

Factors Influencing the Layered to Spinel-like Phase Transition in Layered Oxide Cathodes

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 $Li_{0.5}MO_2$ [M = Mn, Co, Ni, $Ni_{1-y}Co_y$, $Ni_{1-y}Mn_y$, and $Mn_{1-y}(Cr,Al,Mg)_y$] compositions obtained by chemically extracting lithium with $Na_2S_2O_8$ from LiMO₂ have been investigated by X-ray diffraction after heating at various temperatures. While $Li_{0.5}MnO_2$ obtained from both the monoclinic (O3 stacked layer structure) and orthorhombic LiMnO₂ transforms to the spinel-like phases at ambient temperature during the lithium extraction process due to cation migration, $Li_{0.5}NiO_2$ needs mild heat (~150°C) to transform to the spinel-like phase. $Li_{0.5}CoO_2$ does not transform even after heating at 200°C. The decrease in the structural stability in the order $Li_{0.5}CoO_2 > Li_{0.5}NiO_2 > Li_{0.5}MnO_2$ is explained on the basis of crystal field stabilization energies. Additionally, the incorporation of foreign cations into the transition metal planes via cationic substitutions is found to increase the structural stability by perturbing the cooperativity among the transition metal ions and thereby suppressing the cation migration. © 2002 The Electrochemical Society. [DOI: 10.1149/1.1497171] All rights reserved.

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The rapid growth in portable electronic devices has intensified the research activities in lithium-ion batteries as they provide higher voltage and energy density compared to other rechargeable systems. Among the various lithium insertion compounds investigated during the past three decades,¹ transition metal oxides have become attractive cathodes for lithium-ion cells as they offer higher cell voltage than, for example, chalcogenides and pnictides. The higher voltage of oxide cathodes is mainly due to the larger Madelung energy associated with the more ionic oxide lattice and a positioning of the O:2p band at a lower energy compared to the 3p, 4p, or 5p energies of the chalcogenides or pnictides.² In the case of oxides, the LiMO₂ (M= transition metal) layered structure and the LiM₂O₄ spinel structure have become attractive as they provide reversible insertion/ extraction of the lithium ions into/from them with adequate electronic and lithium-ion conductivities.

Among the layered LiMO₂ oxides, LiCoO₂ is widely used in commercial lithium-ion cells as it shows good performance and structural stability during the charge-discharge process.³ However, cobalt is relatively expensive and toxic and only 50% of the theoretical capacity of LiCoO2 could be practically utilized. In this regard, much attention has been focused toward other layered oxides with M = Ni, Mn, Fe, V, and Cr. Unfortunately, the performance of these oxides is inferior to that of $LiCoO_2$. While $LiCrO_2$ is difficult to charge, both layered LiVO24 and LiFeO25 suffer from poor cyclability arising from cationic migrations. Similarly, both the monoclinic (O3 layer structure) $LiMnO_2^{6-9}$ that is generally obtained by an ion exchange of NaMnO₂ and the orthorhombic LiMnO₂¹⁰ transform to a spinel-like structure during the charge-discharge process. LiNiO₂ is difficult to synthesize as an ordered layered material^{11,12} and Ni³⁺ undergoes Jahn-Teller distortion.^{13,14} Moreover, charged $Li_{1-x}NiO_2$ has been found to experience a migration of nickel ions under mild heat to give spinel-like phases at moderate temperatures.¹⁵

However, cationic substitutions have been found to help to improve the electrochemical properties in the case of layered manganese and nickel oxides. For example, the substitution of Cr^{3+} and Al^{3+} for Mn^{3+} in $LiMn_{1-y}M_yO_2^{16-18}$ (M = Cr and Al) has been found not only to access the monoclinic LiMnO₂ by conventional ceramic procedures, but also to improve the stability of the layered phase and the electrochemical performance during cycling. Similarly, the substitution of Co^{3+} for Ni^{3+} in $LiNi_{1-y}Co_yO_2^{19}$ has been found not only to improve the ordering of the cations in the layer lattice, but also to suppress the Jahn-Teller distortion^{13,14} associated

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with Ni³⁺ and improve the electrochemical performance.²⁰ In fact, LiNi_{0.85}Co_{0.15}O₂ shows much higher practical capacity of around 180 mAh/g compared to that of LiCoO₂ (140 mAh/g) with good cyclability. However, LiNi_{0.85}Co_{0.15}O₂ too experiences a migration of nickel ions under mild heat to give spinel-like phases, although to a lesser extent than that found with unsubstituted LiNiO₂.¹⁵

The transformation of the layered $Li_{1-r}MO_2$ (charged cathode) phase to a spinel-like phase become facile as both of them have a cubic close-packed oxygen array. For example, transformation of the layered $Li_{0.5}MO_2$ into the ideal cubic spinel phase $(Li)_{8a}[M_2]_{16d}O_4$ requires a migration of 25% of the transition metal ion $M^{3+/4+}$ from the octahedral sites (3b sites) of the M planes into the empty octahedral sites (3a sites) of the lithium planes and a displacement of the lithium ions from the 3a sites into the neighboring tetrahedral sites. The migration of the transition metal ions can be achieved via the neighboring tetrahedral sites (designated as T1 and T2), as illustrated in Fig. 1. Such a migration of the transition metal ions can impede the lithium-ion diffusion in the lithium layer and degrade the electrochemical performance of the layered phases. Moreover, recent theoretical calculations based on first principles modeling have shown that the spinel structure is energetically more stable compared to the layer structure for the $\mathrm{Li}_{0.5}\mathrm{MO}_2$ compositions with M =Ti, Cr, Mn, Fe, Co, and Ni.²¹



Figure 1. Illustration of the paths for the migration of the transition metal ion M^{n+} from the octahedral sites in the transition metal layer to the octahedral sites in the lithium layer via the neighboring tetrahedral sites (T₁ and T₂).

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Figure 2. XRD patterns of (a) $LiCoO_2$, (b) $Li_{0.5}CoO_2$ obtained by extracting lithium from $LiCoO_2$, (c) $Li_{0.5}CoO_2$ after heating at 150°C, (d) $Li_{0.5}CoO_2$ after heating at 250°C, and (e) $Li_{0.5}CoO_2$ after heating at 400°C for 3 days in air.

Despite the observation of the formation of spinel-like phases during the electrochemical cycling of certain layered oxides, no systematic study focusing on the factors driving such transformations is available in the literature. Identification of the various factors influencing the layered to spinel-like phase transition can help to design structurally stable cathode hosts with high energy density. We present here a systematic investigation of the layered to spinel-like phase transition by evaluating the structural stability of bulk $Li_{0.5}MO_2$ [M = Mn, Co, Ni, $Ni_{1-v}Co_v$, $Ni_{1-v}Mn_v$, and $Mn_{1-\nu}(Cr,Al,Mg)_{\nu}]$ compositions obtained by chemically extracting lithium from the corresponding LiMO₂ phase. The structural stability is assessed by comparing the X-ray diffraction (XRD) patterns recorded before and after heating the bulk Li_{0.5}MO₂ samples at various temperatures. From the results obtained, the factors that drive the transformation and help to suppress the transformation are identified. Additionally, the understanding gained with cationic substitutions is applied to design structurally stable layered lithium manganese oxides.

Experimental

LiCoO₂ was synthesized by solid-state reaction between required amounts of Li₂CO₃ and Co₃O₄ at 800°C in air. LiNi_{1-y}Co_yO₂ samples with $0 \le y \le 0.75$ were synthesized by a sol-gel procedure described elsewhere,¹⁶ in which the gel obtained with an acetic acid solution containing required amounts of Li₂CO₃, cobalt acetate, and nickel acetate was fired at 800°C under flowing oxygen for 24 h. LiNi_{1-y}Mn_yO₂ samples with $0 \le y \le 0.5$ were synthesized by firing coprecipitated hydroxides of nickel and manganese with lithium hydroxide at 800°C under flowing oxygen. The coprecipitation of the nickel and manganese hydroxides were achieved by adding KOH to the corresponding acetate solution followed by filtering, washing, and drying of the product. Orthorhombic LiMnO₂ was synthesized by solid-state reaction between Li₂CO₃ and Mn₂O₃ at 1000°C under flowing nitrogen. Monoclinic LiMnO₂ was obtained by ion-exchanging α -NaMnO₂ with LiBr in hexanol at 150°C. Monoclinic LiMn_{1-y}M_yO₂ (M = Cr, Al, or Mg) samples were synthesized by solid-state reactions of required amounts of LiOH, Mn_2O_3 , Cr_2O_3 , Al_2O_3 , and $Mg(OH)_2$ at 1050°C under inert atmosphere (nitrogen or argon) with one intermittent grinding.

Chemical extraction of lithium from the various LiMO₂ phases to obtain $Li_{0.5}MO_2$ was accomplished by stirring for 2 days the LiMO₂ powders in an aqueous solution containing appropriate quantities of the oxidizer, sodium perdisulfate (Na₂S₂O₈). The following chemical reaction occurs during this process

$$\begin{array}{l} 2\text{LiMO}_2 \,+\, 0.5\text{Na}_2\text{S}_2\text{O}_8 \rightarrow 2\text{Li}_{0.5}\text{MO}_2 \,+\, 0.5\text{Na}_2\text{SO}_4 \\ \\ &+\, 0.5\text{Li}_2\text{SO}_4 \end{array} \tag{1}$$

After the chemical extraction reaction, the product $Li_{0.5}MO_2$ formed was washed with deionized water several times to remove the soluble Na_2SO_4 , Li_2SO_4 , and any unreacted $Na_2S_2O_8$. The $Li_{0.5}MO_2$ samples thus obtained were then heated in air for 3 days at various temperatures to assess the ease of formation of spinel-like phases.

Lithium contents in the products were determined by atomic adsorption spectroscopy (AAS). Structural characterizations were carried out by fitting the XRD data with the Rietveld program. Electrochemical properties were evaluated with coin-type cells using circular cathodes of 0.64 cm² area, metallic Li anodes, and LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte. The cathodes were fabricated by hand-mixing the samples with 25 wt % fine carbon for about 30 min and mixing the composite with 5 wt % polytetrafluoroethylene (PTFE).

Results and Discussion

Comparison of the structural stability of $Li_{0.5}MO_2$ (M=Mn, Co, and Ni).-Figure 2 gives the XRD patterns of LiCoO₂ and $Li_{0.5}CoO_2$ that was obtained by chemical lithium extraction and the evolution of the phases on subjecting $Li_{0.5}CoO_2$ to mild heat. The as-prepared Li_{0.5}CoO₂ maintains the rhombohedral layer structure of the parent $LiCoO_2$ as indicated by the separation between the (018) and (110) reflections centered around $2\theta = 66^{\circ}$ (Fig. 2a and b). The Li_{0.5}CoO₂ sample also maintains the layer structure even after heating at moderate temperatures (Fig. 2c and d), although the (018) and (110) reflections have moved slightly toward each other. At high enough temperatures, Li_{0.5}CoO₂ disproportionates to give Co₃O₄ impurity (Fig. 2e). These observations reveal the good structural stability of LiCoO₂ and attest to its excellent cyclability in the lithium-ion cells. Although the formation of a spinel phase has been claimed from transmission electron microscopy (TEM) studies in cycled $LiCoO_2$ cathodes by Wang *et al.*,²² our experiments with chemically prepared bulk Li_{0.5}CoO₂ reveal that no spinel-like phase is formed even after heating to 250°C (Fig. 2).

Figure 3 shows the evolution of the phases on subjecting the chemically prepared $\text{Li}_{0.5}\text{NiO}_2$ to mild heat. The as-prepared $\text{Li}_{0.5}\text{NiO}_2$ (Fig. 3b) maintains the rhombohedral layer structure like the parent LiNiO₂ (Fig. 3a), as indicated by the separation between the (018) and (110) reflections centered around $2\theta = 65^{\circ}$. However, on heating to 200°C, the rhombohedral $\text{Li}_{0.5}\text{NiO}_2$ transforms to a cubic phase (Fig. 3c), as indicated by the merger of the (018) and (110) reflections into a single reflection of (440). On further heating to $T > 200^{\circ}$ C, the cubic phase begins to disproportionate with a loss of oxygen to give LiNiO₂ and NiO (Fig. 3e).

Rietveld analysis of the cubic phase obtained at 200°C with $Fd\bar{3}m$ space group indicates the formation of a spinel-like phase, but with the nickel ions present in both the 16d and 16c sites (Fig. 4). As pointed out in the introduction, transformation of the layered $\text{Li}_{0.5}\text{NiO}_2$ into the ideal spinel phase $(\text{Li})_{8a}[\text{Ni}_2]_{16d}O_4$ requires the migration of 25% of the nickel ions from the nickel planes (3b sites) into the lithium planes (3a sites) of the initial rhombohedral layer structure. The presence of nickel ions in both the 16d and 16c sites indicates that the migration is incomplete at the moderate tempera-



Figure 3. XRD patterns of (a) LiNiO₂, (b) Li_{0.5}NiO₂ obtained by extracting lithium from LiNiO₂, (c) Li_{0.5}NiO₂ after heating at 150°C, (d) Li_{0.5}NiO₂ after heating at 200°C, and (e) Li_{0.5}NiO₂ after heating at 300°C for 3 days.

tures of 200°C. Further increase in temperature to complete the migration and obtain the ideal spinel $(Li)_{8a}[Ni_2]_{16d}O_4$, however, results in a disproportionation of the phase to give NiO impurity. The results thus clearly reveal that it is difficult to access the ideal spinel $(Li)_{8a}[Ni_2]_{16d}O_4$, although it has been suggested^{11,23} to be formed before by simply looking at the merger of the (018) and (110) reflections in the X-ray pattern. Nevertheless, the tendency of nickel ions to migrate to the lithium planes under mild heat may pose some



Figure 4. Rietveld refinement results of $Li_{0.5}NiO_2$ after heating at 200°C for 3 days in air. The observed and calculated X-ray profiles, peak positions, and the difference between the observed and calculated profiles are shown. Also, the cation distribution, R factors, and lattice parameter are given.



Figure 5. XRD patterns of (a) orthorhombic LiMnO₂, (b) Li_{0.5}MnO₂ obtained from orthorhombic LiMnO₂, (c) monoclinic LiMnO₂, (d) Li_{0.5}MnO₂ obtained from monoclinic LiMnO₂, and (e) sample d after heating at 150°C.

difficulties in the long-term cyclability of LiNiO₂ cathodes at elevated temperatures, unlike in the case of LiCoO₂ cathodes. 15

Figure 5 gives the XRD patterns of monoclinic and orthorhombic LiMnO₂ and the Li_{0.5}MnO₂ samples obtained from them by chemical lithium extraction. The data reveal that in both cases, a nearly spinel-like phase is already formed during the chemical delithiation process at ambient temperature, which is consistent with that found by several groups during electrochemical cycling.⁶⁻¹⁰ Between the two systems, the orthorhombic LiMnO₂ appears to form the spinel-like phase more readily compared to the monoclinic LiMnO₂, as indicated by the formation of a single nearly spinel-like phase at ambient temperature in the former case. In the case of monoclinic LiMnO₂, a spinel-like phase with some additional unidentified reflections is found after lithium extraction at room temperature, and a single spinel-like phase is formed on heating at 150°C.

A comparison of the results obtained with the three systems with M = Co, Ni, and Mn indicates that the tendency of the layered $Li_{0.5}MO_2$ to transform to cubic spinel-like phase decreases in the order $Li_{0.5}MO_2 > Li_{0.5}NiO_2 > Li_{0.5}CoO_2$. While a spinel-like phase is readily formed during lithium extraction for M = Mn, a mild temperature is needed for the case of M = Ni. It is difficult to obtain a spinel-like phase for M = Co even after heating at 200°C. As pointed out earlier, the transformation of the layered phase to a spinel-like phase involves the migration of the M^{n+} ions from the octahedral sites of transition metal layer to the octahedral sites of the lithium layer via the nearby tetrahedral sites. Therefore, the relative stability of the M^{n+} ions in the octahedral vs. tetrahedral sites may play a critical role in the relative ease of formation of the spinel-like phases.

Table I. Croiss and Obolis of Incert, count, and manganese tons.										
	Octahedral coordination				Tetrahedral coordination					
	Configuration ^a				Configuration ^a					
Ion	t_{2g}	eg		CFSE	e	t ₂		CFSE ^b	OSSE	
Ni ³⁺ :3d ⁷	6	1	(LS)	-18 Dq	4	3	(HS)	-5.33 Dq	-12.67 Dq	
Ni ⁴⁺ :3d ⁶	6	0	(LS)	-24 Dq	3	3	(HS)	-2.67 Dq	-21.33 Dq	
$Co^{3+}:3d^{6}$	6	0	(LS)	-24 Dq	3	3	(HS)	-2.67 Dq	-21.33 Dq	
Co ⁴⁺ :3d ⁵	5	0	(LS)	-20 Dq	2	3	(HS)	0.00	-20.00 Dq	
$Mn^{3+}:3d^{4}$	3	1	(HS)	-6 Dq	2	2	(HS)	-1.78 Dq	-4.22 Dq	
$Mn^{4+}:3d^{3}$	3	0	(HS)	-12 Dq	2	1	(HS)	-3.56 Dq	-8.44 Dq	

Table I. CFSEs and OSSEs of nickel, cobalt, and manganese ions.

^a LS and HS refer, respectively, to low spin and high spin configurations.

^b Obtained by assuming $\Delta_t = 4/9\Delta_o$; Δ_t and Δ_o refer, respectively, to tetrahedral and octahedral splittings.

Table I gives the crystal field stabilization energies (CFSEs) for the octahedral and tetrahedral coordination along with the octahedral site stabilization energies (OSSEs), which is the difference between the CFSE values of octahedral and tetrahedral coordination, for various ions. For the M^{3+} ions [low-spin (LS) configurations for Ni³⁺ and Co³⁺ and high-spin (HS) configuration for Mn³⁺ in octahedral geometry], the OSSE values increase in the order Mn³⁺ < Ni³⁺ < Co³⁺. A larger OSSE value for the Co³⁺ ions makes the migration via the tetrahedral site difficult, and therefore, the formation of a spinel-like phase becomes difficult for M = Co. A smaller OSSE value for Mn³⁺ makes the formation of spinel-like phase easier.

Additionally, the ability of the M^{3+} ions to disproportionate to M^{2+} and M^{4+} may also play a role in assisting the formation of spinel-like phases. Mn^{3+} is well known to disproportionate easily to Mn^{4+} and Mn^{2+} .²⁴ The Mn^{2+} ions formed by disproportionation can readily migrate to the lithium planes via the empty tetrahedral sites as the HS Mn^{2+} with a d⁵ electronic configuration has no OSSE. Compared to Mn^{3+} , the disproportionation of both Co^{3+} and Ni^{3+} is energetically less favorable.

The observed trend in cation migration and structural stability correlates with the electrochemical performance of the layered oxide cathodes. LiCoO₂ with a good structural stability provides the best electrochemical performance, while LiMnO₂ with a poor structural stability provides the worst electrochemical performance among the three layered LiMO₂ systems compared here. One of the ways that has been found to improve the electrochemical performance is cationic substitutions. For example, as pointed out previously, the substitutions of cobalt for nickel in LiNi_{1-y}Co_yO₂²⁰ and chromium for manganese in LiMn_{1-y}Cr_yO₂^{16,17} have been found to improve the electrochemical performance. In the next section, we examine how the cationic substitutions influence the cationic migration and structural stability.

Structural stability of cation-substituted $Li_{0.5}Ni_{1-y}Co_yO_2$ and $Li_{0.5}Ni_{1-y}Mn_yO_2$.—With an objective to understand the influence of cationic substitutions on structural stability, we investigated the $Li_{0.5}Ni_{1-y}Co_yO_2$ ($0 \le y \le 1$) and $Li_{0.5}Ni_{1-y}Mn_yO_2$ ($0 \le y \le 0.5$) systems. Figure 6 compares the XRD patterns of $Li_{0.5}Ni_{1-y}Co_yO_2$ ($0 \le y \le 1$) after heating at 200°C. The data reveal that the structural stability increases with increasing cobalt content, as indicated by the separation between the (018) and (110) reflections. It is clear that the substitution of cobalt for nickel suppresses the formation of spinel-like phase.

Figure 7 shows the XRD patterns of $Li_{0.5}Ni_{0.5}Mn_{0.5}O_2$ (y = 0.5) before and after heating at various temperatures. The (018) and (110) reflections centered around $2\theta = 65^{\circ}$ do not merge even after heating at 150°C, suggesting the difficulty of formation of the spinel-like phase. It is interesting to note that while both $Li_{0.5}NiO_2$ (Fig. 3) and $Li_{0.5}MnO_2$ (Fig. 5) transform to cubic spinel-like phases, respectively, at 150-200°C and room temperature, the

cation-substituted Li_{0.5}Ni_{0.5}Mn_{0.5}O₂ does not, even after heating at 150°C. The increased stability achieved by the substitution of Mn for Ni suggests that the presence of multiple cations (mixed cations) in the transition metal plane suppresses cation migration and the formation of spinel-like phases, since the structural stability of Li_{0.5}MnO₂ is poorer than that of Li_{0.5}NiO₂. Further increase in temperature leads to a segregation of the layered Li_{0.5}Ni_{0.5}Mn_{0.5}O₂ into a layered and a spinel phase, as indicated by the Rietveld refinement of the data for the sample heated at 200°C. We have also carried out a Rietveld refinement of the X-ray data of other Li_{0.5}Ni_{1-y}Mn_yO₂ compositions with y = 0.1 and 0.3 after heating at 200°C. A comparison of the phase fractions obtained after heating the Li_{0.5}Ni_{1-y}Mn_yO₂ compositions at 200°C indicates that the fraction of the spinel phase decreases and that of the layered phase increases





Figure 7. XRD patterns of (a) $Li_{0.5}Mn_{0.5}Ni_{0.5}O_2$, (b) $Li_{0.5}Mn_{0.5}Ni_{0.5}O_2$ after heating at 150°C, (c) $Li_{0.5}Mn_{0.5}Ni_{0.5}O_2$ after heating at 200°C, (d) $Li_{0.5}Mn_{0.5}Ni_{0.5}O_2$ after heating at 300°C, and (e) $Li_{0.5}Mn_{0.5}Ni_{0.5}O_2$ after heating at 500°C for 3 days in air.

with increasing Mn content y (Fig. 8). It is possible that the layered phase may be richer in nickel and the spinel phase may be richer in manganese. This observation of a decrease in the spinel fraction with increasing manganese substitution again suggests that the presence of mixed cations in the transition metal plane suppresses cation migration.



Figure 8. Variations with manganese content y of the molar percent of the layered and spinel-like phases present in the 200°C heated $Li_{0.5}Ni_{1-y}Mn_yO_2$.

Table II. List of cation-substituted $LiMn_{1-y}(Cr,Al,Mg)_yO_2$ phases.

Sample	Composition
1	$Li_{0.5}Cr_{0.1}Mn_{0.9}O_2$
2	$Li_{0.5}Cr_{0.07}Al_{0.03}Mn_{0.9}O_2$
3	Li _{0.5} Cr _{0.15} Mn _{0.85} O ₂
4	Li _{0.5} Cr _{0.07} Al _{0.06} Mg _{0.02} Mn _{0.85} O ₂
5	$Li_{0.5}Cr_{0.15}Al_{0.05}Mn_{0.80}O_2$

Cation-substituted $Li_{0.5}Mn_{1-y}(Cr,Al,Mg)_yO_2$, structural stability.—Recognizing that the presence of mixed cations helps to suppress the cation migration and the spinel phase formation, we then applied this strategy to improve the structural stability of layered $Li_{1-x}MnO_2$, which tends to form spinel-like phases at room temperature during electrochemical cycling.⁶⁻⁹ As discussed in the introductory remarks, the substitution of a small amount of Cr^{3+} and Al^{3+} for Mn^{3+} in $LiMn_{1-y}M_yO_2$.¹⁶⁻¹⁸ (M=Cr and Al) is known to improve the electrochemical performance. Such substitutions also help to access the monoclinic LiMnO₂ by conventional high-temperature synthesis procedures without requiring the ion exchange of NaMn_{1-y}M_yO₂. We investigated the substitution of several cations such as Mg²⁺, Al³⁺, Ti⁴⁺, Cr³⁺, and Co³⁺ for manganese. While the substitution of Ti⁴⁺ and Co³⁺ resulted in the formation of impurity phases, single-phase samples could be obtained with the substitution of Cr³⁺, Mg²⁺, and Al³⁺ as given in Table II, and illustrated by the XRD patterns in Fig. 9.

The samples in Table II were subjected to lithium extraction to obtain $Li_{0.5}Mn_{1-y}(Cr,Al,Mg)_yO_2$ and then heated at various temperatures: $T = 100, 120, 150, \text{ and } 200^{\circ}\text{C}$. The XRD patterns of the as-prepared $Li_{0.5}Mn_{1-y}(Cr,Al,Mg)_yO_2$ are shown in Fig. 10. The extent of layered to spinel-like transformation was assessed by monitoring the variation of the c/a ratio with heating temperature.



Figure 9. XRD patterns of LiMn_{1-y}(Cr,Al,Mg)_yO₂: (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4, and (e) sample 5 in Table II.



Figure 10. XRD patterns of the $Li_{0.5}Mn_{1-y}(Cr,Al,Mg)_yO_2$ samples obtained by extracting 50% of lithium from (a) LiMnO₂, (b) sample 1, (c) sample 2, (d) sample 3, (e) sample 4, and (f) sample 5 in Table II. The magnification of the pattern over a small 2 θ range is shown on the right.

As the transformation of the layered phase to the spinel-like phase progresses, the c/a ratio decreases and reaches the ideal value of 4.90 at the cubic symmetry.

Figure 11 shows the variations of c/a ratio with heating temperatures for the samples listed in Table II along with that for Li_{0.5}MnO₂. In the case of as-prepared samples, the cationsubstituted Li_{0.5}Mn_{1-y}(Cr,Al,Mg)_yO₂ compositions have a higher c/a ratio compared to that of Li_{0.5}MnO₂. The c/a ratios of all the samples decrease with increasing temperature, but for a given heating temperature, the cation-substituted compositions have a higher c/a ratio than Li_{0.5}MnO₂. The Li_{0.5}MnO₂ sample becomes cubic with a c/a ratio of 4.90 at 120°C, while most of the cationsubstituted samples maintain a c/a ratio of >4.90, even after heat-



Figure 11. Variations of the c/a ratios of the $Li_{0.5}Mn_{1-y}(Cr,Al,Mg)_yO_2$ samples with heating temperature.

ing at 200°C. The data clearly demonstrate that the cationic substitutions help to suppress the migration of cations and the formation of spinel-like phases.

Several additional points could also be recognized by having a close examination of the data in Fig. 11. First, the structural stability increases with increasing degree of substitution. For example, sample 5 in Table II that has the highest degree (15% Cr and 5% Al) of substitution shows the best structural stability by maintaining the highest c/a ratio of 4.94, even after heating at 200°C. The structural stability of sample 5 is also evident by the clear separation between the (018) and (110) reflections in Fig. 10. Second, at a given degree of substitution, the substitution of two different types of cations instead of a single type of cation gives better structural stability. For example, sample 2 with 7% Cr and 3% Al substitutions exhibits slightly better stability than sample 1 with 10% Cr substitution on heating. However, between samples 3 and 4, sample 4 with three different types of substituents (7% Cr, 6% Al, and 2% Mg) tends to show a faster decrease in the c/a ratio on heating compared to that of sample 3 that has a single substituent (15% Cr). Although sample 4 has a higher c/a ratio in the as-prepared state compared to sample 3, the latter has a higher c/a ratio than the former after heating at $T > 100^{\circ}$ C. Thus, the effectiveness of suppressing the cation migration also depends on the nature of the substituent cation. The data reveal that Cr^{3+} with strong preference for octahedral sites (larger OSSE value) is more effective than the other substituents indicated in Table II in suppressing the cation migration.

It appears that the migration of the transition metal ions requires cooperation of the neighboring cations, which is perturbed and suppressed by the presence of other foreign cations (mixed cations) in the transition metal plane. Additionally, as stated previously, the migration of manganese ions may involve first a disproportionation



Figure 12. Charge/discharge curves indicating the cyclability of (a) orthorhombic LiMn₂, (b) monoclinic layered LiMnO₂, (c) sample 3 in Table II, and (d) sample 5 in Table II in the voltage range 2.5-4.0 V at a rate of 0.03 mA/cm^2 .

of Mn^{3+} ions into Mn^{2+} and Mn^{4+} and then a migration of the Mn^{2+} ions from the octahedral sites to the tetrahedral sites. If so, the substitution of other cations can perturb such a disproportionation and the cation migration.

With an objective to correlate the structural stability to the electrochemical properties, we have also investigated the electrode performance of some of the compositions listed in Table II. The electrochemical cycling data of samples 3 and 5 in Table II that show the best structural stability are compared with those of monoclinic LiMnO₂ and orthorhombic LiMnO₂ in Fig. 12. Both the monoclinic and orthorhombic LiMnO₂ show a clear development of the 3 V plateau characteristic of the formation of spinel-like phases within ten cycles (Fig. 12a and b). Both samples 3 and 5 do not show the development of a clear 3 V plateau at least within the first ten cycles. However, the cation-substituted samples also show capacity fading, since the layered to spinel-like transformation is not fully eliminated, as evidenced from the X-ray patterns and the change in the c/a ratio.

Conclusions

Bulk samples of $Li_{0.5}MO_2$ [M = Mn, Co, and Ni, $Ni_{1-v}Co_v$, $Ni_{1-\nu}Mn_{\nu}$, and $Mn_{1-\nu}(Cr,Al,Mg)_{\nu}$ have been synthesized by chemically extracting lithium from the corresponding LiMO₂ using $Na_2S_2O_8$. The ease of transformation of the layered $Li_{0.5}MO_2$ phases to cubic spinel-like phases decrease in the order Li_{0.5}MnO₂ >Li_{0.5}NiO₂ > Li_{0.5}CoO₂, which could be explained on the basis of crystal field stabilization energies. The ease of transformation is related directly to the ability of the transition metal ions to occupy the tetrahedral sites, and ions with a large octahedral site stabilization energy suppress such a transformation. Additionally, the presence of foreign ions in the transition metal plane (mixed cations) is found to be effective in suppressing the cation migration and the formation of spinel-like phases, possibly by perturbing the cooperativity among the ions. In the case of manganese oxides, the migration may also involve a disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+} , and the presence of other cations may suppress the disproportionation and thereby the formation of spinel-like phases. The mixed cation strategy may prove effective in designing structurally stable cathode hosts for lithium-ion cells.

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