Electronic Supplementary Information

Further Findings of X-ray Absorption Near-Edge Structure in Lithium Manganese Spinel Oxide with First-Principles Calculations

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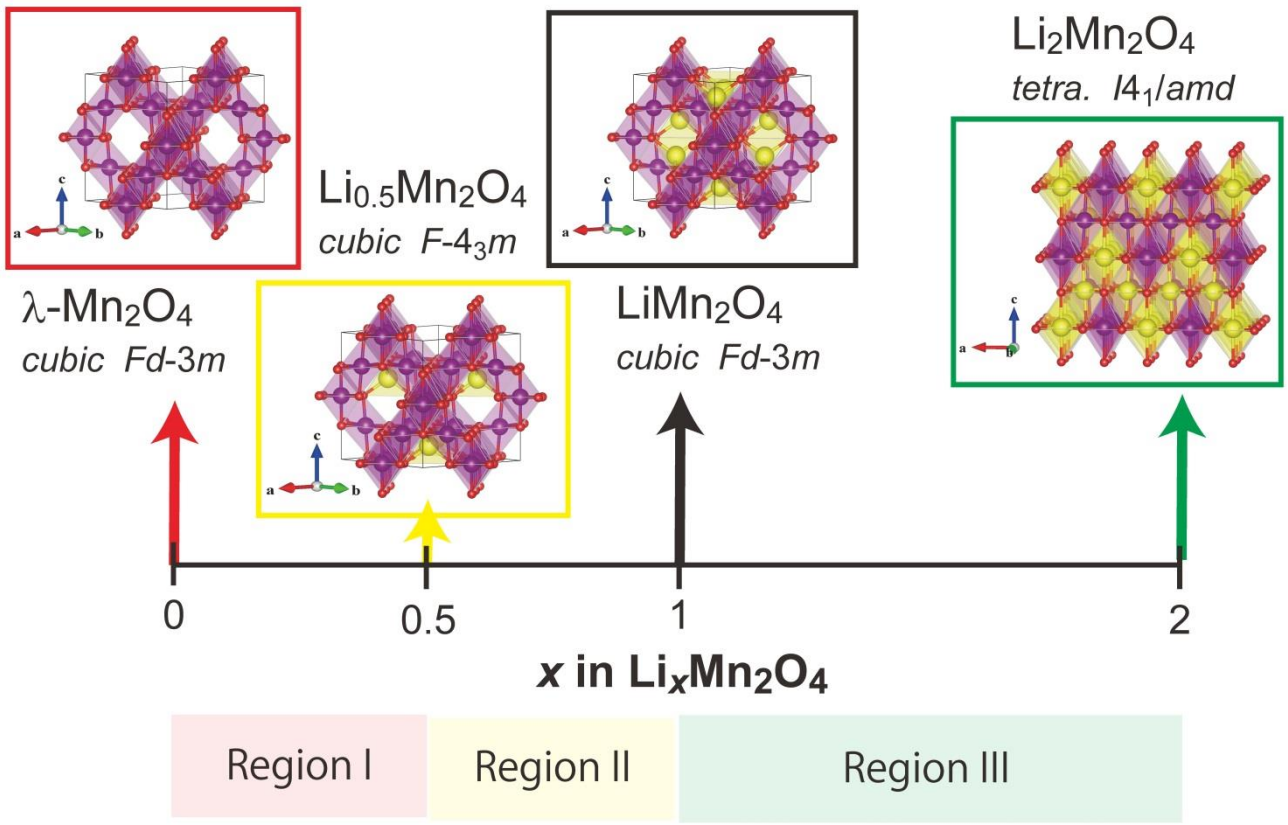

Fig. S1 Schematic diagram of the phase transitions during de-intercalation or intercalation from $Li_xMn_2O_4$ (x = 1). Purple octahedrons represent MnO_6, red balls indicate oxide ions, and yellow balls represent lithium ions.

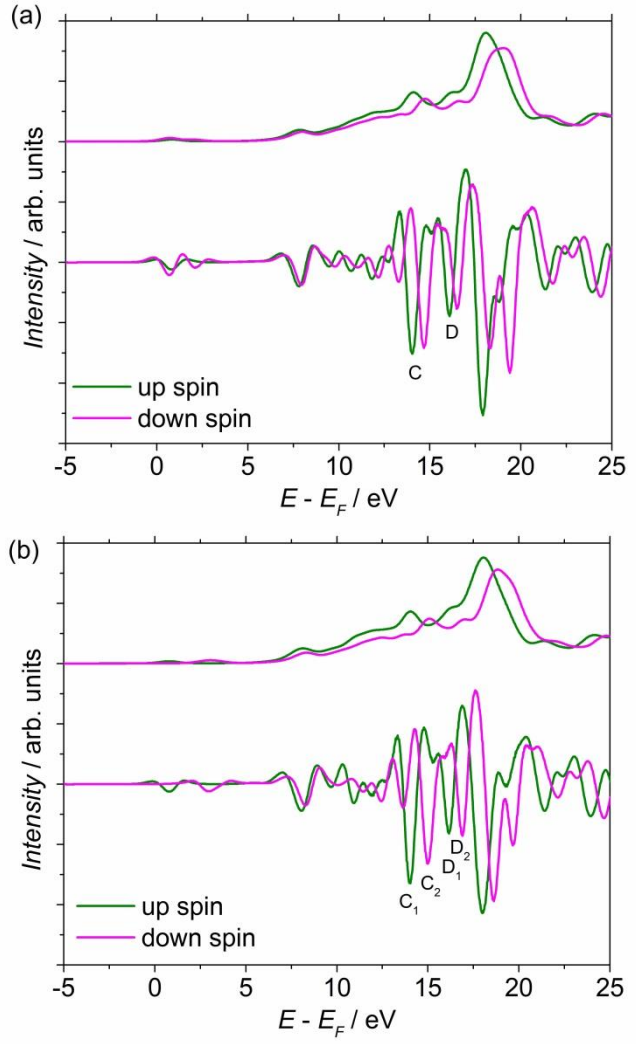

Fig. S2 Theoretical Mn *K*-edge XANES spectra corresponding to up spins (green curves) and down spins (pink curves) of $LiMn_2O_4$ calculated by (a) GGA and (b) GGA+*U*. Second-order differential curves of the XANES spectra are also shown on the bottom to clearly visualize each peak.

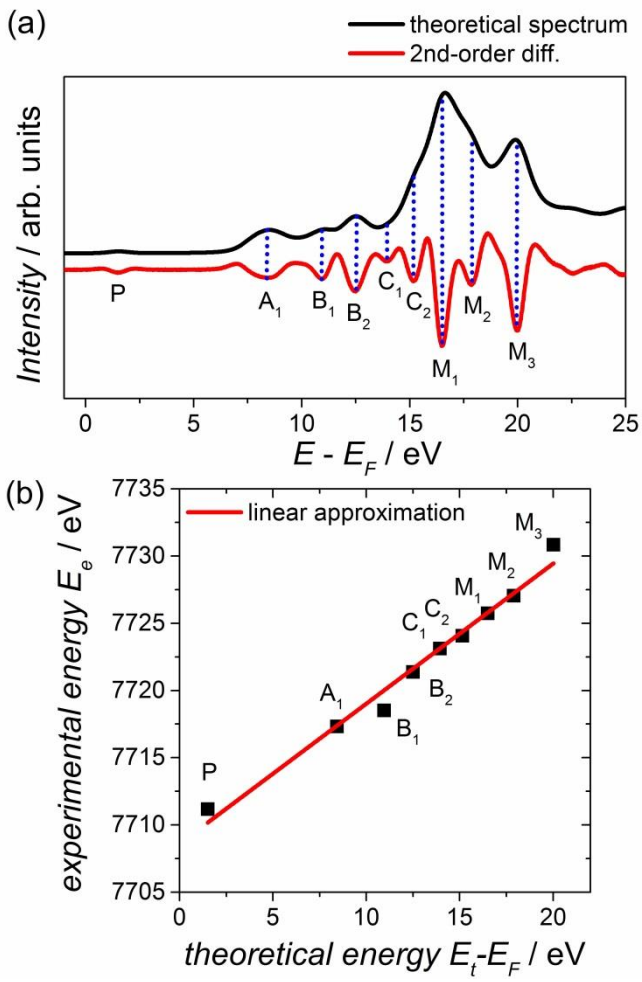

Fig. S3 (a) Theoretical Co *K*-edge XANES spectra of O3-$LiCoO_2$ calculated by GGA (black curves). Second-order differential curves of the XANES spectra are also shown to clearly visualize each peak (red curves). (b) The comparative plots of the theoretical peak energies with experimental energies ($E_t - E_F = \alpha E_e + \beta$, $\alpha = 1.04$, $\beta = 7708.60$, $R^2 = 0.977$).

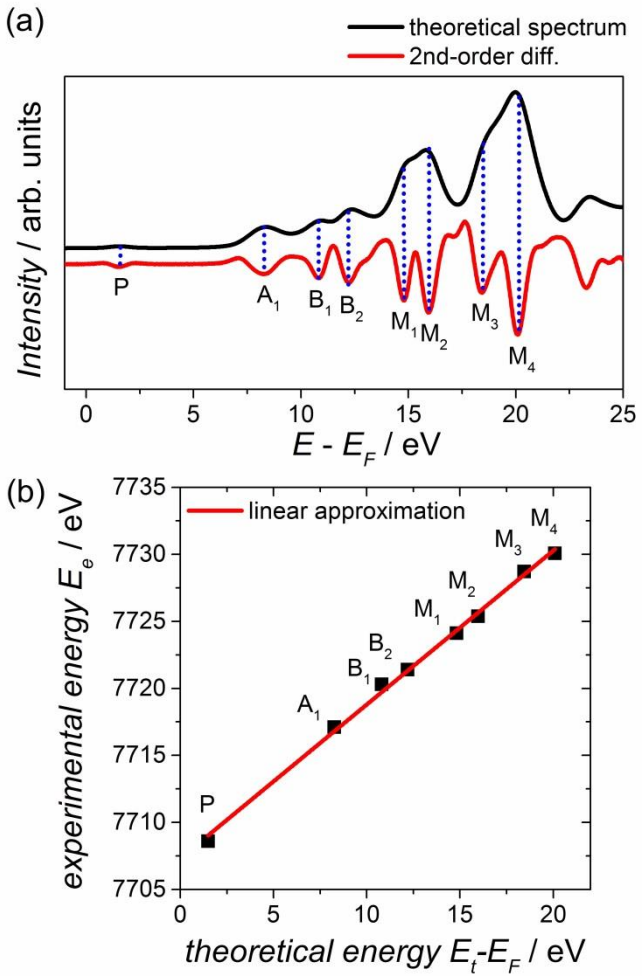

Fig. S4 (a) Theoretical Co *K*-edge XANES spectra of O2-$LiCoO_2$ calculated by GGA (black curves). Second-order differential curves of the XANES spectra are also shown to clearly visualize each peak (red curves). (b) The comparative plots of the theoretical peak energies with experimental energies ($E_t - E_F = \alpha E_e + \beta$, $\alpha = 1.15$, $\beta = 7707.32$, $R^2 = 0.997$).

Table S1 Crystallographic parameters of models and XANES simulating conditions for DFT calculation

Model	*Unit-cell formula*	*Space Group*	*Lattice parameter / Å*[a]				*Super cell*	*k-point grid*[b]	
			a	*b*	*c*			SCF (GS)	SCF & XANES (ES)
$LiMn_2O_4$	$Li_8Mn_{16}O_{32}$	*Fd*-3*m*	8.248	= *a*	= *a*		1 x 1 x 1	12 x 12 x 12	4 x 4 x 4
$LiMn^{3+}Mn^{4+}O_4$ AFM-1[c]	$Li_4(Mn_4^{3+}Mn_4^{4+})O_{16}$	*C*2/*c*	8.137	8.386	5.839	β = 47.63	1 x 2 x 1	12 x 12 x 12	4 x 4 x 4
$LiMn^{3+}Mn^{4+}O_4$ AFM-2[c]	$Li_4(Mn_4^{3+}Mn_4^{4+})O_{16}$	*Imma*	5.750	= *b*	8.707		2 x 2 x 1	12 x 12 x 12	4 x 4 x 4
$Li_{0.5}Mn_2O_4$	$Li_4Mn_{16}O_{32}$	*F*-4$_3$*m*	8.144	= *a*	= *a*		1 x 1 x 1	12 x 12 x 12	4 x 4 x 4
□-Mn_2O_4	$Mn_{16}O_{32}$	*Fd*-3*m*	8.033	= *a*	= *a*		1 x 1 x 1	12 x 12 x 12	4 x 4 x 4
$Li_2Mn_2O_4$	$Li_8Mn_8O_{16}$	*I*4$_1$/*amd*	5.649	= *a*	9.198		2 x 1 x 1	12 x 12 x 12	4 x 4 x 4

a) Lattice parameters were input with Ref [1]-[4]. ([1] *Chem. Mater.* **2000**, 12, 3246., [2] *J. Cryst. Growth* **2001**, 229, 405., [3] *J. Electrochem. Soc.* **2004**, 151, A296., [4] *Chem. Mater.* **1999**, 11, 1936.)

b) GS and ES denote the ground and exctited states, respectively.

c) Two anti-ferromagnetic (AFM) structures were modeled and full-optimized under each space group using Wien2k DFT-code.

Table S2 Ratios of crystal phases in lithium-ion intercalated/de-intercalated $Li_xMn_2O_4$ samples estimated by Rietveld analysis of synchrotron X-ray diffraction

Model	*Phase*	*Space Group*	R_{wp}	*S*	*Molar Ratio / %*
$LiMn_2O_4$	1	*Fd*-3*m*	5.888	1.5285	100
$Li_{0.75}Mn_2O_4$	1	*Fd*-3*m*	6.038	1.6654	100
$Li_{0.5}Mn_2O_4$	1	*Fd*-3*m*	6.301	1.7461	100
$Li_{0.25}Mn_2O_4$	1	*Fd*-3*m*	4.062	0.9689	43.3
	2	*Fd*-3*m*			56.7
$Li_{0.08}Mn_2O_4$	1	*Fd*-3*m*	5.651	1.5534	100
$Li_{1.25}Mn_2O_4$	1	*Fd*-3*m*	5.780	1.6483	68.6
	2	*I*4$_1$/*amd*			31.4
$Li_{1.5}Mn_2O_4$	1	*Fd*-3*m*	6.312	1.7795	37.8
	2	*I*4$_1$/*amd*			62.2
$Li_{1.66}Mn_2O_4$	1	*Fd*-3*m*	6.261	1.7916	22.6
	2	*I*4$_1$/*amd*			77.4