fluoride) in 80:12:8 weight ratio coated on an aluminum foil current collector. Cells contained lithium metal as the anode, a glass-fiber separator, and 1 M LiPF_6 in (50 wt % ethylene carbonate + 50 wt % dimethylene carbonate) electrolytic solution. The cells were assembled under a dry (<1 ppm H_2O) argon atmosphere. Charge-discharge studies were performed between 4.4 and 2.0 V with an Arbin series BT2043 automated battery cyclers.

Results and Discussion

Crystal structure.—Figure 1 shows XRD data for $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ materials prepared at various levels of substitution up to $x = 0.10$. The main peaks for layered (monoclinic) phase are labeled with their *hkl* indices. Positions for peaks characteristic of orthorhombic o - LiMnO_2 phase are indicated.

For Cr substitution, $x = 0.03$ was sufficient to obtain >90% layered phase, and at $x = 0.05$ and $x = 0.10$, the materials were phase-pure layered $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$. For Al substitution, $x = 0.05$ was the minimum amount of Al for which >90% layered phase could be obtained. The remaining peaks in the diffraction pattern correspond to o - LiMnO_2 . Even at $x = 0.10$, some orthorhombic phase persisted in the $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ samples.

The peaks for the layered $\text{LiM}_x\text{Mn}_{1-x}\text{O}_2$ phases correspond to the monoclinic (space group $C2/m$) crystal structure described by

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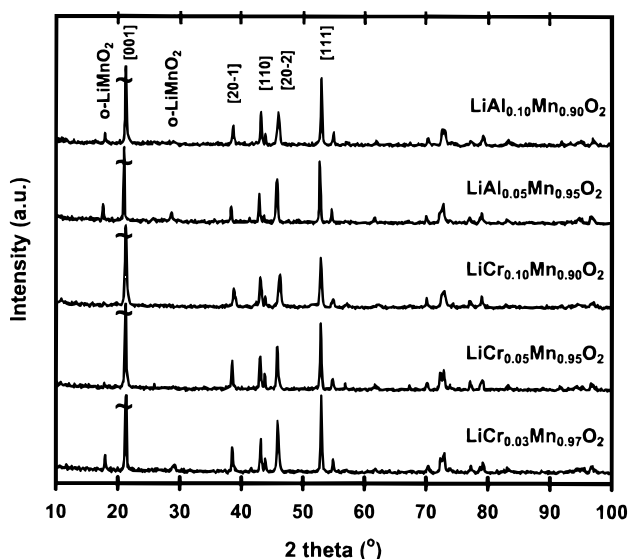


Figure 1. XRD patterns of $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ materials. The $[0\ 0\ 1]$ peaks at ca. 21° 2θ have been cut at 50% intensity for convenient viewing of other peaks.

previous authors for layered LiMnO_2 compounds obtained by soft chemistry.^{2,3} However, for the monoclinic LiMnO_2 phases obtained by soft chemistry, cation disorder corresponding to the presence of some spinel-related phase has been reported.⁵ Rietveld analyses of the XRD data for the $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ compounds described here show that the structures are well ordered with no evidence for Mn, Al, or Cr in the Li layer sites. A typical Rietveld fit is shown in Fig. 2 for $\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$.

Unit cell parameters for the monoclinic layered $\text{LiM}_x\text{Mn}_{1-x}\text{O}_2$ phases are reported in Table I, compared with literature data for non-substituted LiMnO_2 prepared by ion exchange from NaMnO_2 .² The $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ compounds show contracted crystal lattices by comparison with nonsubstituted $m\text{-LiMnO}_2$ materials. In the ab plane, the contraction is more significant along the a axis than the b axis. The extent of monoclinic distortion is reflected in the magnitude of the a/b ratio and is related to the average degree of distortion of the octahedron of oxygen ions around the cations in the Mn layer. Therefore a greater contraction along the a axis is consistent with substitution at the Mn sites by trivalent Al or Cr, which typically have highly regular octahedral coordination compared with the elongated $[\text{Mn}^{3+}\text{O}_6]$ octahedra. The lattice contraction is greater

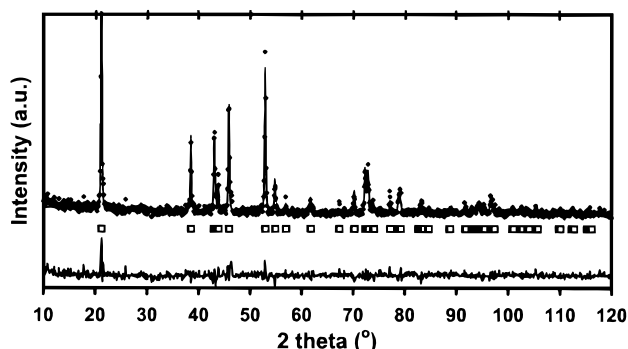


Figure 2. Rietveld fit (solid line) to the XRD data (points) for $\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$, in space group $C2/m$: Li at $(0, 0.5, 0.5)$, Mn/Cr at $(0, 0, 0)$, O at $(0.273, 0, 0.773)$, all at full site occupancy (unit cell parameters in Table I). The $[0\ 0\ 1]$ peak at ca. 21° 2θ has been cut at 50% intensity for convenient viewing of other peaks.

Table I. Unit cell parameters (Å) for $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ materials.

	<i>a</i>	<i>b</i>	<i>c</i>	β
$\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$	5.419(2)	2.802(1)	5.381(2)	115.89(2)°
$\text{LiAl}_{0.10}\text{Mn}_{0.90}\text{O}_2$	5.416(1)	2.804(1)	5.382(2)	115.91(2)°
$\text{LiCr}_{0.03}\text{Mn}_{0.97}\text{O}_2$	5.438(2)	2.808(1)	5.386(2)	115.98(2)°
$\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$	5.431(1)	2.807(1)	5.385(2)	115.98(2)°
$\text{LiCr}_{0.10}\text{Mn}_{0.90}\text{O}_2$	5.405(2)	2.815(2)	5.375(2)	115.61(2)°
LiMnO_2 (Ref. 2)	5.439(3)	2.809(2)	5.395(4)	115.9(4)°

at $x = 0.05$ for Al than for Cr, consistent with the smaller ionic radius of Al (0.54 Å for Al^{3+} compared with 0.62 Å for Cr^{3+}). However, at $x = 0.10$, the compound with Cr has smaller lattice parameters. The relatively small decrease in lattice parameters going from $x = 0.05$ to $x = 0.10$ for Al suggests that very little additional Al was dissolved in the LiMnO_2 lattice at $x = 0.10$. Chiang *et al.* have reported only limited solubility for Al in LiMnO_2 .⁶ For Cr, solid solution has been reported for $0.05 \leq x < 1$ in $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$.⁸

With increasing substitution by Al or Cr, the XRD data for the monoclinic phases show the greatest shift, and also increased broadening, in the $[2\ 0\ -l]$ diffraction peaks relative to other peaks in the diffraction pattern. Figure 3 shows an enlarged view of the region of the XRD patterns containing the $[2\ 0\ -1]$ and $[2\ 0\ -2]$ peaks for the 5 and 10% substituted materials. The broadening effect is particularly observable for the $[2\ 0\ -2]$ peak at 46° 2θ . The $[2\ 0\ 2]$ planes are directly perpendicular to the long axial bonds of the Jahn-Teller distorted $[\text{Mn}^{3+}\text{O}_6]$ octahedra, and the spacing of these planes (ca. 2.30 Å) corresponds to the length of these long axial Mn-O bonds. Typical $\text{Al}^{3+}\text{-O}$ and $\text{Cr}^{3+}\text{-O}$ bond lengths in octahedral coordination are ca. 1.92 and 2.00 Å, respectively. The substitution of Mn^{3+} by these species therefore results in disorder perpendicular to the $[2\ 0\ -2]$ planes as oxygen ions relax up to 0.4 Å out of the plane toward the substituent ions. Atomic displacements are less significant along other crystal vectors because the four equatorial $\text{Mn}^{3+}\text{-O}$ bond lengths (typically 1.90-1.95 Å) are closer to the lengths of the $\text{Al}^{3+}\text{-O}$ or $\text{Cr}^{3+}\text{-O}$ bonds. The broadening of the $[2\ 0\ -l]$ diffraction peaks not only confirms the presence of the substituent ions in the Mn sites of monoclinic LiMnO_2 , but also provides further evidence

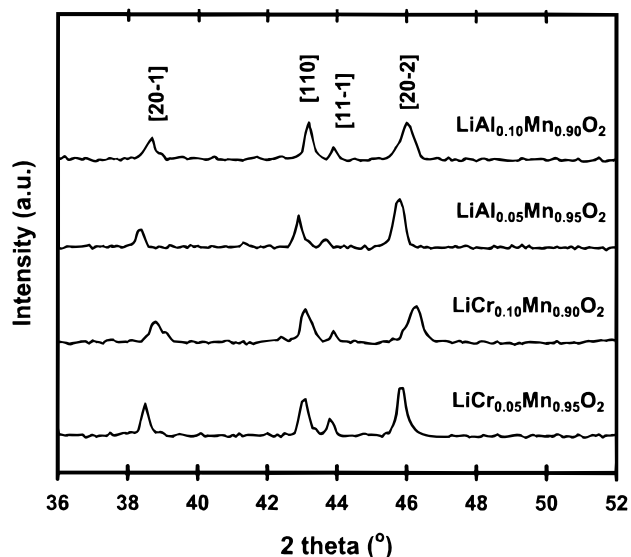


Figure 3. Enlargement of the region from 36 to 52° 2θ of the XRD patterns for the 5 and 10% substituted monoclinic phases, showing the broadening of the $[2\ 0\ -l]$ peaks with increasing substitution.

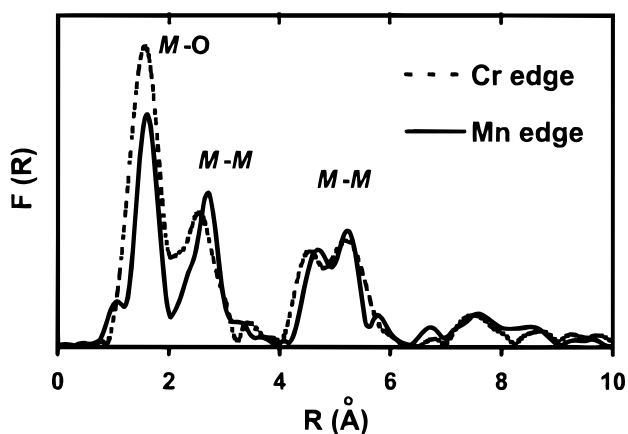


Figure 4. Fourier transformed EXAFS data at the Cr and Mn K-edges for $\text{LiCr}_{0.10}\text{Mn}_{0.90}\text{O}_2$.

of a more regular local coordination symmetry around the substituent species than around Mn^{3+} .

These differences in local coordination symmetry have been more specifically probed by X-ray absorption spectroscopy. Fourier transformations of the EXAFS spectra recorded at the Cr and Mn K-edges for $\text{LiCr}_{0.10}\text{Mn}_{0.90}\text{O}_2$ are shown in Fig. 4. The Fourier transformed data provide a pseudoradial distribution of the atomic ordering around the absorbing element (however, the peaks are shifted ca. 0.3 Å to lower values relative to the true interatomic distances, due to uncorrected phase shifts). Qualitatively, the Fourier transformations show that the coordination around Mn and Cr is identical beyond 4 Å, consistent with the elements occupying the same crystallographic site in the compound. The peaks at distances less than 4 Å correspond to the first coordination shell of oxygen and the ions occupying the six nearest-neighboring octahedral sites in the transition metal layer. These peaks show some differences between the Cr and Mn coordination in the compound. Interatomic distances calculated for these coordination shells from the EXAFS spectrum are given in Table II. The values for Mn-O and Mn-M ($M = \text{Mn or Cr}$) show the Jahn-Teller effect on the octahedral coordination around the Mn^{3+} ions and are consistent with the monoclinic crystal structure determined by XRD. The oxygen coordination around Cr ions is highly regular with six equal Cr-O distances, confirming the conclusions from the peak broadening in the XRD discussed above. The six neighboring M ions are also more closely distributed in the local structure around Cr than around Mn.

Electrochemistry.—Coin cells comprising layered monoclinic $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ materials were cycled over more than 200 cycles at ambient temperature and at 55°C. At ambient temperature, the materials show electrochemical characteristics described for the layered monoclinic LiMnO_2 system in previous works^{3,6-8}: a high first-charge capacity (up to 280 mAh/g), followed by discharge capacities up to 180 mAh/g at low current rates, but with a relatively high dependence of capacity on current rate. The dependence of capacity on current rate indicates that discharge is diffusion limited, although the mechanism for this limitation has not yet been elucidated. However since Al-substituted LiMnO_2 materials show good cycling stability at elevated temperature,⁶ we were particularly interested in comparing the performance of the Al- and Cr-substitut-

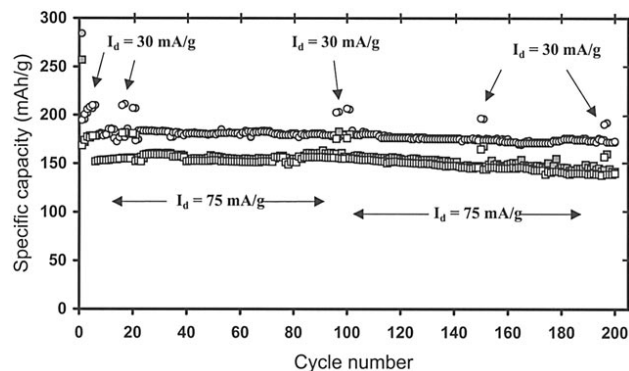


Figure 5. Cycling data at 55°C for Li cells containing $\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$ (squares) and $\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$ (circles). Charge = gray, discharge = white.

ed materials at 55°C. For Cr-substituted materials, cycling data at 55°C has not been previously reported, to our knowledge.

The cycling performance at 55°C is shown for $x = 0.05$ materials in Fig. 5. Cells were first charged and discharged at a current rate of 30 mA/g for five cycles and were then switched to the higher current rate of 75 mA/g for subsequent cycles. To verify the discharge capacity at the lower current rate after extended cycling, cells were periodically discharged at 30 mA/g (cycles 16, 20, 96, 100, 150, 196, and 200). Note two features in particular; the capacities obtained with the Cr-substituted material are ca. 15% higher than those obtained with the Al-substituted material, and the capacity retention at 55°C is high (>90%) over 200 cycles for both the Al- and the Cr-substituted material.

Although both Al- and Cr-substituted compounds show remarkable cycling stability at 55°C, significant differences were observed in the voltage profiles. Figure 6 compares discharge curves at different cycle number for the cells of Fig. 5. For $\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$, the first discharge is characterized by a relatively featureless sloping profile between 4 and 3 V. However, with continued cycling, the voltage in the first half of discharge evolves to higher potential, and the voltage in the second part of discharge evolves to lower potential. By cycle 16, the discharge profile shows two distinct plateaus at around 4 and 3 V, with a sharp drop between the two plateaus. This profile strongly resembles that observed for a spinel-type manganese oxide structure, where the 4 V plateau relates to insertion of Li into tetrahedral sites, and the 3 V plateau relates to insertion into octahedral sites. Therefore, the data for $\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$ are fully consistent with recent structural analyses showing that this compound transforms to a spinel-related structure during cycling.⁹ The layered LiMnO_2 compounds prepared by soft chemistry have also undergone transformation to spinel with cycling.⁵

The discharge curves for the Cr-substituted material also show an evolution with cycling, but the evolution is different from that observed for the Al-substituted material. On the first discharge, the voltage profile is similar to that for the Al-substituted compound, but shows more structure with distinct inflections in the curve at ca. 60 and 120 mAh/g, which divide the discharge into three regions. On subsequent cycles, there is some movement of the middle part of the discharge to lower voltage, but the curve continues to be characterized by three distinct steps. The most important observation is that no significant additional capacity is evolved at 4 V beyond the first

Table II. Interatomic distances (number of atoms at this distance in parentheses) determined from EXAFS for $\text{LiCr}_{0.10}\text{Mn}_{0.90}\text{O}_2$.

Mn-O	Mn-M ($M = \text{Mn or Cr}$)	Cr-O	Cr-M ($M = \text{Mn or Cr}$)
1.94 Å ($\times 4$)	2.82 Å ($\times 2$)	1.99 Å ($\times 6$)	2.81 Å ($\times 2$)
2.29 Å ($\times 2$)	3.05 Å ($\times 4$)	—	2.97 Å ($\times 4$)

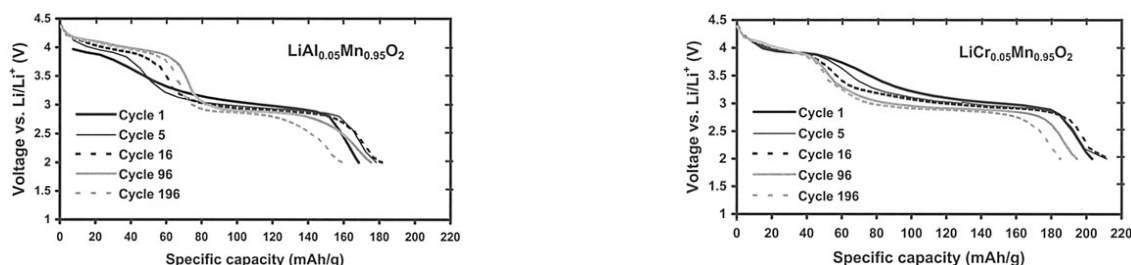


Figure 6. Discharge curves for Li cells containing $\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$ (left) and $\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$ (right) at cycles 1, 5, 16, 96, and 196 (current rate 30 mA/g, temperature 55°C).

cycle, even after 200 cycles, indicating little or no formation of additional spinel-type tetrahedral sites for Li with cycling.

Evolution of crystal structure during cycling.—The differences between the shapes of the discharge curves evolved by the Cr- and Al-substituted compounds suggest that different structural processes take place during lithium deintercalation and reintercalation. Therefore, cycled materials were investigated by XRD on cathodes extracted from cells in various states of charge and discharge. Cell parameters calculated from the XRD data are compared in Table III for Al- and Cr-substituted ($x = 0.05$) materials during the first cycle and after 100 cycles. XRD patterns are shown in Fig. 7. Figure 8 compares cell parameters of Al- and Cr-substituted materials with those reported for unsubstituted LiMnO_2 ¹⁴ as a function of Li content during the first cycle.

The first charge capacity for both Al- and Cr-substituted materials corresponds to almost complete removal of Li from the compounds. As observed for layered LiMnO_2 prepared by soft chemistry, this deintercalation is accompanied by a relaxation of the starting monoclinic crystal structure to a more regular hexagonal crystal structure, as a result of oxidation of Mn^{3+} to Mn^{4+} . However, data reported for LiMnO_2 show that the hexagonal c parameter undergoes a sharp decrease at the end of charge, to 13.41 Å.¹⁴ Such a low c parameter at the end of charge was not observed in this study for the Al- or Cr-substituted compounds.

On the first discharge, XRD shows that both Al- and Cr-substituted compounds retain a hexagonal structure to 2.0 V. The hexagonal a parameter increases with discharge, consistent with reduction of Mn^{4+} to Mn^{3+} . The c parameter initially increases during discharge and then decreases with further intercalation of Li. If the cells are discharged below 2.0 V, a monoclinic and/or tetragonal phase appears in the XRD pattern.¹⁰

Cathodes extracted from cells after further charge-discharge cycles reveal that different processes take place for Al- and Cr-substituted samples on subsequent cycling. Cycled Al-substituted compounds show a decrease in the hexagonal c/a ratio relative to the first cycle. After 100 cycles, the c/a ratio has a value of 4.9, and it is no longer possible to distinguish whether the phase is hexagonal or cubic from the XRD patterns. The diffraction peaks in the dis-

charged sample correspond well to a cubic spinel system with a cell parameter of $a = 8.23$ Å, comparable with LiMn_2O_4 . Recent studies of cycled Al-substituted LiMnO_2 by transmission electron microscopy and electron diffraction have shown that the cycled phase is mainly spinel-type.⁹ This is consistent with the evolution of the discharge voltage profiles with cycling.

However, cathodes extracted from cells containing Cr-substituted compounds after 100 cycles show c/a ratios greater than 5.0. Figure 7 shows the diffraction pattern for the Cr-substituted compound in the charged state. The XRD pattern corresponds to a hexagonal structure and is clearly distinguishable from that expected for a spinel-type compound, which should be cubic ($c/a \sim 4.9$) and would have a cell volume < 100 Å³ in the charged state. The diffraction peaks are broader than those observed for the Al-substituted material after 100 cycles, particularly the peak at $ca. 52^\circ 2\theta$, indicating a more disordered structure for the cycled Cr-substituted material. The disorder may result from changes in the crystal structure underlying the type of evolution of the discharge profile shown in Fig. 6. However, we have not yet been able to determine the nature of these changes in any more detail by *ex situ* XRD.

The reasons for the differences between the Cr- and Al-substituted materials with respect to structural evolution during cycling are currently under investigation in a more detailed study by *in situ* XRD and X-ray absorption fine structure spectroscopy, the results of which are reported separately. However, the structural data reported to date indicate that the most significant structural transformations take place in layered transition metal oxides in the highly charged (delithiated) state. These structural transformations are typically accompanied by a decrease in the interlayer distance. Our data for $\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$ show some decrease in the hexagonal c parameter ($c = 3 \times$ the interlayer distance) on the first charge, although the effect is not as large as that reported for unsubstituted LiMnO_2 . For $\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$, we observe a small decrease in c at the end of the first charge, but the c parameter remains 0.1 Å higher than that for fully charged $\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$. These observations suggest that the layered structure of the Cr-substituted material is more stable to delithiation than either the Al-substituted material or the unsubstituted material.

Table III. Unit cell parameters calculated from X-ray diffraction data for hexagonal phases in cycled cathodes.

Starting material	Cycle no.	State of charge	a (Å)	c (Å)	Cell volume (Å ³)	c/a
$\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$	1	Charged to 4.4 V	2.86	14.53	102.9	5.08
	1	Discharged to 3.5 V	2.86	14.61	103.7	5.11
	1	Discharged to 2.0 V	2.88	14.56	105.0	5.05
	100	Discharged to 2.0 V	2.91	14.24	104.4	4.90
$\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$	1	Charged to 4.4 V	2.86	14.62	103.7	5.11
	1	Discharged to 3.2 V	2.87	14.66	104.7	5.11
	1	Discharged to 2.0 V	2.89	14.58	105.5	5.05
	100	Charged to 4.4 V	2.87	14.60	104.2	5.09

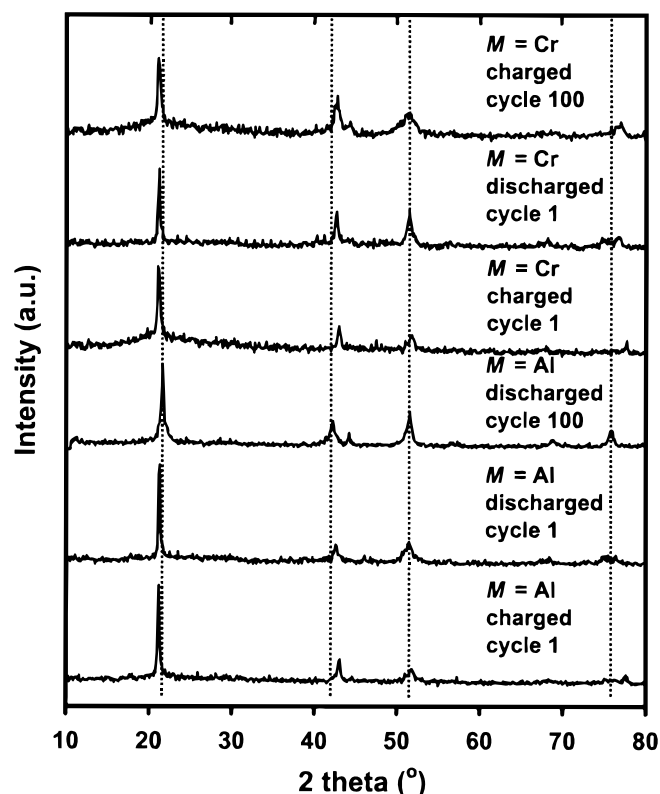


Figure 7. XRD patterns of cycled $\text{LiM}_x\text{Mn}_{1-x}\text{O}_2$ ($x = 0.05$) cathodes. Dotted lines indicate the main peak positions calculated for a cubic spinel oxide with unit cell parameter of 8.23 Å.

Conclusions

Although the $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ systems prepared by the solid-state routes show similarities in crystal structure, significant differences are observed in the electrochemical properties with cycling. In both cases, XRD studies on cycled cathodes show that during the first charge the monoclinic structure undergoes a relaxation to a hexagonal structure, which is retained on the first discharge to a cutoff of 2 V vs. Li/Li^+ . The similarity in the shapes of the first cycle discharge curves between the Al- and the Cr-containing materials is further evidence that the crystal structures at this stage are nearly identical. On further cycling, our data for the Al-substituted materials agree with other reports that the crystal structure of these compounds transforms to a spinel-type. However, low levels of Cr substitution seem to be able to prevent significant transformation to a spinel-type structure on extended cycling between 4.4 and 2.0 V.

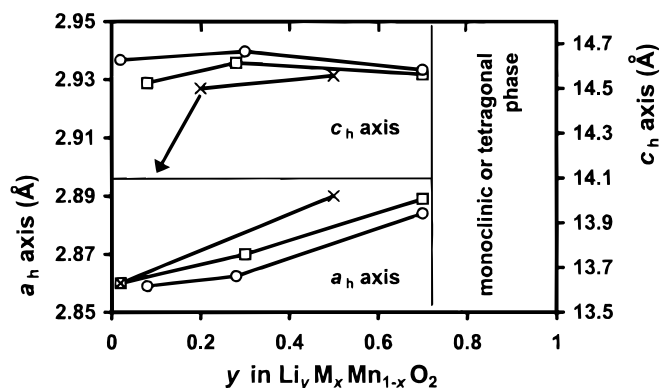


Figure 8. Hexagonal unit cell parameters as a function of Li content in the first cycle for $\text{LiAl}_{0.05}\text{Mn}_{0.95}\text{O}_2$ (squares), $\text{LiCr}_{0.05}\text{Mn}_{0.95}\text{O}_2$ (circles), and LiMnO_2 (crosses; Ref. 14).

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