Electronic Supplementary Information

X-ray Absorption Near-Edge Structures of LiMn₂O₄ and LiNi_{0.5}Mn_{1.5}O₄ Spinel Oxides for Lithium-Ion Batteries: First-Principles Calculation Study

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Experimental procedure

LiMn₂O₄ was synthesized *via* solid-state reactions.^{1,2} Li₂CO₃ (99.99%, Kojundo Chemical Laboratory Co. Ltd.) and Mn₂O₃, which was obtained by preheating MnCO₃ (99.99%, Kojundo) at 600 °C for 48 h, were used as starting materials. The required amounts of the starting materials were mixed and heated at 800 °C for 2 days in air and then cooled at a rate of 0.5 °C/min. LiNi_{0.5}Mn_{1.5}O₄ was synthesized by the co-precipitation method.³⁻⁶ Ni(CH₃COO)₂·4H₂O (99.9%, Wako Pure Chemical Industries) and Mn(CH₃COO)₂·4H₂O (99.9%, Wako) were dissolved in distilled water, and then mixed with 0.2 mol dm⁻³ NaOH solution, producing a hydroxide sediment. After filtering and drying, the sediment and LiOH·H₂O (Kojundo) were mixed and heated at 700 °C for 18 h in air, and then cooled at a rate of 0.5 °C/min. All the observed X-ray diffraction peaks of the synthesized LiMn₂O₄ and LiNi_{0.5}Mn_{1.5}O₄ could be indexed as cubic spinel phases (space groups: *Fd-3m* and *P*4₃32, respectively).^{2,6}

Synchrotron XAFS analyses of the pristine and electrochemically reacted lithium manganese spinel oxide samples were performed to investigate the lithium ion (de-)intercalation processes. The electrode comprised a suspension containing 80 wt% active material, 10 wt% acetylene black, and 10 wt% polyvinylidene difluoride, which was coated and then pressed on aluminum foil. The electrodes were assembled in a two-electrode cell using metallic lithium foil as the counter/reference electrode. The liquid electrolyte was a 1 mol dm⁻³ ethylene carbonate/dimethyl carbonate solution of LiPF₆. The electrochemical (de-)intercalation of the lithium ion was carried out at a constant current rate of 0.1 C (about 0.067 mA·cm⁻²). Figure S1 shows the electrochemical lithium ion (de-)intercalation profiles from pristine LiMn₂O₄ (black line) and LiNi_{0.5}Mn_{1.5}O₄ (red line). The value of *x* in Li_xMn₂O₄ (x = 0.08, 0.25, 0.5, 0.75, 1.25, 1.5, 1.66) and Li_xNi_{0.5}Mn_{1.5}O₄ (x = 0.06, 0.25, 0.5, 0.75, 1.25, 1.5, 1.66) and Li_xNi_{0.5}Mn_{1.5}O₄ (x = 0.06, 0.25, 0.5, 0.75, 1.25, 1.5, 1.66) and Li_xNi_{0.5}Mn_{1.5}O₄ (x = 0.06, 0.25, 0.5, 0.75, 1.25, 1.5, 1.66) and Li_xNi_{0.5}Mn_{1.5}O₄ (x = 0.06, 0.25, 0.5, 0.75, 1.25, 1.5, 1.78) was calculated by assuming that all electric currents were utilized for the lithium ion (de-)intercalation processes. XANES spectroscopy was conducted at the BL01B1 beamline at SPring-8, Sayo, Japan (2014B1238), using the Mn and Ni *K*-edges to investigate the local electronic structures of the pristine and (de-)intercalated samples.

Theoretical procedure

XANES spectra were calculated using the all-electron full potential linearized augmented plane wave plus local orbitals (FLAPW + lo) method as implemented in the WIEN2k density functional theory (DFT) package.⁷ We adopted the spin-polarized generalized gradient approximation (GGA) and the self-interaction corrected (SIC)⁸ GGA+U approaches within the Perdew-Burke-Ernzerhof (PBE)⁹ exchange-correlation potential. The effective Hubbard parameters U_{eff} were taken to be 5 eV for the Mn 3*d* orbital¹⁰ and 6 eV for the Ni 3*d* orbital.¹¹ All the atomic positions of the Li_xNi_{0.5}Mn_{1.5}O₄ models were optimized under the fixed experimental lattice constants using the GGA level of theory in the package. The crystallographic parameters of the Li_xNi_{0.5}Mn_{1.5}O₄ models are summarized in Table S1. The standard full core hole treatment was taken into account in the present XANES simulations. We used a *k*-point grid of 4 × 4 × 4 throughout this study. The detailed computational procedure was described in our previous papers.² We did not use the supercell technique, due to the sufficient-distances ($\geq ca$. 8Å) between two neighboring X-ray absorbing atoms to avoid interactions (See lattice constants in Table S1).

Model ^{a)}	Unit-cell formula	Space Group	Lattice constant ^{b)} / Å		
			а	b	С
$[Ni_{1/2}Mn_{3/2}]O_4$	[NiMn ₃ O ₈] ₄	P4332	8.005	= a	= a
$Li_{0.5}[Ni_{1/2}Mn_{3/2}]O_4$	Li ₄ [NiMn ₃ O ₈] ₄	P2 ₁ 3	8.092	= a	= a
Li[Ni1/2Mn3/2]O4	Li ₈ [NiMn ₃ O ₈] ₄	P4332	8.167	= a	= a
Li1.5[Ni0.5Mn1.5]O4	$Li_{24}[Ni(Mn^{3+}Mn_2^{4+})O_8]_8$	C 222 ₁	$11.48 (= 2a_0)$	= a	8.689 ^{a)}
$Li_2[Ni_{1/2}Mn_{3/2}]O_4$	$Li_{16}[Ni(Mn_2^{3+}Mn^{4+})O_8]_4$	$P4_{3}2_{1}2$	$8.118 (=\sqrt{2} a_0)$	= a	8.689 ^{a)}

^{*a*)} The models were constructed based on the structures of cubic LiNi_{1/2}Mn_{3/2}O₄ ($P4_332$) in *J. Electrochem. Soc.* 2004, **151**, A296, and tetragonal Li₂Mn₂O₄ ($I4_1/amd$) in *Chem. Mater.* 1999, **11**, 1936.

^{b)} Lattice constants were fixed at the experimental data including a₀ =5.740 Å in J. Electrochem. Soc. 2004, **151**, A296.



Fig. S1 Electrochemical lithium ion (de-)intercalation profiles of $Li_xMn_2O_4$ (black line) and $Li_xNi_{0.5}Mn_{1.5}O_4$ determined by the galvanostatic method (C rate: 0.1 C).



Fig. S2 First-order differential curves of experimental Mn *K*-edge XANES spectra for (a) $Li_xMn_2O_4$ and (b) $Li_xNi_{0.5}Mn_{1.5}O_4$, enabling clear visualization of each peak.



Fig. S3 Experimental Mn *K*-edge XANES spectra for (a) $Li_xMn_2O_4$ (x = (I) 0.08, (II) 0.5, (III) 1, (IV) 1.5, (V) 1.66), and (b) $Li_xNi_{0.5}Mn_{1.5}O_4$ (x = (I) 0.06, (II) 0.5, (III) 1, (IV) 1.5, (V) 1.78). Theoretical Mn *K*-edge XANES spectra for (a)-(i) Mn_2O_4 , (ii) $Li_{0.5}Mn_2O_4$ (iii) $LiMn_2O_4$ (iv) $Li_{1.5}Mn_2O_4$, (v) $Li_2Mn_2O_4$ models, and (b)-(i) $Ni_{0.5}Mn_{1.5}O_4$, (ii) $Li_{0.5}Nn_{1.5}O_4$, (iii) $LiNi_{0.5}Mn_{1.5}O_4$, (v) $Li_{2.N}i_{0.5}Mn_{1.5}O_4$ models are shown. Experimental spectra are broader than theoretical ones due to the limitation of experimental energy-resolution, and then theoretical Mn *K*-edge XANES spectra after smoothing process are also shown for the comparison easily in (I') to (v').



Fig. S4 First-order differential curves of experimental Mn *K*-edge XANES spectra for (a) $Li_xMn_2O_4$ (x = (I) 0.08, (II) 0.5, (III) 1, (IV) 1.5, (V) 1.66), and (b) $Li_xNi_{0.5}Mn_{1.5}O_4$ (x = (I) 0.06, (II) 0.5, (III) 1, (IV) 1.5, (V) 1.78). Those of theoretical Mn *K*-edge XANES spectra for (a)-(i) Mn_2O_4 , (ii) $Li_{0.5}Mn_2O_4$ (iii) $LiMn_2O_4$ (iv) $Li_{1.5}Mn_2O_4$, (v) $Li_2Mn_2O_4$ models, and (b)-(i) $Ni_{0.5}Mn_{1.5}O_4$, (ii) $Li_{0.5}Ni_{0.5}Mn_{1.5}O_4$, (iii) $LiN_{0.5}Mn_{1.5}O_4$, (v) $Li_2Ni_{0.5}Mn_{1.5}O_4$ models are shown. First-order differential curves of theoretical Mn *K*-edge XANES spectra after smoothing process are also shown for the comparison easily in (I') to (v').



Fig. S5 Peak-top positions, M', A' and B', at the first-order differential curves of theoretical Mn K-edge spectra after smoothing process (open squares, circles and triangles) and experimental spectra (closed squares, circles and triangles) at various Li_xMn₂O₄ and Li_xNi_{0.5}Mn_{1.5}O₄.



Fig. S6 First-order differential curves of experimental Ni K-edge XANES spectra for Li_xNi_{0.5}Mn_{1.5}O₄ to clearly visualize each peak.



Fig. S7 (a) Experimental Ni *K*-edge XANES spectra for $Li_xNi_{0.5}Mn_{1.5}O_4$ (x = (I) 0.06, (II) 0.5, (III) 1, (IV) 1.5, (V) 1.78). Theoretical Ni *K*-edge XANES spectra for (i) $Ni_{0.5}Mn_{1.5}O_4$, (ii) $Li_{0.5}Nn_{1.5}O_4$, (iii) $LiN_{0.5}Mn_{1.5}O_4$, (iv) $Li_{1.5}Ni_{0.5}Mn_{1.5}O_4$, (v) $Li_2Ni_{0.5}Mn_{1.5}O_4$ models are shown. Experimental spectra are broader than theoretical ones due to the limitation of experimental energy-resolution, and then theoretical Ni *K*-edge XANES spectra after smoothing process are also shown for the comparison easily in (I') to (v'). (b) First-order differential curves of experimental Ni *K*-edge XANES spectra for $Li_xNi_{0.5}Mn_{1.5}O_4$ (x = (I) 0.06, (II) 0.5, (III) 1, (IV) 1.5, (V) 1.78). Those of theoretical Ni *K*-edge XANES spectra for (i) $Ni_{0.5}Mn_{1.5}O_4$, (ii) $Li_{0.5}Mn_{1.5}O_4$, (iii) $LiNi_{0.5}Mn_{1.5}O_4$, (iv) $Li_{1.5}Ni_{0.5}Mn_{1.5}O_4$, (v) $Li_{2}Ni_{0.5}Mn_{1.5}O_4$ models are shown. First-order differential curves of theoretical Ni *K*-edge XANES spectra for (i) $Ni_{0.5}Mn_{1.5}O_4$, (ii) $Li_{0.5}Mn_{1.5}O_4$, (iii) $LiNi_{0.5}Mn_{1.5}O_4$, (iv) $Li_{1.5}Ni_{0.5}Mn_{1.5}O_4$, (v) $Li_{2}Ni_{0.5}Mn_{1.5}O_4$ models are shown. First-order differential curves of theoretical Ni *K*-edge XANES spectra after smoothing process are also shown for the comparison easily in (I') to (v').



Fig. S8 Peak-top positions, M', A' and B', at the first-order differential curves of theoretical Ni K-edge XANES spectra after smoothing process (open squares, circles and triangles) and experimental spectra (closed squares, circles and triangles) at various Li_xMn₂O₄ and Li_xNi_{0.5}Mn_{1.5}O₄.

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