#### Supplementary Information

#### Effects of cation superstructure ordering on oxygen redox stability in O2-

### type lithium-rich layered oxides

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## **Supplementary Figures**



Fig. S1. Rietveld refinement results of X-ray HRPD patterns of **a**, P2-Na<sub>5/6</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> and **b**, P2-Na<sub>5/6</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub>.



Fig. S2. Rietveld refinement results of neutron HRPD patterns of **a**, P2-Na<sub>5/6</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> and **b**, P2-Na<sub>5/6</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub>.



**Fig. S3.** Comparisons of (002) Bragg peaks between P2- and O2-type layered oxides for the two electrodes. Asterisks in the figure indicate O3-type impurity phase.



Fig. S4. Simulated XRD pattern of O2-type  $Li_2MnO_3$  with *Cmca* space group. A wavelength of  $\lambda$ =1.5209 Å was used for the simulation.



XRD O2-type solid-solution of  $Li_x(Li_{0.25}Ni_{0.125}Mn_{0.625})O_2 -$ Fig. **S5**. patterns of the  $Li_x(Li_{0.25}Co_{0.25}Mn_{0.5})O_2$  series. A wavelength of  $\lambda = 1.5406$  Å was used for the measurement. The results show that the intensities of the superstructure peaks gradually weaken, and the peaks become broaden with increasing cobalt content in the structure. Two peaks, (0-22) and (0-23), began to disappear in the sample containing 30% LLCMO - 70% LLNMO (that is, O2-Lix(Li0.25Ni0.0875Co0.075Mn0.5875)O2), and the two peaks were not observed in the structure with higher cobalt contents. These observations indicate that the presence of cobalt is prone to disrupt the superstructural ordering in the transition metal layers even with a small amount of cobalt ion. It infers that care should be taken when considering the incorporation of cobalt ions into lithium-rich layered oxides since trivalent substituents such as Co3+ can easily randomize the superstructural orderings of (Li<sup>+</sup>-Mn<sup>4+</sup> and Ni<sup>2+</sup>-Mn<sup>4+</sup>).



**Fig. S46.** FFT images for pristine electrodes of **a**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> and **b**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> shown in **Fig. 1**d and e of the main text. The cyan, blue, and purple circles correspond to the (110), (002), and (004) planes along the [1-10] zone axis of the space group  $P6_{3}mc$ , respectively.



Fig. S7. Simulated FFT patterns **a**, along the [100] zone axis of the space group *Cmca* and **b**, along the [1-10] zone axis of the space group  $P6_{3}mc$ .



**Fig. S58.** Average voltage of first discharge and second charge for various C-rates (0.1C, 0.2C, 0.5C, and 1C) of **a**,  $O2-Li_x(Li_{0.25}Ni_{0.125}Mn_{0.625})O_2$  and **b**,  $O2-Li_x(Li_{0.25}Co_{0.25}Mn_{0.5})O_2$  electrodes after cycling at 0.1C, as shown in **Fig. 2**d and e of the main text. Compared with the O2-LLNMO electrode, where symmetrical kinetic properties were confirmed with small variations in the capacity upon increasing the C-rate from 0.1 to 1, significant asymmetric kinetics was identified in the O2-LLCMO electrode, with the capacity decreasing while the polarization increased with the current rate during the discharging process, unlike the behavior observed during the charging process.



Fig. S9. In situ XRD results of **a**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> and **b**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub>. A wavelength of  $\lambda$ =1.54056 Å was used for the measurement. Comparison of the main (002) peak position difference between the full-charged and pristine states in the two electrodes.



**Fig. S610.** In-plane cation arrangements of the most stable structure of O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> according to various Li clustering, whose calculation results are shown in Fig. S711. As indicated by the yellow circles, Fig. S610a, b, and c represent the most stable structures when 1, 2, and 3 Li ions, respectively, are clustered in the TM layer. The calculations in **Fig. 4** of the main text and Supplementary Table 5–6 were calculated based on the structure in Fig. S610b.



Number of Erclaster in the Twildyer

**Fig. S711.** Calculated total energies of Li(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> with different orderings in the transition metal layer. A total of 200, 400, and 400 atomic configurations were enumerated for the case of 1, 2, and 3 Li clusters, respectively. The most stable structures in each case according to the results of this calculation is shown in Fig. S610. The relative energies of the structures in Fig. S610b and c are 8.9 and 22.7 meV/atom, respectively, compared with the configuration of Fig. S610a, which is the most stable structure. Considering that the thermal energy is 25.7 meV/atom at room temperature, all three configurations are thermodynamically feasible.



**Fig. S812.** Schematic diagram of the structure after the transition metal migrates to Path III as shown in **Fig. 4**d. It was confirmed that a significant number of vacancies were clustered around the oxidized oxygen (see around the yellow oxygen). Therefore, the oxidized oxygen is expected to be highly unstable because it coordinates with only one transition metal.



**Fig. S913.** Schematic diagram of the structure before and after relaxation after transition metal migrates to the final site of Path II.



Fig. S1014. SEM images for pristine electrodes of **a**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> and **b**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub>.



Fig. S15. Histogram results of a, O2-Lix(Li\_{0.25}Ni\_{0.125}Mn\_{0.625})O2 and b, O2-Lix(Li\_{0.25}Co\_{0.25}Mn\_{0.5})O2 fortheSTXMmappingimagesinFig.5aandb.



**Fig. S1416.** STXM absorption spectra of O K-edge for **a**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> and **b**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> electrodes during initial charging and discharging. Spectra were collected for the indicated points in the left electrochemical profiles. The differential spectra between the pristine and 4.6-V-charged electrodes and between the 4.6-V-charged and 2.0-V-discharged electrodes are shown together. The shaded region represents the evolution of a new peak at 530.6 eV, which is clear evidence of the redox of lattice oxygen. The spatial distribution of the oxygen redox degree for O2-Li<sub>x</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> and O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> of pristine, 4.6-V-charged, and 2.0-V-discharged electrodes is shown on the right side of the spectra.



**Fig. SH217.** XANES absorption spectra for the **a**, Ni K-edge and **b**, Mn K-edge of the O2-Li<sub>x</sub>(Li<sub>0.25</sub>Mn<sub>0.625</sub>)O<sub>2</sub> electrode. XANES absorption spectra for the **c**, Co K-edge and **d**, Mn K-edge of the O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> electrode. Reference spectra are also plotted. Each inset figure is an enlarged graph of the pink box in each XANES spectrum, indicating the half-edge energy position. During the initial charging of LLNMO to 4.3 V (state #1 $\rightarrow$  state #2), the half-edge energy of Ni K-edge shifted to a higher energy, indicating that Ni was oxidized to a higher oxidation state (here oxidized from 2+ to 4+). The position of the edge did not change even after charging to 4.6 V (state #2 $\rightarrow$  state #3), but the edge energy shifted to the original position when the fully charged electrode was discharged to state #4. During the same process, the edge position of Mn was not changed, which means that Mn was electrochemically inactive in this reaction region (state #1 $\rightarrow$  state #4). However, when the electrode was further discharged to state #5, the inactive Mn was reduced as the half-edge energy of LLNMO, became closer to that of Mn<sup>3+</sup><sub>2</sub>O<sub>3</sub>, while Ni remained unchanged during this process. Like LLNMO, LLCMO exhibited similar sequential redox behavior up to state #4. The charging process to 4.3 V (state #1 $\rightarrow$  state #2) was compensated by the cationic redox of Co<sup>3+/4+</sup> and the position of Co K-edge was not changed further until 4.6 V (state #3). Similar to Ni redox, the Co redox was completely reversed to its

original state upon discharging the LLCMO to 3.2 V (state #4). The notable distinct redox behavior of LLCMO is that a new redox center of  $Co^{2+/3+}$  was activated in the low-voltage region (#4 $\rightarrow$ #5) of LLCMO, which was confirmed by the fact that the half-edge energy of LLCMO approached that of  $Co^{+2.67}_{3}O_{4}$ . The partial manganese reduction to Mn<sup>3+</sup> was similarly observed in LLCMO in this reaction region (#4 $\rightarrow$ #5).



**Fig. S1318.** Solid-state <sup>7</sup>Li NMR spectra of pristine and 1-, 5-, and 10-cycled **a**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> and **b**, O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> electrodes. The green and pink shaded areas represent Li<sub>TM</sub> and Li<sub>Li</sub> signals, respectively. The right panel is an enlarged image of the green area in the left panel, showing the <sup>7</sup>Li signal in the TM layer.



Fig. S1419. The spatial distribution of oxygen redox degree of pristine and 1-, 5-, and 10-cycled **a**,  $O2-Li_x(Li_{0.25}Ni_{0.125}Mn_{0.625})O_2$  and **b**,  $O2-Li_x(Li_{0.25}Co_{0.25}Mn_{0.5})O_2$  electrodes.



**Fig. S1520.** XANES absorption spectra for the **a**, Ni K-edge and **b**, Mn K-edge of pristine and 1-, 5-, and 10-cycled O2-Li<sub>x</sub>(Li<sub>0.25</sub>Ni<sub>0.125</sub>Mn<sub>0.625</sub>)O<sub>2</sub> electrode. XANES absorption spectra for the **c**, Co K-edge and **d**, Mn K-edge of pristine and 1-, 5-, and 10-cycled O2-Li<sub>x</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> electrode. As observed in XANES results, the cationic redox behaviors significantly differed for the two electrodes. For the O2-LLNMO electrode, as shown in Fig. S1520a and b, the half-edge energy positions of Ni and Mn were well conserved during the cycles, except that the edge of Mn undergoes a slight change after the first cycle. In contrast, in O2-LLCMO (Fig. S1520c and d), the edges of Co and Mn continue to shift to lower energies even after the irreversible redox transitions of the first cycle, confirming that the redox irreversibility continued to deteriorate during the repeated electrochemical cycling.

# Supplementary Tables

Table S1.	Rietveld	refinements	of X-ray	HRPD	patterns	of P2-Na	a <sub>5/6</sub> (Li <sub>0.25</sub> N	i <sub>0.125</sub> Mn <sub>0.62</sub>	$_{25})O_2 1$	naterials.
$(R_p = 13.9)$	9%)									

Phase	Atom	X	Y	Z	Occupancy	B <sub>iso</sub>
<b>P2</b> P6 <sub>3</sub> /mmc ( <b>82.19</b> wt%)	Nal	0.3333	0.6667	0.75	0.833	1
	Lil	0	0	0	0.25	1.88 (32)
	Ni1	0	0	0	0.125	1.88 (32)
	Mn1	0	0	0	0.625	1.88 (32)
	01	0.3333	0.6667	0.4108 (7)	0.978 (4)	1.42 (67)
	a (Å)		b (Å)		<b>c</b> (Å)	
-	2.8	839 (1)	,	2.8839 (1)	11.	.0100 (4)
	Atom	X	У	Z	Occupancy	B <sub>iso</sub>
O3 R3m (17.81 wt%)	Li1	0	0	0	0.833	1
	Li2	0.3333	0.6667	0.1667	0.25	1.19 (83)
	Ni1	0.3333	0.6667	0.1667	0.125	1.19 (83)
	Mn1	0.3333	0.6667	0.1667	0.625	1.19 (83)
	01	0	0	0.2396	1	0.83 (52)
-	8	ı (Å)		b (Å)		c (Å)
	2.8	449 (2)		2.8449 (2)	14.2	2094 (22)

Phase	Atom	X	Y	Z	Occupancy	B <sub>iso</sub>
	Na1	0.3333	0.6667	0.75	0.833	1
P2 P6 <sub>3</sub> /mmc (83.4 wt%)	Li1	0	0	0	0.25	1.49 (32)
	Ni1	0	0	0	0.125	1.49 (32)
	Mn1	0	0	0	0.625	1.49 (32)
	01	0.3333	0.6667	0.4133 (7)	0.988 (4)	1.26 (76)
	a (Å)			b (Å)	<b>c</b> (Å)	
	2.8	381 (1)		2.8381 (1)	11.	.0595 (3)
	Atom	X	У	Z	Occupancy	B <sub>iso</sub>
O3 R3m (16.6 wt%)	Lil	0	0	0	0.833	1
	Li2	0.3333	0.6667	0.1667	0.25	1.33 (86)
	Ni1	0.3333	0.6667	0.1667	0.125	1.33 (86)
	Mnl	0.3333	0.6667	0.1667	0.625	1.33 (86)
	01	0	0	0.2387 (11)	0.962 (8)	0.74 (78)
	8	u (Å)		b (Å)		c (Å)
	2.8	443 (2)		2.8443 (2)	14.2	2406 (15)

**Table S2.** Rietveld refinements of X-ray HRPD patterns of P2-Na<sub>5/6</sub>(Li<sub>0.25</sub>Co<sub>0.25</sub>Mn<sub>0.5</sub>)O<sub>2</sub> materials. ( $R_p = 11.7 \%$ )

 $\textbf{Table S3.} Rietveld refinements of neutron HRPD patterns of P2-Na_{5/6}(Li_{0.25}Ni_{0.125}Mn_{0.625})O_2 \ materials.$ 

$\langle \rho \rangle$	$(R_p)$	=	7	.6	%)
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Phase	Atom	X	Y	Z	Occupancy	B <sub>iso</sub>	
P2 P6 <sub>3</sub> /mmc (82.53 wt%)	Na1	0.3333	0.6667	0.75	0.833	1	
	Li1	0	0	0	0.25	1.86 (33)	
	Ni1	0	0	0	0.125	1.86 (33)	
	Mn1	0	0	0	0.625	1.86 (33)	
	01	0.3333	0.6667	0.4084 (4)	1	0.74 (7)	
	a (Å)		b (Å)	c (Å)			
	2.8872	2(1)	2.8872 (1)		11.0032 (	5)	
	Atom	X	У	Z	Occupancy	B <sub>iso</sub>	
O3 R3m (17.47 wt%)	Li1	0	0	0	0.833	1	
	Li2	0.3333	0.6667	0.1667	0.25	0.99 (18)	
	Ni1	0.3333	0.6667	0.1667	0.125	0.99 (18)	
	Mn1	0.3333	0.6667	0.1667	0.625	0.99 (18)	
	01	0	0	0.2377 (12)	1	1.51 (36)	
	a (Å)			b (Å)	c (Å)		
	2.8	521 (3)	2	.8521 (3)	14.0	0742 (30)	

 $\label{eq:s4.Relation} \textbf{Table S4. Rietveld refinements of neutron HRPD patterns of P2-Na_{5/6}(Li_{0.25}Co_{0.25}Mn_{0.5})O_2\ materials.$ 

Phase	Atom	X	Y	Z	Occupancy	B <sub>iso</sub>	
	Nal	0.3333	0.6667	0.75	0.833	1	
	Li1	0	0	0	0.25	1.56 (24)	
P2	Ni1	0	0	0	0.125	1.56 (24)	
P6 <sub>3</sub> /mmc	Mn1	0	0	0	0.625	1.56 (24)	
(83.85 wt%)	01	0.3333	0.6667	0.4097 (2)	1	0.96 (5)	
-	a (Å)			b (Å)	c (Å)		
-	2.8	442 (1)	,	2.8442 (1)	11.	.0358 (3)	
	Atom	X	У	Z	Occupancy	B <sub>iso</sub>	
-	Lil	0	0	0	0.833	1	
O3 R3m (16.15 wt%)	Li2	0.3333	0.6667	0.1667	0.25	0.91 (18)	
	Nil	0.3333	0.6667	0.1667	0.125	0.91 (18)	
	Mn1	0.3333	0.6667	0.1667	0.625	0.91 (18)	
	01	0	0	0.2454 (5)	1	1.82 (22)	
-	a (Å)			b (Å)		c (Å)	
	2.8	453 (2)	2	2.8453 (2)	14.2	2462 (11)	

Table S5. Relative site energies of intermediate and final sites calculated along the other poss ible migration paths of TM ions (O1: octahedral site in the TM layer, O2: octahedral site in the Li layer, T: tetrahedral site in the Li layer,  $V_{Li}$ : lithium vacancy).

Site	Dimer	Local environment	Relative Site E (eV)
Initial O1		Edge-share with (2 Li, 4 TM)	0
Intermediate O2			0.21
	Formed (~ 1.31 Å)	Face-share with $V_{Li}$	-3.96
		Face-share with TM	Not relaxed
Final T		Face-share with TM	2.37
Fillat 1		Edge-share with (2 $V_{Li}$ , 1 TM)	1.19
		Edge-share with (2 $V_{Li}$ , 1 TM)	1.34
		Edge-share with (1 $V_{Li}$ , 2 TM)	Not relaxed

**Table S6.** Relative site energies of intermediate and final sites calculated along the other poss ible migration paths of TM ions (O1: octahedral site in the TM layer, O2: octahedral site in the Li layer, T: tetrahedral site in the Li layer,  $V_{Li}$ : lithium vacancy).

Site	Dimer	Local environment	Relative Site E (eV)
Initial O1		Edge-share with (2 Li, 4 TM)	0
Intermediate T			-0.54
	Formed (~ 1.36 Å)	Face-share with $V_{Li}$	-2.54
Final O2	Formed (~ 1.35 Å)	Face-share with TM	0.44
		Face-share with TM	3.04