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Role of Composition on the Atomic Structure, Oxygen Loss, and Capacity of Layered Li−Mn−Ni Oxide Cathodes

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Supporting Information

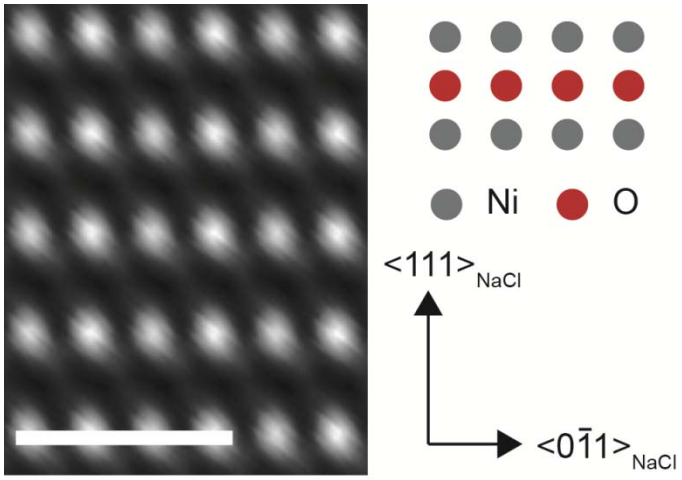

Fig. S1 Simulated HAADF-STEM image of NiO with the rock-salt structure, viewed down the $<\bar{2}\,11>_{NaCl}$ zone axis. The scale bar is 0.5 nm.

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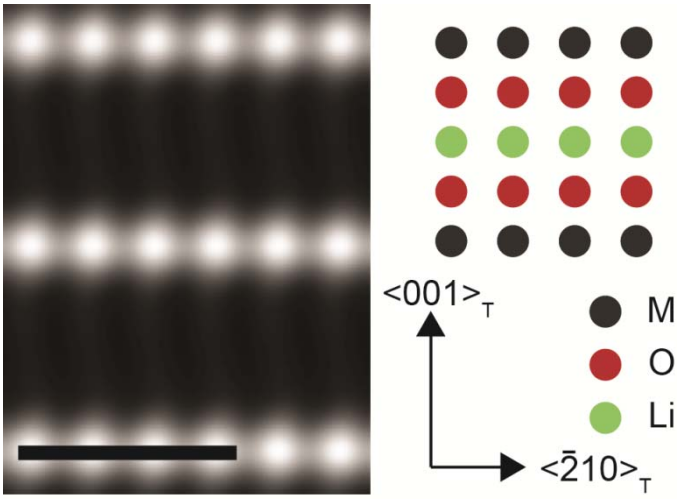

Fig. S2 Simulated HAADF-STEM image of $Li[Mn_{0.5}\ Ni_{0.5}]O_2$ viewed down the $[120]_T$ zone axis. The scale bar is 0.5 nm.

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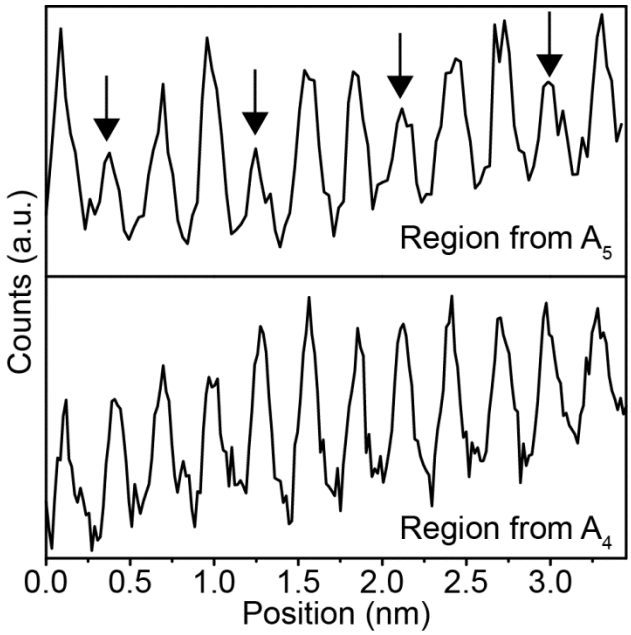

Fig. S3 Intensity profiles along the $[01\bar{1}]_{NaCL}$ direction from regions with an A_4 atomic arrangment and an A_5 atomic arrangment. The arrows show the position that exhibits reduced intensity, which occurs every third atomic column in A_5.

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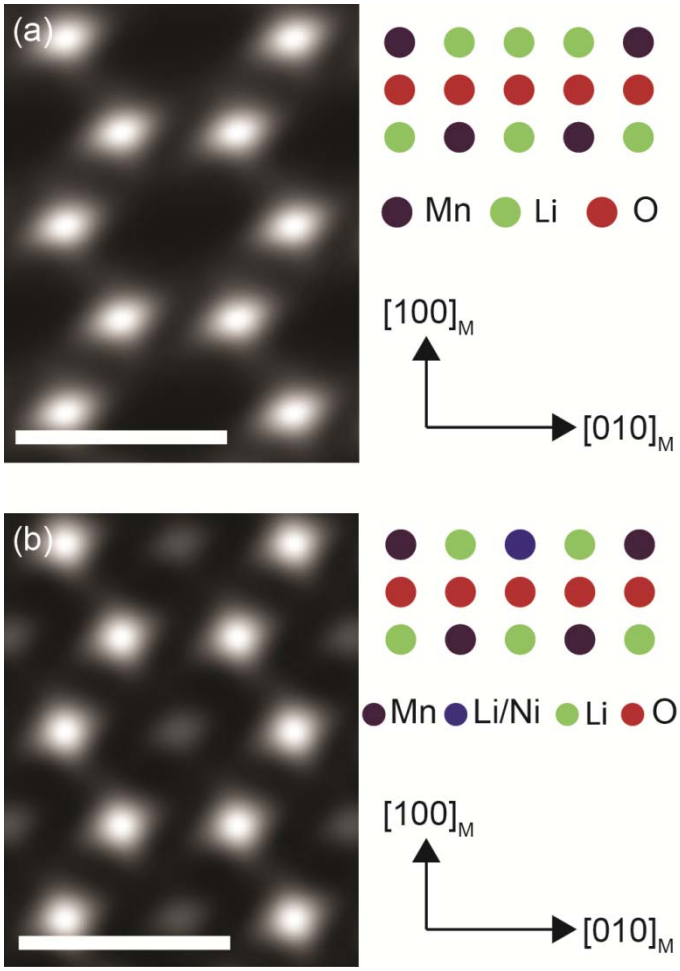

Fig. S4 Simulated HAADF-STEM image of (a) Li_2MnO_3 viewed down the $[001]_M$ zone axis and (b) $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ viewed down the $[001]_M$ zone axis. The scale bars are 0.5 nm.

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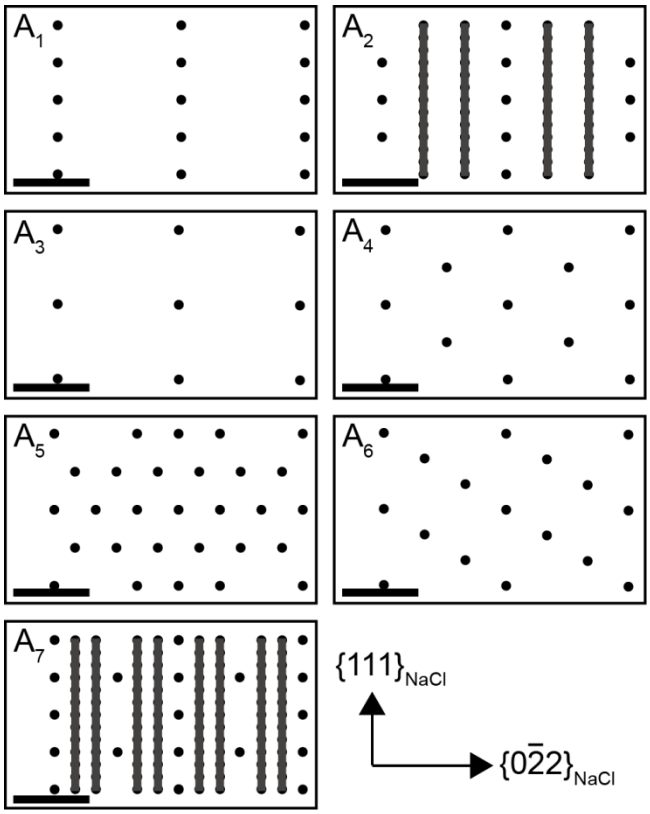

Fig. S5 Simulated electron diffraction patterns corresponding to the seven types of arrangements A_1 to A_7 found for the $Li[Li_{1/3-2x/3}Mn_{2/3-x/3}Ni_x]O_2$ series, viewed down the $<\bar{2}\,11>_{NaCl}$ zone axis. The directions indicated assume the most basic structure for layered oxides, the NaCl structure. The simulations are meant to show the positions of the allowed reflections and not the intensity of each allowed reflection. Therefore, each spot is given the same size and intensity. The scale bars are all 1 nm^{-1}.

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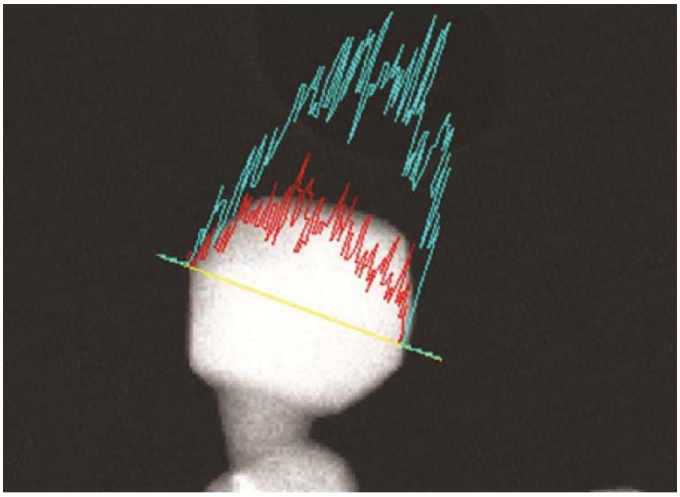

Fig. S6 EDS line scan (yellow) across a particle of $Li[Li_{0.2}Mn_{0.6}Ni_{0.2}]O_2$, showing the distribution of Mn (blue) and Ni (red).

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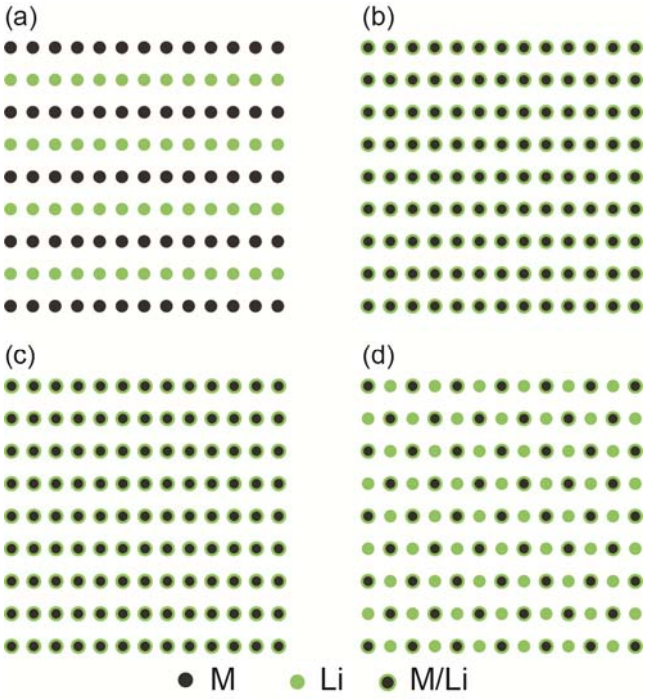

Fig. S7 Two-dimensional atomic models of $LiMO_2$, viewed down the NaCl $[\bar{2}\,11]_{NaCl}$ zone axis with the M and Li layers alternating on the (a) $(111)_{NaCl}$ (b) $(11\,\bar{1})_{NaCl}$, (c) $(1\,\bar{1}\,1)_{NaCl}$, and (d) $(\bar{1}\,11)_{NaCl}$ planes.

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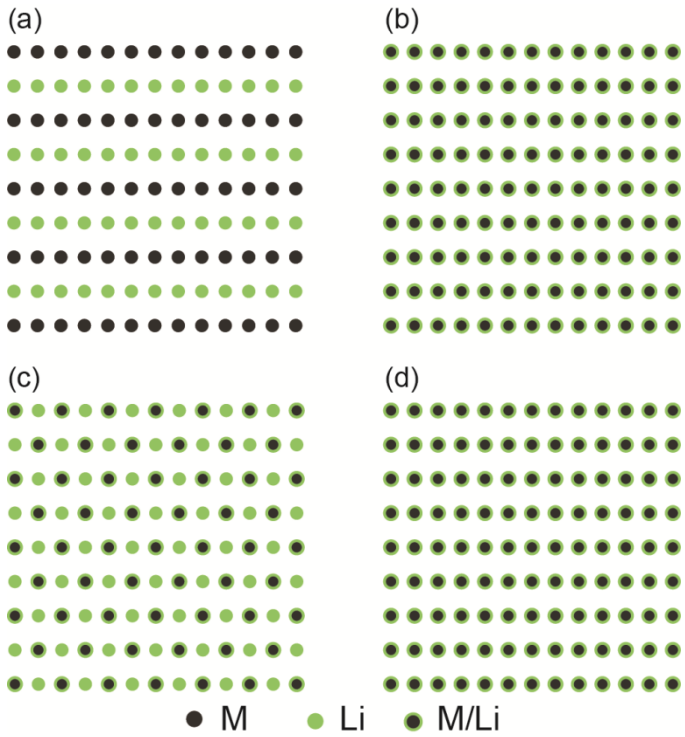

Fig. S8 Two-dimensional atomic models of $LiMO_2$, viewed down the NaCl $[1\ \bar{2}\ 1]_{NaCl}$ zone axis with the M and Li layers alternating on the (a) $(111)_{NaCl}$ (b) $(11\ \bar{1})_{NaCl}$, (c) $(1\ \bar{1}\ 1)_{NaCl}$, and (d) $(\bar{1}\ 11)_{NaCl}$ planes.

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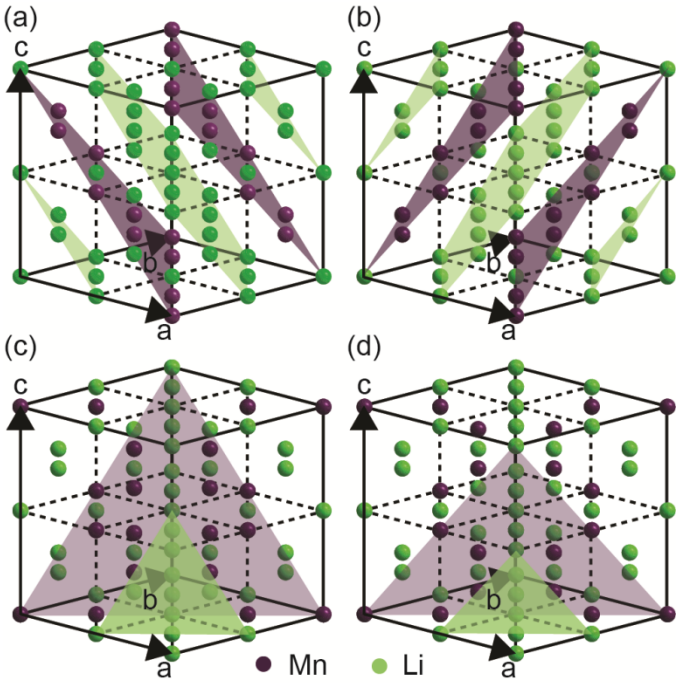

Fig. S9 Three-dimensional atomic models of various NaCl {111} planes in which the M and Li layers reside in Li_2MnO_3. (a) $(111)_{NaCl}$, (b) $(11\bar{1})_{NaCl}$, (c) $(1\bar{1}1)_{NaCl}$, and (d) $(\bar{1}11)_{NaCl}$.

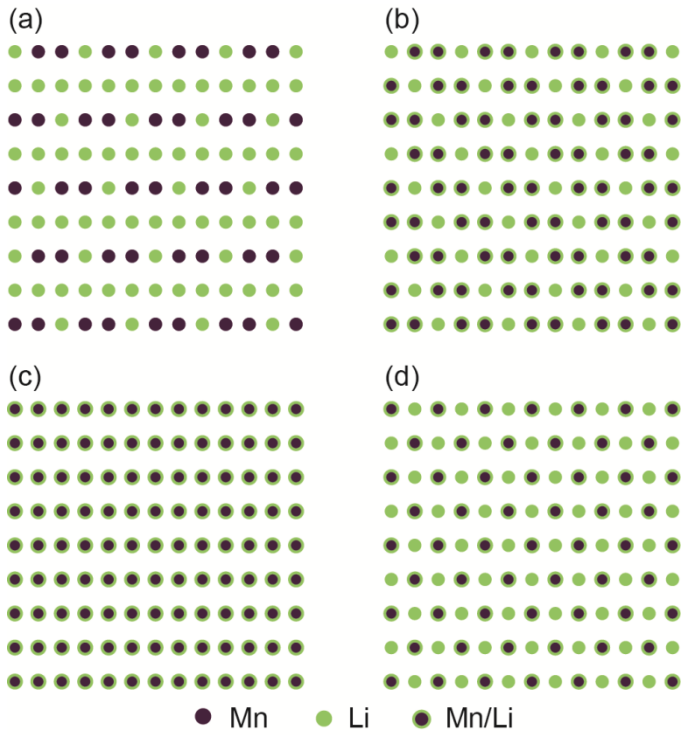

Fig. S10 Two-dimensional atomic models of Li_2MnO_3, viewed down the NaCl $[\bar{2}\,11]_{NaCl}$ zone axis with the M and Li layers alternating on the (a) $(111)_{NaCl}$ (b) $(11\,\bar{1})_{NaCl}$, (c) $(1\,\bar{1}\,1)_{NaCl}$, and (d) $(\bar{1}\,11)_{NaCl}$ planes.

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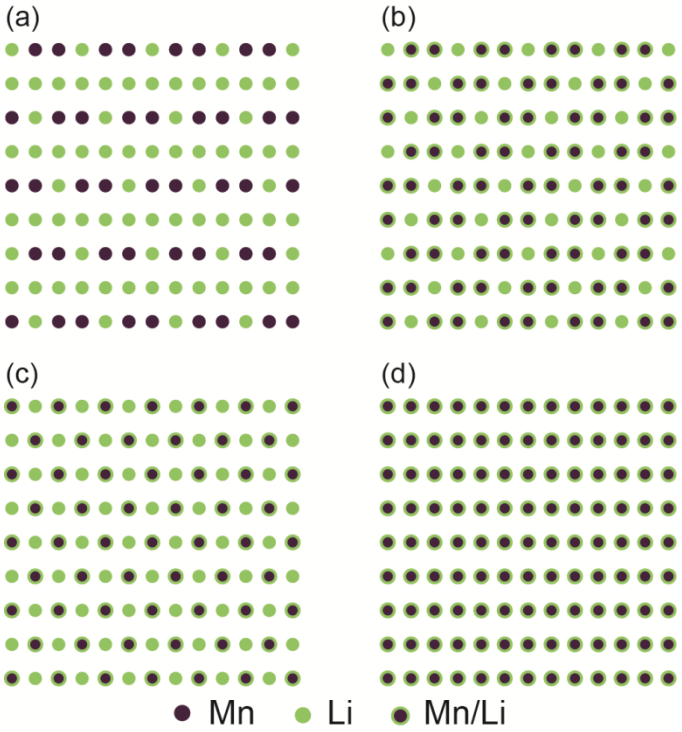

Fig. S11 Two-dimensional atomic models of Li_2MnO_3, viewed down the NaCl $[1\ \bar{2}\ 1]_{NaCl}$ zone axis with the M and Li layers alternating on the (a) $(111)_{NaCl}$ (b) $(11\ \bar{1})_{NaCl}$, (c) $(1\ \bar{1}\ 1)_{NaCl}$, and (d) $(\bar{1}\ 11)_{NaCl}$ planes

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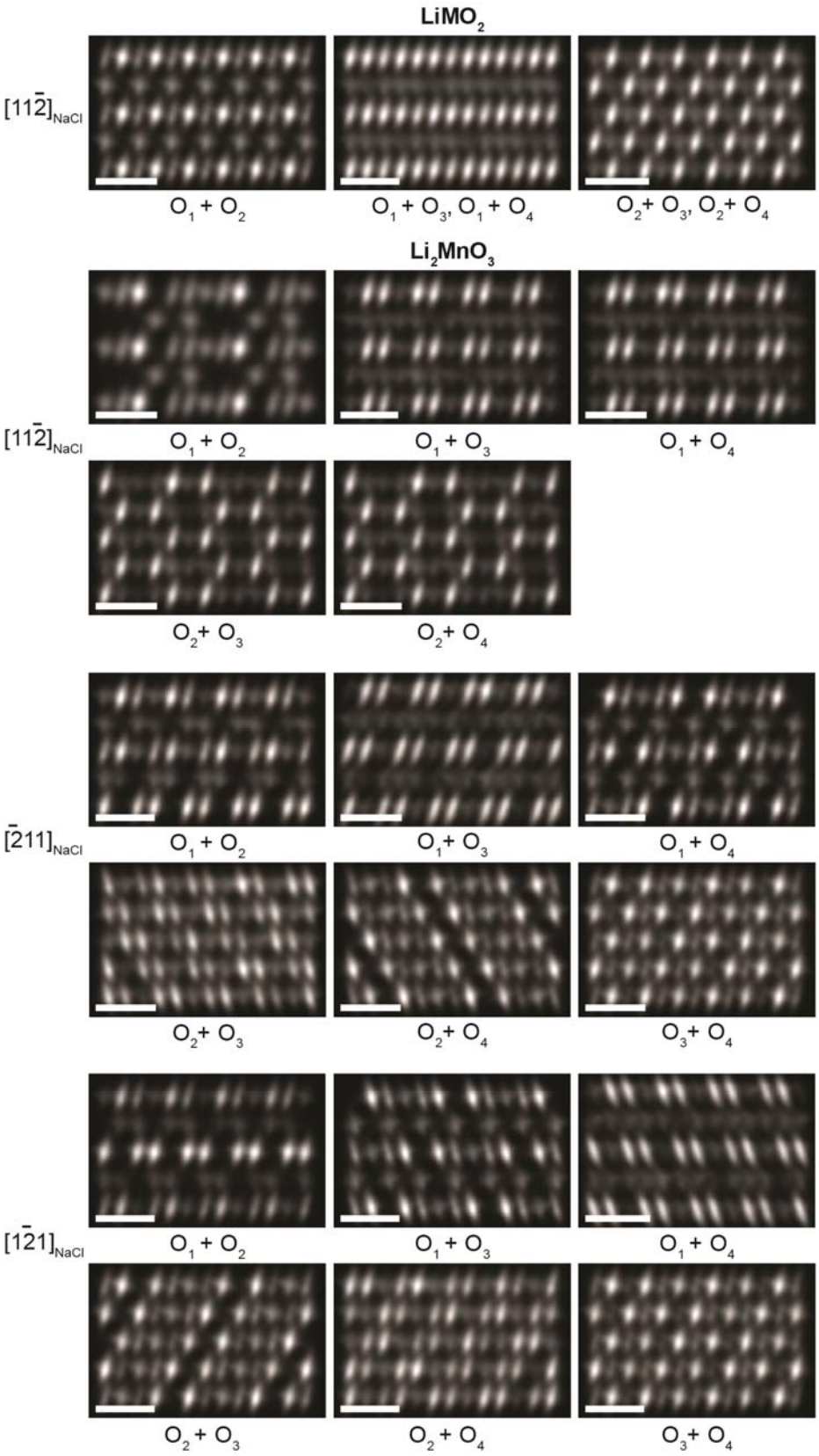

Fig. S12 Simulated HAADF-STEM images of $LiMO_2$ and Li_2MnO_3 showing possible combinations of overlapping one set of $\{111\}_{NaCl}$ type planes ordering across half of the crystal thickness and a different set of $\{111\}_{NaCl}$ type planes ordering across the other half of the crystal thickness. The beam direction is shown on the left, while the combination of overlapping two different sets of $\{111\}_{NaCl}$ types planes across the specimen thickness is, indicated by $O_n + O_m$. The scale bars are 0.5 nm.

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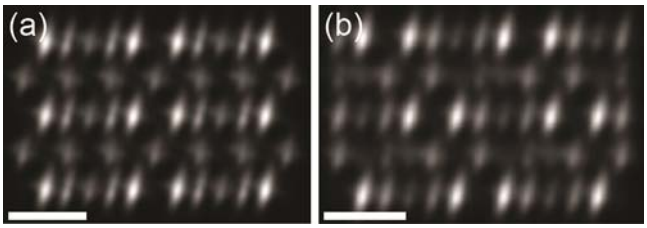

Fig. S13 Simulated HAADF-STEM image of Li_2MnO_3 with (a) half of the crystal ordered on the $(111)_{NaCl}$ planes with a $[100]_M$ orientation variant and the other half ordered down the $(\bar{1}\ 11)_{NaCl}$ planes. The beam direction is $[\bar{2}\ 11]_{NaCl}$. And, (b) a third of the cation layers ordered on the $(111)_{NaCl}$ planes with a $[110]_M$ orientation variant, a third ordered on the $(\bar{1}\ 11)_{NaCl}$ planes also with a $[110]_M$ orientation variant and the last third ordered on the $(11\ \bar{1})_{NaCl}$ planes with a $[1\ \bar{1}\ 0]_M$ orientation variant viewed in the $\{\bar{2}\ 11\}_{NaCl}$ direction. The scale bars are about 0.5 nm.

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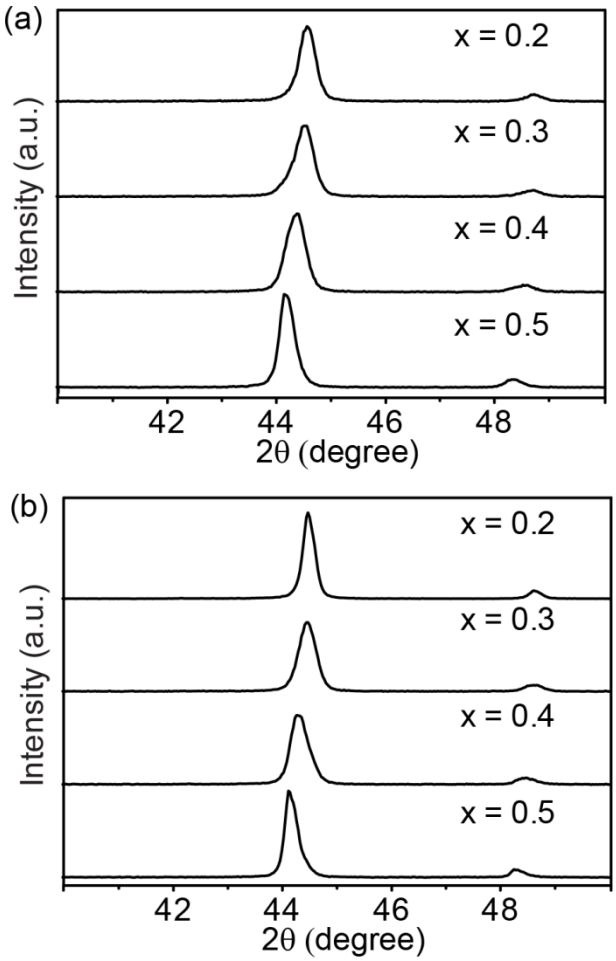

Fig. S14 XRD patterns scanned 40° to 50° of four compositions for the $Li[Li_{1/3-2x/3}Mn_{2/3-x/3}Ni_x]O_2$ ($0 < x \leq ½$) series (x = 0.5, 0.4, 0.3 and 0.2) prepared by (a) EDTA and (b) hydroxide precursor methods.

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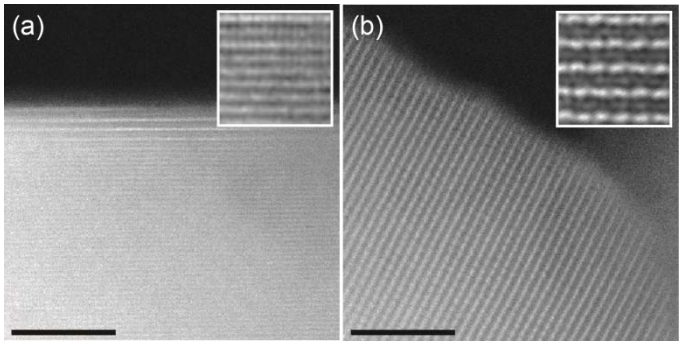

Fig. S15 Aberration-corrected HAADF-STEM images of $LiMn_{0.5}Ni_{0.5}O_2$ viewed down (a) the $[\bar{2}\,11]_{NaCl}$ zone axis and (b) the $[\bar{1}\,21]_{NaCl}$ zone axis. The scale bars are 5 nm. The insets show images at higher magnification and have been deconvoluted to reduce noise.[51]

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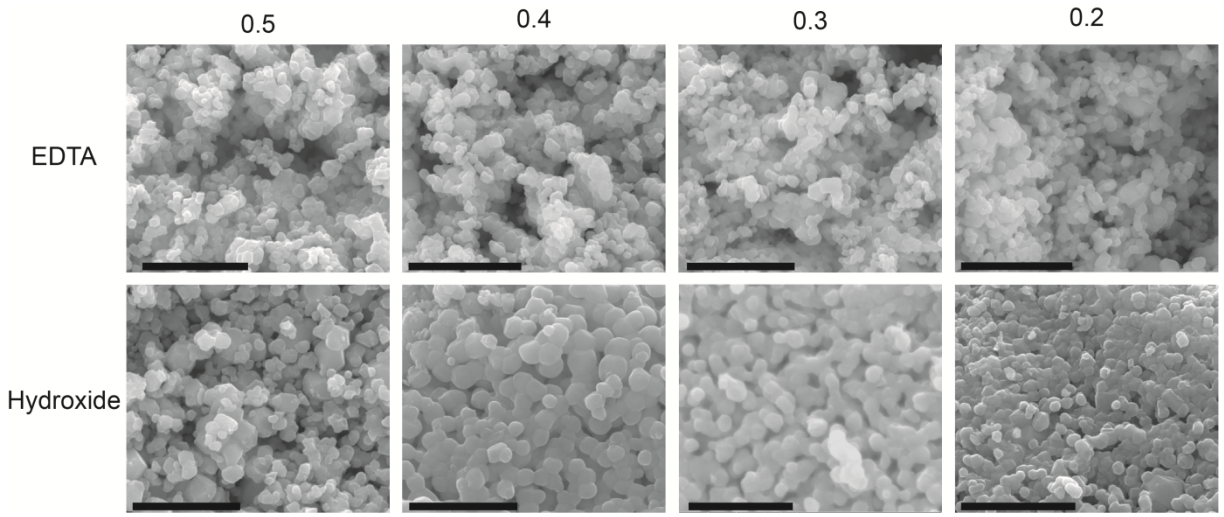

Fig. S16 Secondary electron SEM images of four compositions for the $Li[Li_{1/3-2x/3}Mn_{2/3-x/3}Ni_x]O_2$ ($0 < x \leq ½$) series prepared by the EDTA and hydroxide methods. The scale bars are 2 μm.

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Table S1. Equivalent directions for $LiMO_2$ with ordering on the four {111} planes of NaCl

Viewing direction (NaCl)	Plane of cation ordering in NaCl			
	1 1 1	1 1 $\bar{1}$	1 $\bar{1}$ 1	$\bar{1}$ 1 1
1 1 $\bar{2}$	1 2 0 (A_1)[a]	1 2 $\bar{1}$ (A_4)	10 8 $\bar{1}$ (A_3)	2 $\bar{8}$ 1 (A_3)
$\bar{2}$ 1 1	$\bar{2}$ $\bar{1}$ 0 (A_1)	8 $\bar{2}$ 1 (A_3)	8 10 1 (A_3)	2 1 1 (A_4)
1 $\bar{2}$ 1	1 $\bar{1}$ 0 (A_1)	10 2 $\bar{1}$ (A_3)	$\bar{1}$ 1 1 (A_4)	2 10 1 (A_3)

[a] The corresponding arrangements, as defined in the manuscript, are shown in parenthesis.

Table S2. Equivalent directions for Li_2MnO_3 with ordering on the four {111} planes of NaCl

Viewing direction (NaCl)	Plane of cation ordering in NaCl			
	1 1 1	1 1 $\bar{1}$	1 $\bar{1}$ 1	$\bar{1}$ 1 1
1 1 $\bar{2}$	1 0 0 (A_2) [a]	0 0 1 (A_5)	$\bar{3}$ 2 3(A_3)	$\bar{3}$ $\bar{2}$ 3(A_3)
$\bar{2}$ 1 1	1 1 0 (A_2)	0 $\bar{1}$ 1 (A_6)	6 $\bar{1}$ 3 (A_3)	3 $\bar{1}$ 6(A_4)
1 $\bar{2}$ 1	1 $\bar{1}$ 0 (A_2)	0 1 1 (A_6)	3 1 6 (A_4)	6 1 3 (A_3)

[a] The corresponding arrangements, as defined in the manuscript, are shown in parenthesis.

Table S3 Observed lithium content of $Li[Li_{1/3-2x/3}Mn_{2/3-x/3}Ni_x]O_2$ with x = 0.2, 0.3, 0.4, and 0.5

$Li[L_{i1/3-2x/3}Mn_{2/3-x/3}Ni_x]O_2$	Li content (observed)	
	Co	SG
x = 0.2 (Li 1.20)	1.22	1.182
x = 0.3 (Li 1.13)	1.11	1.10
x = 0.4 (Li 1.07)	1.05	1.03
x = 0.5 (Li 1.00)	1.00	1.01

[a] Co: Co-precipitation method SG: Sol-gel method.