Supplementary Information

Intra-layer ordering and inter-layer disordering of Li_2MnO_3 phase in $Li_{1.07}Mn_{1.93}O_{4-\delta}$ cathode materials: electron diffraction investigation and DIFFaX simulation of XRD patterns

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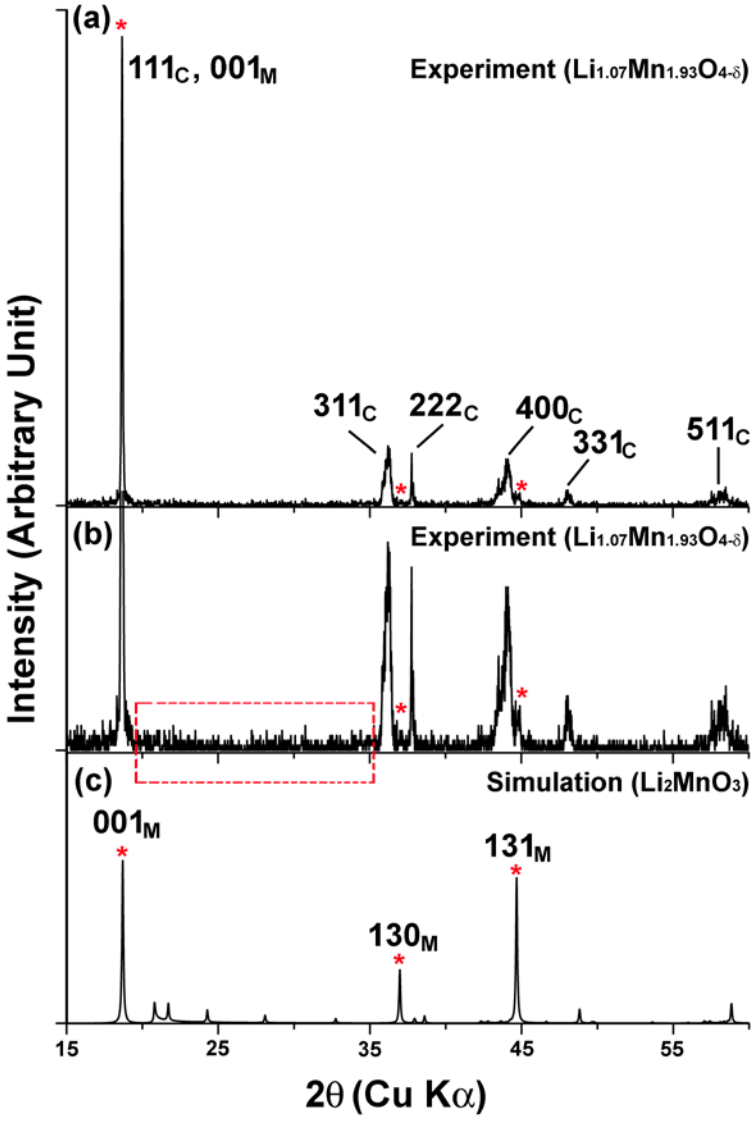

Figure S1 (*a*) Experimental XRD pattern of $Li_{1.07}Mn_{1.93}O_{4-\delta}$ (δ = 0.182) with dominant cubic spinel $LiMn_2O_4$ and monoclinic Li_2MnO_3 phases. The experiment was carried out on D8 Advance (Bruker AXS inc.) X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å); (*b*) A close-up view of the diffraction peaks in (*a*). (*c*) Simulated XRD pattern (λ = 1.54 Å) of Li_2MnO_3 with inter-layer stacking disordering when *x* equals to 0.33 (Table 1) (also shown in Fig. 3(*e*)). The subscripts "C" and "M" refer to the cubic and monoclinic indexing, respectively.

A characteristic DIFFaX simulation file in regard of studying the inter-plane disordering effect on XRD pattern with *x* equals to 0.33 (Table 1) is shown as follows:

INSTRUMENTAL {Header for instrumental section}
X-ray {Simulate X-ray diffraction}
1.5406 {X-ray wavelength}
{gaussian 0.1 trim} {Instrumental broadening (much faster)}
LORENTZIAN 0.1

STRUCTURAL {Header for structural section}
4.93 4.93 14.23 120.0 {unit cell coordinates, a, b, c, gamma}
UNKNOWN 1.0
9 {Number of layers}
infinite {Layers are very wide in the a-b plane}

LAYER 1 {atomic coordinates}
None

Atoms	Number	Coordinate (x)	Coordinate (y)	Coordinate (z)
Li	1	0	0	0
Li	2	-0.667	0.333	0.167
Li	3	-0.328	-0.006	0.167
Li	4	-0.006	0.672	0.167
Mn	1	0.333	0.667	0
Mn	2	0.667	0.333	0
O	1	0.643	0.643	0.076
O	2	0.308	0.666	0.259
O	3	0.666	0.308	0.259
O	4	0.023	0.023	0.258
O	5	0.359	0.001	0.074
O	6	0.001	0.359	0.074

LAYER 2
None

Atoms	Number	Coordinate (x)	Coordinate (y)	Coordinate (z)
Li	1	0	0	0
Li	2	1	0.667	0.167
Li	3	0.322	0.328	0.167
Li	4	0.678	0.006	0.167
Mn	1	0.333	-0.333	0
Mn	2	-0.333	-0.667	0
O	1	0	-0.643	0.076
O	2	0.358	-0.308	0.259
O	3	-0.358	-0.666	0.259

O	4	0	-0.023	0.258
O	5	-0.358	-0.359	0.074
O	6	0.358	-0.001	0.074

LAYER 3

None

Atoms	Number	Coordinate (x)	Coordinate (y)	Coordinate (z)
Li	1	0	0	0
Li	2	-0.333	-1.000	0.167
Li	3	0.006	-0.322	0.167
Li	4	-0.672	-0.678	0.167
Mn	1	-0.667	-0.333	0
Mn	2	-0.333	0.333	0
O	1	-0.643	0	0.076
O	2	-0.666	-0.358	0.259
O	3	-0.308	0.358	0.259
O	4	-0.023	0	0.258
O	5	-0.001	0.358	0.074
O	6	0.359	-0.358	0.074

LAYER 4 = 1

LAYER 5 = 1

LAYER 6 = 2

LAYER 7 = 2

LAYER 8 = 3

LAYER 9 = 3

STACKING {Header for stacking description}

recursive {Statistical ensemble}

infinite {Infinite number of layers}

TRANSITIONS {Header for stacking transition data}

{Transitions from layer 1}

Stacking transition Probability (α)	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
1	-0.333	-0.333	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333

{Transitions from layer 2}

Stacking transition probability	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
1	0.333	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333

{Transitions from layer 3}

Stacking transition probability	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
1	0	0.333	0.333
0	0	0	0.333

{Transitions from layer 4}

Stacking transition probability	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
1	-0.333	-0.333	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333

{Transitions from layer 5}

Stacking transition probability	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0.34	-0.333	-0.333	0.333
0.33	-0.333	-0.333	0.333
0.33	-0.333	-0.333	0.333

0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333

{Transitions from layer 6}

Stacking transition probability	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
1	0.333	0	0.333
0	0	0	0.333
0	0	0	0.333

{Transitions from layer 7}

Stacking transition probability	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0.33	0.333	0	0.333
0.34	0.333	0	0.333
0.33	0.333	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333

{Transitions from layer 8}

Stacking transition probability	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
1	0	0.333	0.333

{Transitions from layer 9}

Stacking transition probability	Stacking vector (R_x)	Stacking vector (R_y)	Stacking vector (R_z)
0.33	0	0.333	0.333
0.33	0	0.333	0.333
0.34	0	0.333	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333
0	0	0	0.333