

Local Structure and Electronic States of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ Studied by X-ray Absorption Spectroscopy

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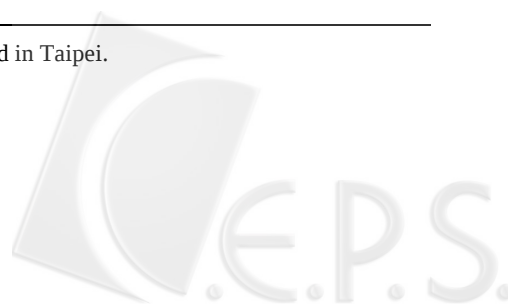
The local structure and electronic states of Co^{3+} substituted lithium manganate spinels of the composition $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$) have been probed by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies at the Mn and Co edges. The substitution of Co^{3+} into the Mn sites causes an oxidation of Mn^{3+} to Mn^{4+} , decreasing the localized Jahn-Teller distortion of the lattice. This in turn leads to a shortening of the Mn-O(M) bond length and a reduction in local structural disorder of the $\text{Mn}(\text{Co})\text{O}_6$ octahedra. The data show that the replacement of $d^4 \text{Mn}^{3+}$ by $d^6 \text{Co}^{3+}$ in the octahedral sites of the spinel structure eliminates the local disorder in the lattice around the Mn^{3+}O_6 octahedra which are distorted by Jahn-Teller stabilization of the electronic state.

INTRODUCTION

High voltage cathode materials for use in lithium-ion based secondary battery systems have been of considerable interest in recent years.^{1,2} In all lithium-ion battery systems, energy storage is associated with a reversible lithium ions intercalation into the positive electrode material. High energy density, small change in voltage during discharge, high power density, excellent reversibility, limited environmental impact and low cost materials are necessary for ideal commercial lithium ion batteries. Commercially available lithium cells with lithium cobalt oxide cathodes have high cost and are limited in working potential. Enhancement of the working potential leads to a collapse of the LiCoO_2 structure; to prevent this, an additional device would be necessary, increasing the cost of the cell. Among the materials under study at present, manganese oxides were found to be promising in terms of specific energy, nontoxicity, low cost and environmental benignancy. Lithium spinel LiMn_2O_4 is nowadays the most promising candidate for innovative lithium-ion (rocking chair) batteries.³⁻⁵

LiMn_2O_4 possesses cubic $Fd\bar{3}m$ symmetry at room temperature with an average manganese valence of 3.5, where the Mn exists in Mn^{4+} ($t_{2g}^3 e_g^0$) and Jahn-Teller active Mn^{3+} ($t_{2g}^3 e_g^1$) configurations. One of the problems for commercial application of LiMn_2O_4 is the poor cyclability of the charge-discharge process in the 4-V region. Some serious defects responsible for the capacity loss of the LiMn_2O_4 material are as

follows:^{6,7} (i) The more stable one-phase structure in the low-voltage region transforms to an unstable two-phase mixture in the high-voltage region. (ii) The Mn^{3+} ions of $\text{LiMn}^{3+}\text{Mn}^{4+}\text{O}_4$ cathode materials undergo a self-redox reaction to Mn^{2+} and Mn^{4+} at high voltages, inducing capacity loss due to a loss of the cathode. The Mn^{2+} so generated irreversibly dissolves into the electrolyte, causing an increase in resistance of the cell. Several studies have been aimed at improving the properties of LiMn_2O_4 , particularly for its efficiency in maintaining electrochemical capacity over a large number of cycles without sacrificing initial reversible capacity and also its performance at room temperature.⁸ Partial substitution of manganese by another cation, such as Ni,⁸ Co,^{3,8} Cr,^{8,9} or Ti¹⁰..., can be used to tailor the properties of LiMn_2O_4 both to improve the cyclability and to change the electrochemical behavior of the rechargeable battery cathode. Guohua et al.⁸ have shown that the substitution of M ions at the Mn site, $\text{Li}(\text{Mn},\text{M})_2\text{O}_4$ (M = Cr, Co and Ni), stabilizes the lattice through a reduction in Jahn-Teller distortion of the lattice at the local level. However, substitution was found to lower the capacity of the cell by reducing the quantity of oxidisable Mn^{3+} and replacing it with a non-oxidisable cation. X-ray absorption spectroscopy is the most effective tool for probing the chemical environment of the metal atom, since it does not require a long range structural order.¹¹⁻²⁰ Ammundsen et al.^{19,20} have investigated the chromium substitution in LiMn_2O_4 and have found that stabilization of the short-range structure occurs when Cr^{3+} is substituted for



Mn³⁺. The reversible chemical extraction and re-insertion of lithium takes place with changes in the oxidation states. The replacement of Jahn-Teller distorted Mn³⁺ by Cr³⁺ reduces local disorder in the lattice. Aitchison et al.¹¹ and Ammundsen et al.²⁰ have observed that the Co³⁺ is favorable as a dopant into LiM_xMn_{2-x}O₄ due to the similarity in size between Co³⁺ and Mn⁴⁺. The extended X-ray absorption fine structure (EXAFS) data confirm that cobalt is homogeneously distributed in the lattice and is responsible for an increase in local structural order. The improvements in cyclability when Mn³⁺ is substituted by the cobalt ion can be attributed to an increase in lattice stability driven by a reduction in the local lattice distortion by Jahn-Teller stabilized Mn³⁺. However, the ion substitution induces local structural and electronic perturbation, which can affect lithium diffusion in the lattice and hence the electrochemical performance.

In this work, we applied X-ray absorption near-edge structure (XANES) and EXAFS spectroscopic investigations of the Li(Mn_{2-x}Co_x)O₄ (0 ≤ x ≤ 0.4) system. Using these techniques, we have studied the variations in the local structure surrounding metal ion Mn(Co)O₆ octahedral (16d sites) which are related to its long range structure and performance as a battery cathode material.

EXPERIMENTAL

Samples of the system Li(Mn_{2-x}Co_x)O₄ (0 ≤ x ≤ 0.4) were synthesized by the solid state reaction of Li₂CO₃, MnO₂ and Co₃O₄. Well ground mixtures of the starting materials were heated at 800 °C in air for 24 h, followed by two additional treatments each of 24 h at 800 °C with intermediate grindings. The process was repeated to minimize the impurities Mn₂O₃ and Li₂MnO₃.

Powder X-ray diffraction analyses were carried out with a SCINTAG (X1) diffractometer (Cu Kα radiation, λ = 1.5406 Å) at 40 keV and 30 mA. Data for the Rietveld refinement were collected in the 2θ range 15° ~ 120° with a step size of 0.02° and a count time of 10 s per step. The GSAS program²¹ was used for the Rietveld refinement in order to obtain the information about the crystal structures of Li(Mn_{2-x}Co_x)O₄. In all cases the XRD patterns could be indexed on the basis of a cubic cell. The valence of Mn was determined by chemical titration. The samples were dissolved in an excess of 20 mL K₂C₂O₄ and 2 mL H₂SO₄ around 65 °C maintained by a water bath to reduce all Mnⁿ⁺ to Mn²⁺ (2 < n ≤ 4), and then the excess C₂O₄²⁻ ions in the solution were determined by titration at 65 °C with a standard solution of KMnO₄.²² The chemical compositional analyses were performed using a Perkin-

Elmer AA-3100 atomic absorption spectrometer and EDAX-DX4 energy dispersive X-ray spectrometer.

The X-ray absorption experiments were carried out at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan, with an electron beam energy of 1.5 GeV and a maximum stored current of 200 mA. All the spectra were collected at room temperature. The XANES measurements at the Mn L₂₃ edge were performed at the 6-m high-energy spherical grating monochromator (HSGM) beamline BL20A. The samples were in powder form, attached on conducting tape, and then put into an ultrahigh vacuum chamber (10⁻⁹ Torr) in order to avoid surface contamination. The spectra were recorded in the sample current mode. The incident photon flux (*I*₀) was monitored by a Ni mesh located downstream the exit slit of the monochromator. The reproducibility of the absorption spectra of the same sample in different runs was found to be extremely good. The photon energies were calibrated within an accuracy of ~0.1 eV using the known O K-edge absorption peaks of CuO.

The EXAFS measurements at Mn K and Co K edges were performed in transmission mode at the Wiggler beamline BL17C with a double-crystal Si (111) monochromator. It is important that the size of the particles be smaller than one absorption length in the material, μd < 1, where *d* is the particle size and μ is the total absorption coefficient. Thus, all samples for the EXAFS measurements were finely ground to pass through a 400 mesh sieve. After this treatment, the resultant powder was rubbed homogeneously onto Scotch tape. Furthermore, to avoid the sample thickness effect, the condition Δμx ≤ 1 must be satisfied, where Δμx is the edge step. Therefore, the thickness of the samples was adjusted by folding the sample-coated Scotch tape to achieve Δμx ~ 1. All the spectra were obtained at room temperature using gas-ionization chambers as detectors with a scan step of ~0.4 eV for the XANES region and ~1.5 eV for the EXAFS region. Moreover, to ensure reliability of the spectra, the spectrum of Mn(or Co) metal foil was also monitored to evaluate the stability of the energy scale for each measurement.

The data analysis for the experimental EXAFS spectra was performed using the UWXAFS package.²³ The AUTOBK²⁴ code was used for background subtraction. Background subtraction was by linear extrapolation of the pre-edge and EXAFS spectra were individually normalized in the μ(*k*) - μ₀(*k*) convention, simulating μ₀(*k*) with third order spline functions. The normalized EXAFS spectrum obtained is

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\Delta\mu_0(0)} \quad (1)$$

Where $k = \sqrt{2m(E - E_0)} / \hbar$ is the wavenumber, *E* is the pho-

ton energy, E_0 is the threshold energy, $\hbar$ is $6.62608 \times 10^{-34}/2\pi$ Js, $\mu(k)$ is the measured absorption coefficient, $\mu_0(k)$ is the background, and $\Delta\mu_0(0)$ is the edge jump. The resulting EXAFS spectra were k^3 -weighted and Fourier transformed in the range $2.95 \leq k \leq 13.85 \text{ \AA}^{-1}$ with a Hanning apodization function. A nonlinear least-squares curve fitting procedure in the FEFFIT code²⁵ was carried out in the range $1.28 \leq R \leq 3.45 \text{ \AA}$, corresponding to the first shell of M-O and second shell of M-M, where M was Mn or Co. Based on the plane wave single scattering, the general EXAFS formula²⁶ can be expressed as a summation over all shells i by the equation

$$\chi(k) = S_0^2 \sum_i \frac{N_i F_i(k)}{k R_i^2} \sin [2kR_i + \delta_i(k)] e^{-2R_i/\lambda} e^{-2k^2 \sigma_i^2} \quad (2)$$

where $F_i(k)$ is the backscattering amplitude from each of the N_i atoms in the shell i at distance R_i , with Debye-Waller factor σ_i^2 . S_0 , $\delta_i(k)$ and $\lambda(k)$ are respectively the amplitude reduction factor, the total phase shift, and the photoelectron mean free path. The values of $F_i(k)$, $\delta_i(k)$, and $\lambda(k)$ were theoretically calculated by a curved wave *ab initio* procedure in the code FEFF 7.0.²⁷ The refinements were based on the minimization of the R factor,²⁸ which is defined as follows:

$$\mathfrak{R} = \frac{\sum_{i=1}^N \left\{ [\text{Re}(f_i)]^2 + [\text{Im}(f_i)]^2 \right\}}{\sum_{i=1}^N \left\{ [\text{Re}(\tilde{\chi}_{\text{data}_i})]^2 + [\text{Im}(\tilde{\chi}_{\text{data}_i})]^2 \right\}} \quad (3)$$

where $f_i = \tilde{\chi}_{\text{data}_i} - \tilde{\chi}_{\text{model}_i}$ is the function to be minimized, $\tilde{\chi}$ is the χ function weighted by k^3 , and N is the number of function evaluations. When fitting in R -space, $N = 2(R_{\text{max}} - R_{\text{min}})/\delta R$, where δR is the grid spacing in R -space. The M-O(M) distance and the corresponding Debye-Waller factor represented another two refinable parameters ($\Delta R_{\text{M-O(M)}}$ and $\sigma_{\text{M-O(M)}}^2$). In the fitting procedure, only ΔE_0 (shift of the photoelectron energy origin), $\Delta R_{\text{M-O}}$, $\Delta R_{\text{M-M}}$, $\sigma_{\text{M-O}}^2$ and $\sigma_{\text{M-M}}^2$ were varied, and the coordination number N_i and S_0^2 were fixed. Here, $S_0^2 = 0.56$ was found from fitting the spectrum for the $x = 0.0$ sample, with the Mn-O distances and the coordination number fixed on the basis of the values from the known crystal structure.^{13,16}

RESULTS AND DISCUSSION

The powder XRD patterns of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$) are shown in Fig. 1. After the three heat treatments with intermediate grindings, the samples are of single phase. The powder X-ray diffraction data can be indexed on the basis of an $Fd\bar{3}m$ cubic unit cell.²⁹ The cell symmetry of spinel was

identified by the observation of the reflections with the limiting condition on hkl : h, k, l either all odd or all even, with the F centering of the unit cell. The observed and calculated X-ray diffraction profiles of the sample with $x = 0.1$ are shown in Fig. 2. The ideal crystal structure of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ with a cubic cell is shown in the inset of Fig. 2. We assume that the Co^{3+} ions substitute the Mn sites homogeneously while retaining the $Fd\bar{3}m$ space group symmetry. Low spin Co^{3+} ion has an ionic radius of $0.545 \text{ \AA}$ for C.N. (coordination number) = 6, compared to Mn^{3+} ($0.645 \text{ \AA}$ for C.N. = 6, in low crystal field) and Mn^{4+} ($0.53 \text{ \AA}$ for C.N. = 6, in low crystal field).³⁰

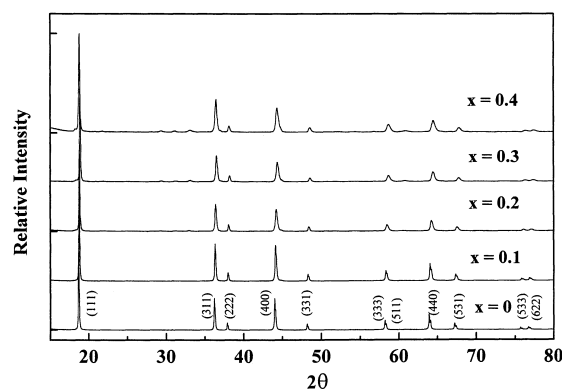


Fig. 1. X-ray powder diffraction patterns of the $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$) samples.

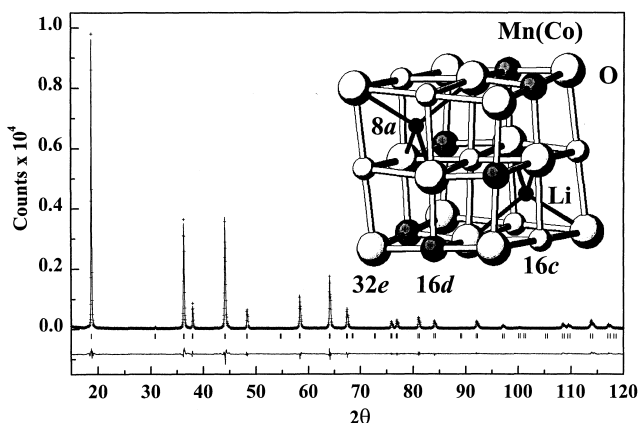


Fig. 2. Rietveld plot of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ with $x = 0.1$ at 300 K. The experimental data points are shown as plus (+) signs. The solid line is the calculated profile. The tick marks below the profile indicate the positions of the allowed Bragg reflections. The difference plot (observed minus calculated) is shown at the bottom. A portion of cubic $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ spinel structure with O at $32e$ site, Mn(Co) at $16d$ site and Li at $8a$ site is shown in the inset.

Table 1. Average Mn Valence, Refined Fractional Atomic Positions, Cell Parameters and Reliability Factors (%) of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$. The Atomic Positions are Li: (0.125, 0.125, 0.125), Mn(Co): (0.5, 0.5, 0.5), O: (x, x, x) for Fd3m Space Group at Room Temperature

		x = 0	x = 0.1	x = 0.2	x = 0.3	x = 0.4
Li						
	$10^2 u_{\text{iso}}(\text{\AA}^2)$	3.3(6)	4.0(5)	2.4(6)	2.4(7)	4.6(7)
Mn (Co)						
	$10^2 u_{\text{iso}}(\text{\AA}^2)$	2.37(3)	2.02(3)	2.42(4)	2.42(5)	2.31(5)
O						
	x	0.2641(2)	0.2623(2)	0.2635(2)	0.2645(3)	0.2625(3)
	$10^2 u_{\text{iso}}(\text{\AA}^2)$	3.81(7)	3.7(1)	3.03(9)	3.2(1)	2.8(1)
a	(\AA)	8.2422(2)	8.2336(2)	8.2178(6)	8.1996(9)	8.173(1)
Volume	(\AA ³)	559.93(2)	558.17(3)	554.98(7)	551.3(1)	546.0(1)
R_p	(%)	9.78	8.99	10.16	10.99	10.06
R_{wp}	(%)	12.91	12.18	13.96	15.2	14.3
χ^2	(%)	1.08	1.32	1.65	2.35	3.28
Mn-Mn x 6	(\AA)	2.91406(6)	2.91101(7)	2.9055(2)	2.8990(2)	2.8897(4)
Mn ⁿ⁺		3.51(1)	3.52(1)	3.56(1)	3.58(1)	3.61(1)

$$R_p = \sum |y_{oi} - y_{ci}| / \sum y_{oi} \text{ (R-pattern)}, R_{\text{wp}} = [\sum W_i (y_{oi} - y_{ci})^2 / \sum W_i (y_{oi})^2]^{1/2} \text{ (R-weighted pattern)},$$

$$\chi^2 = \frac{M}{(N_o - N_p)} \text{ (goodness of fit),}$$

where y_{oi} is the observed intensity at the i th step, y_{ci} is calculated at the i th step, W_i is $1/y_i$, M is residual, N_o is the number of observations, N_p is the number of parameters adjusted. U_{iso} is the thermal parameter and Mn-Mn is the average Mn-Mn bond distance.

The formula can thus be written as $\text{LiMn}^{4+}_{1-x}\text{Mn}^{3+}_{1-x}\text{Co}^{3+}_x\text{O}_4$. The lattice constant a and the cell volume of the $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ decrease with the addition of Co at room temperature as shown in Table 1. The Co ion prefers to substitute at the octahedral Mn site and substitutes for the Mn^{3+} ion. This causes the M-M ($M = \text{Mn}, \text{Co}$) bond lengths to depend not only on the valence state of Mn, but also on the concentration and valence state of Co.

The Mn and Co K-edge XANES spectra are shown in Fig. 3. The K-edge energies of all the target elements were defined as the energy at half the height of the absorption edge.³¹ The Mn K-edge X-ray absorption spectrum of the Co substituted lithium manganate, $\text{Li}(\text{Mn}_{1.8}\text{Co}_{0.2})\text{O}_4$, is shown together with the reference spectra of $\text{Mn}^{3+}_2\text{O}_3$, $\text{LiMn}^{3.5+}_2\text{O}_4$, and Mn^{4+}O_2 in Fig. 3(a). The edge energy of $\text{Li}(\text{Mn}_{1.8}\text{Co}_{0.2})\text{O}_4$ is found to be lower than that of the Mn^{4+} reference but higher than that of the $\text{Mn}^{3.5+}$ reference, indicating the mixed oxidation state of manganese ($\text{Mn}^{3+}/\text{Mn}^{4+}$) in these compounds. Fig. 3(b) clearly shows that there is a large difference in the edge position between Co^{2+} in CoO and the octahedral Co^{3+} of Co_2O_3 and LiCoO_2 . The Co K-edge energy of all the substituted manganese spinel is observed at the same energy as that of LiCoO_2 . The similarity in the feature of the XANES spectra at the Co and Mn edges of spinel strongly supports the fact that cobalt is predominantly trivalent and is present in 16d oc-

tahedral sites.^{11,19,20} The cobalt ion is randomly distributed in the spinel structure and is trivalent, replacing Mn^{3+} . The Co^{3+} ion stabilizes the lattice through a reduction in Jahn-Teller distortion of the lattice at the local level, but can limit the fraction of lithium that may be extracted due to its redox inactivity at potentials up to $\sim 4\text{V}$. The 5V plateau reported during the electrochemical extraction of Li from $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ appears to be due to the oxidation of Co^{3+} to Co^{4+} .^{4,5,11}

The XANES spectra of the $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ spinel manganates are characterized by the features labeled A to D shown in Fig. 4. Pre-edge features A_1 and A_2 result from transitions to bound final states in the 3d orbital. The main absorption edge rises in two distinct steps, which may be distinguished as two inflection points B_1 and B_2 . There is a relatively intense and symmetric resonance above the absorption edge (C), and a broader structure to high energy (D).¹²⁻¹⁹ To obtain detailed information on the electronic and geometric structures around the manganese ion, each spectrum has been investigated by examining the second derivative method, which is quite effective in amplifying small differences in the spectral features as shown in Fig. 4(b). Each spectrum shows doubly split pre-edge peaks, A_1 and A_2 , which are attributed to the quadrupole-allowed transitions from the core 1s level to unoccupied 3d states.^{17,18} Such a splitting of the pre-edge peak definitely originates from the separation of degenerate

$3d$ level under the octahedral crystal field. For the $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ spinel compounds with a weak crystal field, the $1s^1 3dt_{2g}^3 e_g^1$ final state, due to the $1s$ to $3de_g$ transition, is expected to be more stable than the $1s^1 3dt_{2g}^4 e_g^0$ state resulting from the $1s$ to $3dt_{2g}$ transition. Therefore, the lower energy peak, A_1 , is attributed to a transition from $1s$ to $3de_g$, while the higher one, A_2 , is assigned as a transition from $1s$ to $3dt_{2g}$, even though the energy of $3dt_{2g}$ level is lower than that of $3de_g$ level. The stronger intensity of A_2 compared to A_1 can be understood from the fact that Mn in $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ has the mixed oxidation state with Mn^{4+} and Mn^{3+} . The shift in the edge position for $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ to higher energy corresponds to an increased average Mn oxidation state with increasing x .

The Mn L-edge XANES spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ are shown in Fig. 5. The spectra show two broad multiple structures separated by spin-orbital splitting (Mn $2p_{3/2}$ and Mn $2p_{1/2}$).^{17,32} The chemical shift is caused by the change in the electrostatic energy at the Mn site, driven by varying the ionic valence in the compounds. The $2p_{3/2}$ absorption peaks of

MnO_2 and Mn_2O_3 are marked by solid and dashed lines, respectively. The $2p_{3/2}$ peak of the $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ contains both Mn^{3+} and Mn^{4+} absorption transitions, which implies that Mn^{3+} and Mn^{4+} are distributed randomly in the structure and the electrons in the $3d$ orbital of Mn^{3+} are localized.^{32,33} Thus, it is seen that charge localization and mixed valence of Mn^{3+} and Mn^{4+} are found in the system. The Mn valence of the samples from $x = 0$ to $x = 0.4$ was determined by chemical titration. The calculated average Mn valence for $x = 0$ to $x = 0.4$ in $\text{LiMn}^{4+}_1\text{Mn}^{3+}_{1-x}\text{Co}^{3+}_x\text{O}_4$ is 3.50, 3.53, 3.56, 3.59 and 3.63, respectively, whereas the actual experimental values are 3.51 ± 0.02 , 3.52 ± 0.01 , 3.56 ± 0.01 , 3.58 ± 0.01 and 3.61 ± 0.03 as shown in Table 1. At noted, there is a good agreement between the calculated and observed values.

The effect of substitution in the Mn sites of LiMn_2O_4 spinel oxide has been investigated by K-edge EXAFS. The experimental k^3 -weighted Mn and Co K-edge EXAFS spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$) are shown in Figs. 6(a) and (b), and the corresponding Fourier transforms (FTs) in the k range of 2.95 – $13.85 \text{ \AA}^{-1}$ and 2.95 – $11.9 \text{ \AA}^{-1}$ are shown in Fig. 7

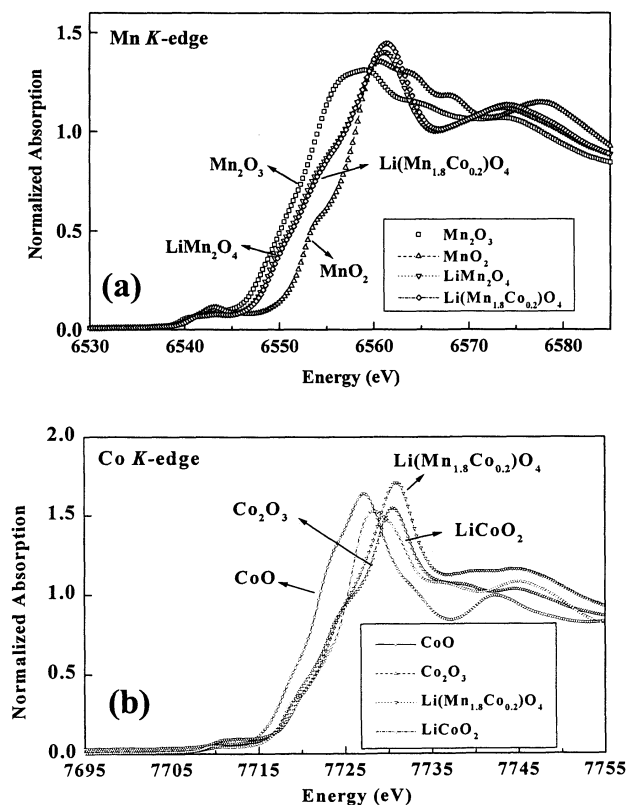


Fig. 3. (a) Mn K-edge XANES spectra of Mn_2O_3 , MnO_2 , LiMn_2O_4 and $\text{Li}(\text{Mn}_{1.8}\text{Co}_{0.2})\text{O}_4$ and (b) Co K-edge XANES spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$, where the spectra are identical for $x = 0.1$ to 0.4 , and the spectra of CoO , Co_2O_3 and LiCoO_2 .

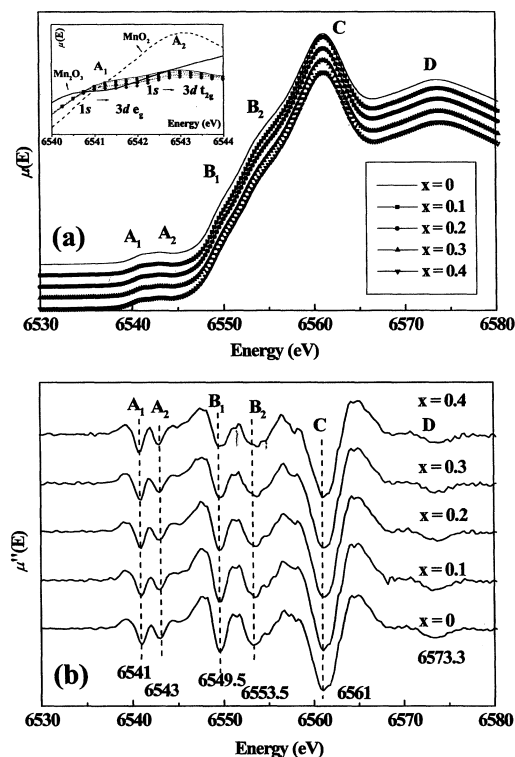


Fig. 4. (a) Mn K-edge XANES spectra and (b) the second-derivative spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$) in the range 6530–6580 eV. The inset of (a) shows the expanded view of the pre-edge range 6540–6544 eV.

and Fig. 8, respectively. As can be seen from Fig. 6, the overall spectral features of EXAFS oscillation of the $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ compositions are quite similar. The experimental EXAFS signal contains all contributions from different scattering paths including single scattering and multiple scatterings. The comparison between experimental and simulated data suggests that the multiple scatterings are neglected for the

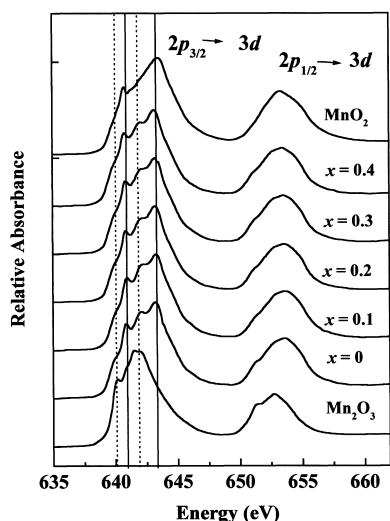


Fig. 5. Mn 2p-edge XANES spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$) along with two standards, MnO_2 (Mn^{4+} , shown by the solid line) and Mn_2O_3 (Mn^{3+} , shown by the dashed line) for comparisons.

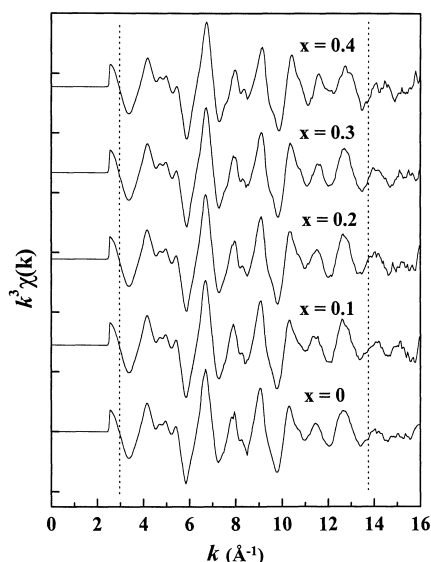


Fig. 6. (a) Mn and (b) Co k^3 -weighted K-edge EXAFS spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$).

purpose of structural refinements regarding the nearest oxygen and manganese neighbors. Owing to the high symmetry of the spinel structure, considering only the first and second coordination shells practically all the essential structural information can be derived.^{16,18} At low- k ($< 3 \text{ \AA}^{-1}$) region, multiple scattering contributions become more important, causing some deviation from the fit, which uses a single scattering formulation. The observed spectral similarities between the cubic spinel LiMn_2O_4 and chemically substituted $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0.1 \leq x \leq 0.4$) suggest that both phases possess nearly the same local atomic arrangement.

The Fourier transforms of the Mn and Co K-edge EXAFS spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$) are shown in Figs. 7 and 8, respectively. The first prominent peak in the Fourier transform is assigned to the M-O ($\text{M} = \text{Mn}$ and Co) contribution, and is followed by the second peak corresponding to the Mn-M and Co-M ($\text{M} = \text{Mn}$ or Co) contribution. The best-fit results (solid lines) are compared to the experimental spectra (circles) and the fitted structural parameters for M-O shell and M-M shell are listed in Table 2. For all samples, the first coordination shell around both Co and Mn ions was fixed

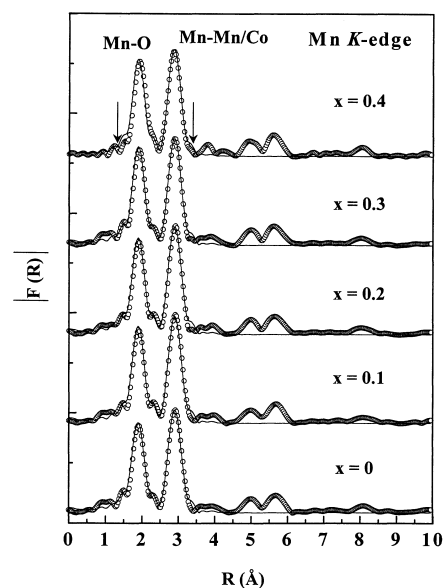


Fig. 7. Fourier transforms $F(R)$ of the k^3 -weighted Mn K-edge EXAFS spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$). The range using the Fourier filtering is shown by the arrows. The solid lines and circles represent the fitted and experimental data, respectively. The first prominent peak in the Fourier transform is assigned to the Mn-O contribution, and is followed by the second peak corresponding to the Mn-Mn and Mn-Co contributions.

at six oxygen atoms, in agreement with the expected number for an octahedral site. Substituting Co^{3+} for Mn^{3+} in LiMn_2O_4 leads to a shortening of the Mn-O bond length with increasing cobalt substitution.¹¹ The Debye-Waller factor ($\sigma_{\text{Mn-O}}$) for the Mn-O shell of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ obtained from EXAFS data is shown in Fig. 9(a) as a function of the degree of substitution. A decrease in the Debye-Waller factor is observed, consistent with an enhanced symmetry of the average Mn environment caused by the reduction in the number of Mn^{3+} ions. Contributions from the Jahn-Teller distortion manifest primarily as damping of the oscillations in EXAFS due to incoherence in the photoelectron waves, producing a reduced intensity Fourier transformed peak and higher Debye-Waller factor in the analysis.¹⁵⁻¹⁹ The removal of the contribution from Mn^{3+} ions by increasing Co^{3+} substitution is seen in the data as a marked decrease in the Debye-Waller factors for the Mn-O shell. In Fig. 9(b), a slight increase in Co-O bond length ($R_{\text{Co-O}}$) and a decrease in the Debye-Waller factor ($\sigma_{\text{Co-O}}$) are also observed for $x = 0.1$ to 0.4 . The Co-O Debye-Waller factors are notably smaller than those for Mn-O, and significantly lower in the doped spinels than in LiMn_2O_4 , indicating a higher degree of

regularity of the CoO_6 octahedron in the three-dimensional spinel framework. Coordination numbers for the manganese-metal and cobalt-metal shells were fixed to 6 in fitting. In Fig. 10, a difference is observed between the Mn-M ($R_{\text{Mn-M}}$) and Co-M ($R_{\text{Co-M}}$) bond length ($M = \text{Co}$ or Mn). As x increases, the Mn-M distance ($R_{\text{Mn-Mn/Co}}$) and the Debye-Waller factor ($\sigma_{\text{Mn-Mn/Co}}$) were found to decrease (as shown in Fig. 10(a)). This result is consistent with the decrease in the lattice parameter a on increasing x as studied by XRD. Substituting Mn^{3+} with the smaller non-Jahn Teller Co^{3+} ion reduces lattice strain at the $16d$ site, and the shorter Co-M distance ($\sim 2.86 \text{ \AA}$) observed by EXAFS shows that the Mn lattice contracts about Co (as shown in Fig. 10(b)). This local contraction and the difference in coulombic repulsion between $\text{Co}^{3+}/\text{Mn}^{4+}$ and $\text{Mn}^{4+}/\text{Mn}^{4+}$ indicate that the average Co-M bond length is shorter than Mn-M.¹⁹⁻²⁰ With increasing cobalt content, the Debye-Waller factor $\sigma_{\text{Mn-Mn/Co}}$ decreases whereas $\sigma_{\text{Co-Co/Mn}}$ increases. At low levels of substitution, lower Debye-Waller factors are observed for the Co-M shell than

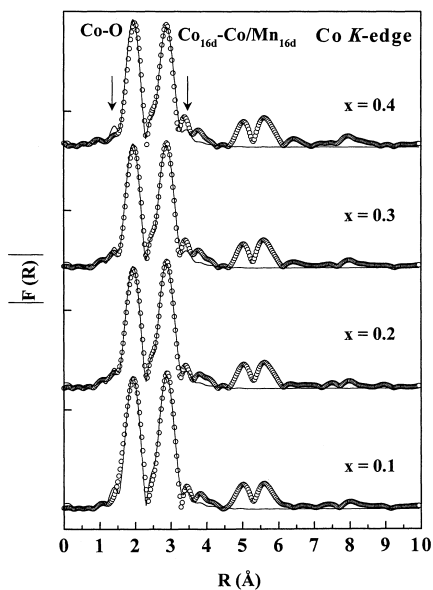


Fig. 8. Fourier transforms $F(R)$ of the k^3 -weighted Co K-edge EXAFS spectra of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0.1 \leq x \leq 0.4$). The range applying the Fourier filtering is shown by the arrows. The solid lines and circles represent the fitted and experimental data, respectively. The first prominent peak in the Fourier transform is assigned to the Co-O contribution. The second peak corresponds to the Co-Mn and Co-Co contributions.

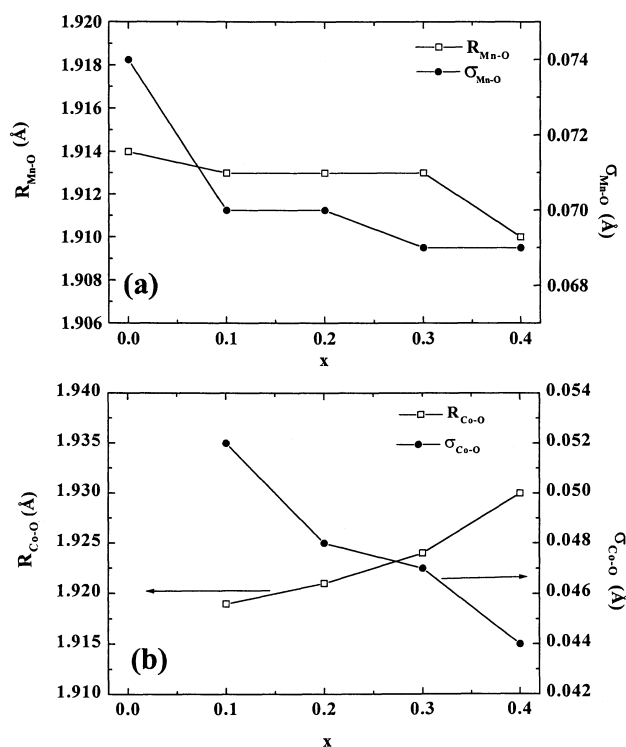


Fig. 9. The M-O ($M = \text{Mn}$ or Co) bond lengths ($R_{\text{M-O}}$) and Debye-Waller factor ($\sigma_{\text{M-O}}$) as a function of the compositional parameter x for (a) Mn K-edge EXAFS data of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ with $x = 0 \sim 0.4$ and (b) Co K-edge EXAFS data of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ with $x = 0.1 \sim 0.4$.

Table 2. Structural Parameters of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ Determined from EXAFS

$\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$	Mn-O		Mn-Mn(Co)		Residue (%)
	R (Å)	σ (Å)	R (Å)	σ (Å)	
x = 0	1.914 (26)	0.074	2.9150 (2)	0.076	2.4
x = 0.1	1.913 (50)	0.070	2.9130 (2)	0.075	1.6
x = 0.2	1.913 (36)	0.070	2.9082 (2)	0.075	1.6
x = 0.3	1.913 (25)	0.069	2.9008 (2)	0.075	1.7
x = 0.4	1.910 (35)	0.069	2.8889 (18)	0.074	2.6

$\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$	Co-O		Co-Co(Mn)		Residue (%)
	R (Å)	σ (Å)	R (Å)	σ (Å)	
x = 0.1	1.919 (45)	0.052	2.864 (46)	0.065	2.2
x = 0.2	1.921 (41)	0.048	2.864 (46)	0.067	1.3
x = 0.3	1.924 (38)	0.047	2.863 (47)	0.068	1.3
x = 0.4	1.930 (32)	0.044	2.865 (45)	0.070	1.8

for the Mn-M shell, indicating a higher degree of cation ordering around the Co ions than around the Mn ions. This can be attributed to the fact that unlike the tetragonally distorted Mn^{3+}O_6 octahedra, the Co^{3+}O_6 octahedra do not induce distortions in the surrounding local lattice structure.

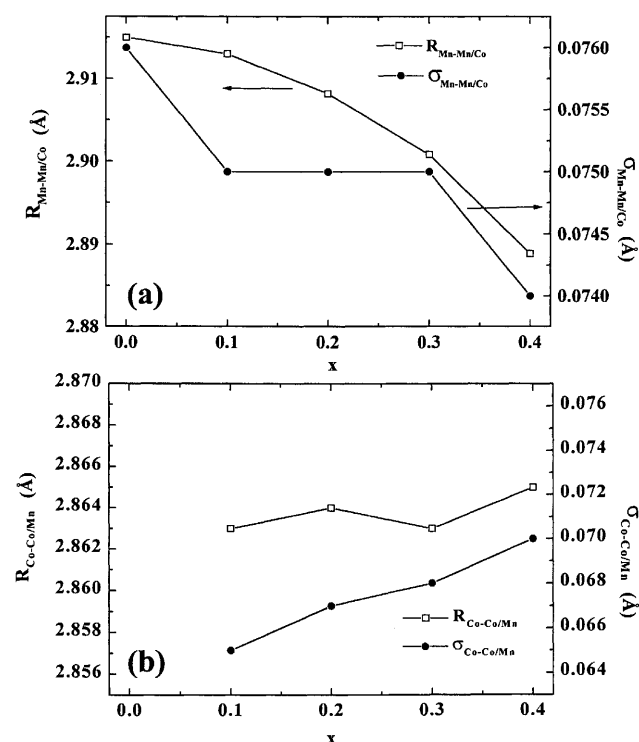


Fig. 10. The M-M (M = Mn or Co) distances ($R_{\text{M-M}}$) and Debye-Waller factor ($\sigma_{\text{M-M}}$) as a function of the compositional parameter x for (a) Mn K-edge EXAFS data of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ with $x = 0 \sim 0.4$ and (b) Co K-edge EXAFS data of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ with $x = 0.1 \sim 0.4$.

Increasing the number of Co-M interactions caused a change in the long-range structural order, which appears as a continuous decrease in the cell parameters. Oxidation of manganese from Mn^{3+} to Mn^{4+} , the Mn sites substituted with Co^{3+} is reflected in a shortening of the Mn-O(M) bond length and a reduction in $\sigma_{\text{Mn-O(M)}}$ due to the reduced localized Jahn-Teller distortion of the lattice. A similar decrease is seen in Mn-Mn/Co distance, compared to the smaller change in Co-Co/Mn distance due to the reduction in cell volume.

The substitution of Co^{3+} on the framework would be localized to the 16d site, which is similar to excess Li^+ being substituted into the Mn site.³⁴ From the chemical formula $\text{LiMn}^{4+}_1\text{Mn}^{3+}_{1-x}\text{Co}^{3+}_x\text{O}_4$ ($0 \leq x \leq 0.4$), the theoretical capacities based on a one-electron charge-discharge reaction were calculated to be in the range 148 mAh/g to 96 mAh/g. Since the deintercalation of Li^+ from the spinel structure must be electrically compensated by oxidation of Mn^{3+} to Mn^{4+} , this suggests that even for substituted spinel phases, only the amount of Mn^{3+} contributes to the charge-discharge capacity.³⁵⁻³⁸ Accordingly, the initial capacity of $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.4$) is limited by the initial amount of Mn^{3+} in the 16d sites. At present, the discharge capacity of the doped compositions ($x = 0.1 \sim 0.4$) is more stable than that of the LiMn_2O_4 spinel phase, and the capacity fading was slightly suppressed by increasing the Co content from 0.1 to 0.4.³⁵ Therefore, the spinel structure becomes more tolerant to repeated charge-discharge by doping of Co, which is attributable to the reduction of Mn valence giving rise to the suppression of the Jahn-Teller distortion via Co doping. The improvement in cycling performance is also attributed to stabilization in the spinel structure via doped metal cations.

CONCLUSIONS

We reported the EXAFS results for undoped and doped spinel $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ with $0 \leq x \leq 0.4$. The data show that the replacement of Mn^{3+} (d^4) ions by Co^{3+} (d^6) in the octahedral framework of the spinels eliminates the local disorder present in the lattice around $[\text{Mn}^{3+}\text{O}_6]$ octahedra. Understanding the effect of Co substitution on the local structure of the LiMn_2O_4 provides important insights into how the structure of these materials can be tailored to give optimum chemical and electronic properties.

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Key Words

X-ray absorption near-edge structure (XANES);
Extended X-ray absorption fine structure (EXAFS);
 $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$; Lithium-ion based secondary
battery.

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