## **Supporting Information**

## Revealing the thermodynamics and kinetics of in-plane disordered Li<sub>2</sub>MnO<sub>3</sub> structure in Li-rich cathodes

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Figure S1. Possible distributions and corresponding energy of disordered Li<sub>2</sub>MnO<sub>3</sub>.

Exploring different ordered configurations through DFT calculations and choosing the ground-state structure with the lowest energy is a general idea of modeling disordered phases<sup>[1]</sup>. In order to obtain the specific Li<sub>2</sub>MnO<sub>3</sub> configuration, geometry optimization and energy calculation are performed on all possible distributions by DFT calculations. The in-plane disordered Li<sub>2</sub>MnO<sub>3</sub> configuration (b) with the lowest energy is adopted as the initial structure model for further research. Notably, it is reasonable that the ordered Li<sub>2</sub>MnO<sub>3</sub> exhibits lower energy than the disordered, the fact that the disordered structure is not at the lowest point of thermodynamic energy explains well why it cannot be obtained through conventional unassisted routes, but instead relies on molten-salt to step over some certain energy barriers.



Figure S2. XRD spectrum prediction of configuration (b).

XRD prediction is performed on configuration (b) to verify the feasibility as the model for calculation. Compared with the ordered Li<sub>2</sub>MnO<sub>3</sub>, configuration (b) shows weakened superstructure peaks and left-shifted peaks, which is consistent with experimental results. It demonstrates that the utilization of the lowest-energy ground-state structure is appropriate.



Figure S3. The calculated formation energy of (a) disordered and (b) ordered  $Li_{2-x}MnO_3$ . (c) The average delithiation potential of disordered and ordered  $Li_{2-x}MnO_3$ .

Based on the initial models of in-plane disordered and ordered  $Li_2MnO_3$ , each five ground-state configurations at different states of charge are obtained through energy screening. Figure S3a and Figure S3b shows calculated formation energy ( $E_f$ ) of disordered and ordered  $Li_{2-x}MnO_3$  (x=0, 0.25, 0.5, 0.75 and 1) respectively according to the equation (1)<sup>[2]</sup>:

$$E_f(x) = E(\text{Li}_{2-x}\text{MnO}_3) - xE(\text{LiMnO}_3) - (1-x)E(\text{Li}_2\text{MnO}_3)$$
(1)

The formation energy is defined as 0 at x=0 and 1, and the ground-states with the lowest energy are connected to form a convex hull, the energy appears as negative values mean that the delithiation is a global process rather than an average result. The average delithiation potential, estimated by equation  $(2)^{[3]}$ , is shown in Figure S3c. The twostep delithiation potential of the ordered Li<sub>2</sub>MnO<sub>3</sub> is narrowly located from 4.66 V to 4.71 V. For in-plane disordered Li<sub>2</sub>MnO<sub>3</sub>, the delithiation potential is significantly lower at 4.14 V in the first step and 4.40 V in the second step, and it increases to 4.65 V from x=0.5 to 1, still lower than the ordered.

$$V_{ave}(x_1 \sim x_2) = -\frac{E(\text{Li}_{2-x_1}\text{MnO}_3) - E(\text{Li}_{2-x_2}\text{MnO}_3) - (x_2 - x_1)E(\text{Li})}{x_2 - x_1}$$
(2)



Figure S4. Structure configurations of (a) disordered and (b) ordered  $Li_{2-x}MnO_3$ . The quantified Li content at different Li concentrations of (c) disordered and (d) ordered  $Li_{2-x}MnO_3$ . Diagram of Li movement (e) from disorder- $Li_{1.25}MnO_3$  to disorder- $LiMnO_3$  and (f) from order- $Li_{1.5}MnO_3$  to order- $Li_{1.25}MnO_3$ .

To understand the lithium storage mechanism of in-plane disordered  $Li_2MnO_3$  structure, the removal sequence of Li at each site during the delithiation process is clarified from the perspective of thermodynamic energy. Figure S4a and Figure S4b shows the configurations of disordered and ordered  $Li_{2-x}MnO_3$  at different Li concentrations (x=0, 0.25, 0.5, 0.75 and 1). The quantified Li content of disordered and ordered  $Li_{2-x}MnO_3$  is shown in Figure S4c and Figure S4d, respectively. Considering that the symmetry has changed in disordered  $Li_2MnO_3$  structure, but for intuitive

comparison, 2b', 2c' and 4h' are named to represent the 2b, 2c, and 4h sites in ordered  $Li_2MnO_3$  of the visually equivalent. It can be found that in in-plane disordered  $Li_2MnO_3$  structure, the first 0.75 mol Li is contributed by the 4h' and 2c' sites in the Li-layer, while the Li content in the TM-layer has not changed. The interesting phenomenon occurs from  $Li_{1.25}MnO_3$  to  $LiMnO_3$ , the Li in the TM-layer (2b' site) begins to remove for the first time and half of them is retained in LiMnO<sub>3</sub>. At the same time, the Li content in the Li-layer remains unchanged and accompanied by the migration of 0.25 mol Li from 2c' to 4h' site, the diagram is shown in Figure S4e. For ordered  $Li_2MnO_3$ , priority is given to removing all the Li at the 2c site, while the Li at the 4h site remains in place. Starting from x=0.5, the Li in the TM-layer (2b site) begins to remove and completely emptied when x=1. Similarly, 0.5 mol Li at the 4h site is compensated to the 2c site from  $Li_{1.5}MnO_3$  to  $Li_{1.25}MnO_3$ , as shown in Figure S4f. Note that the migration barrier from Li-layer to Li-layer is lower than that from TM-layer to Li-layer.

Materials	Measured Li : Mn : Ni	Actual composition
DR-LNMO	1.58: 0.73: 0.25	$Li_{1.26}Mn_{0.58}Ni_{0.2}O_2$
O-LNMO	1.68: 0.64: 0.21	$Li_{1.44}Mn_{0.55}Ni_{0.18}O_2$

Table S1. Measured Li: Mn: Ni atomic ratio of DR-LNMO and O-LNMO compounds by ICP tests.

According to the ICP results, DR-LNMO and O-LNMO can be described as  $Li_{1.26}Mn_{0.58}Ni_{0.2}O_2$  and  $Li_{1.44}Mn_{0.55}Ni_{0.18}O_2$  respectively. Note that the molten-salt is bound to affect the Li content in the materials, and to a certain extent, the Li content is a driving force for the distribution of cations. The large Li content makes the cations tend to be more ordered, therefore, the highly ordered Li/Mn structure can be successfully constructed.



Figure S5. Overlapping partial XRD spectrum of DR-LNMO and O-LNMO.

Figure S5 shows the overlapping XRD spectra of DR-LNMO and O-LNMO. It is observed that almost all peaks greater than 30° in DR-LNMO are shifted to the left. This is obviously not caused by the crystallinity, because the crystallinity can only affect the intensity of the peak but cannot cause a shift. Therefore, it confirms the structural difference between DR-LNMO and O-LNMO, rather than the dominance of crystallinity.



Figure S6. XRD Rietveld refinements of (a) DR-LNMO and (b) O-LNMO. (c) Raman spectra of fresh electrodes of DR-LNMO and O-LNMO.

Li <sub>2</sub> MnO <sub>3</sub> , <i>a</i> =5.2105 Å, <i>b</i> =8.4125 Å, <i>c</i> =5.9172 Å, β=108.8288°						
Atom	Wyckoff symbol	х	У	Z	Occupancy	Beq.
Li1	4h	0.00000	0.33870	0.50000	1	0
Li2	2c	0.00000	0.00000	0.50000	1	0
Li3	2b	0.00000	0.50000	0.00000	0.3333	0.0026
Mn4	2b	0.00000	0.50000	0.00000	0.6667	0.0026
Li5	4g	0.00000	0.16710	0.00000	0.3333	0
Mn6	4g	0.00000	0.16710	0.00000	0.6667	0
07	8j	0.24510	0.17870	0.77650	1	0
08	4i	0.21920	0.00000	0.22750	1	0

Table S2. Structural parameters for DR-LNMO from Rietveld refinement.

Table S3. Structural parameters for O-LNMO from Rietveld refinement.

Li <sub>2</sub> MnO <sub>3</sub> , <i>a</i> =4.5495 Å, <i>b</i> =8.1766Å, <i>c</i> =6.1838 Å, β=106.8889°						
Atom	Wyckoff symbol	Х	у	Z	Occupancy	Beq.
Lil	4h	0.00000	0.33870	0.50000	1	0.9375
Li2	2c	0.00000	0.00000	0.50000	1	0.1563
Li3	2b	0.00000	0.50000	0.00000	1	0.9375
Mn4	4g	0.00000	0.16710	0.00000	1	2.5
05	8j	0.24510	0.17870	0.77650	1	2.5
06	4i	0.21920	0.00000	0.22750	1	1.731



Figure S7. dQ/dV curves of DR-LNMO and O-LNMO during the initial charge process. Peak 1 and peak 2 correspond to the oxidation of transition metals and oxygen respectively.



Figure S8. Initial charge-discharge profiles of (a) DR-LNMO and (b) O-LNMO. (c) Average discharge voltage of DR-LNMO and O-LNMO during 50 cycles at 0.1C.

Figure S8a and S8b show the initial charge-discharge profiles of DR-LNMO and O-LNMO. After the Li in the TM-layer is removed, the ordered honeycomb superstructure undergoes structural transformation and relaxation, resulting in strong voltage hysteresis<sup>[4,5]</sup>, which is well verified in O-LNMO. The Li/Mn disorder in the TM-layer of DR-LNMO reduces the degree of in-plane migration of the transition metal, and is reflected in the low voltage hysteresis. The average discharge voltage of DR-LNMO during 50 cycles at 0.1C is shown in Figure S8c, the alleviated voltage decay of DR-LNMO during cycling confirms that the Li/Mn disorder in the TM-layer contributes to suppression of the layered-spinel transition.



Figure S9. (a) XRD spectrum of the electrode after 300 cycles of DR-LNMO and O-LNMO. (b) Raman spectra of the electrodes after 300 cycles of DR-LNMO and O-LNMO.

The XRD spectrum of the electrode after 300 cycles of DR-LNMO and O-LNMO is shown in Figure S9a. The peak shape and intensity of DR-LNMO remain relatively intact, the  $I_{(003)}/I_{(104)}$  ratio of DR-LNMO is 1.2, which is significantly greater than that in O-LNMO ( $I_{(003)}/I_{(104)}$ =0.7), indicating a better maintained layered structure in DR-LNMO.

Figure S9b shows the Raman spectra of the electrodes after 300 cycles of DR-LNMO and O-LNMO. The obvious broadening of the peaks is due to structural distortion. The strong weakening of the peak at ~500 cm<sup>-1</sup> in O-LNMO is associated with the migration of Mn to the interlayer and the formation of spinel structure. The merging of the two peaks close to 600 cm<sup>-1</sup> indicates that the cations are rearranged during the cycle, which well explains the phenomenon that the capacity of O-LNMO first increases and then decreases.



Figure S10. Nyquist plots of (a) DR-LNMO and (b) O-LNMO at various states of charge during the initial charge-discharge process.

The semicircle in the high-frequency region corresponds to the resistance  $R_{sf}$ , which represents the solid electrolyte interface (SEI) film on the electrode surface. It slightly decreases with charging and increases with discharge, but the range of change is small throughout the process. The followed semicircle represents the charge transfer resistance and in comparison, it behaves much larger in O-LNMO than in DR-LNMO.



Figure S11. BVEL maps of disorder- $Li_2MnO_3$ , disorder- $LiMnO_3$ , order- $Li_2MnO_3$  and order- $LiMnO_3$  under the isosurface with percolation energy of 1.05 eV.

Based on the exact configurations obtained by DFT, BVS method is performed on disorder-Li<sub>2</sub>MnO<sub>3</sub>, disorder-LiMnO<sub>3</sub>, order-Li<sub>2</sub>MnO<sub>3</sub> and order-LiMnO<sub>3</sub>. The calculated channels and percolation energy are suggested to determine the trend and difficulty of Li<sup>+</sup> migration. The yellow outline corresponds to the isosurface with percolation energy of 1.05 eV, and the inside is the area where Li<sup>+</sup> may transport. The narrowest part of the channel enclosed by the isosurface is the highest energy site in the migration path. The Li<sup>+</sup> diffusion is divided into an intralayer transport along *a* (*b*) axis and an interlayer transport along *c* axis.

		a axis	<i>b</i> axis	c axis
disorder	Li <sub>2</sub> MnO <sub>3</sub>	0.94	2.24	1.00
	LiMnO <sub>3</sub>	0.96	1.90	1.01
order	Li <sub>2</sub> MnO <sub>3</sub>	0.87	2.45	1.07
	LiMnO <sub>3</sub>	1.09	2.03	1.24

Table S4. The calculated percolation energy (eV) above  $E_{min}$  along with a, b and c axis via BVS method.



Figure S12. Contour map mode for in-situ XRD curves of DR-LNMO.

## Methods

**Material synthesis:** The shared precursor of DR-LNMO and O-LNMO is prepared by a co-precipitation method. First, MnSO<sub>4</sub> and NiSO<sub>4</sub> were dissolved in deionized water at a molar ratio of 3:1 to form a 2.0 mol/L transition metal sulfate aqueous solution. And it was uniformly dropped into a continuously stirred tank reactor together with a 2.0 mol/L Na<sub>2</sub>CO<sub>3</sub> aqueous solution and an appropriate amount of NH<sub>3</sub>·H<sub>2</sub>O. The reaction temperature was kept constant at 55°C, pH at 7.5, and stirring speed at 1200 rpm/min, The obtained precipitate was washed with deionized water and dried at 120°C to prepare the Ni<sub>0.25</sub>Mn<sub>0.75</sub>CO<sub>3</sub> precursor. Secondly, the precursor and an appropriate amount of Li<sub>2</sub>CO<sub>3</sub> (4% Li excess), with the addition of KCl or LiNO<sub>3</sub> flux, were manually mixed thoroughly in a mortar. After that, the mixture was sintered at 500°C for 5 h, and then at 700°C, 800°C, and 900°C respectively for 12 hours. The amount of molten-salt is based on the molar ratio of n (KCl/LiNO<sub>3</sub>):n (TM)= 4:1. Finally, the obtained product was repeatedly washed with deionized water to completely remove the soluble molten-salt, and then the powder was dried at 120°C.

**Computational details:** All density functional theory (DFT) calculations were performed with simulation cells size up to 4 formula units. The results of all  $Li_{2-x}MnO_3$  configurations were obtained using the spin-polarized generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional to handle exchange-correlation energy<sup>[6]</sup>. The strong correlation effect of Mn 3d was considered with the DFT+U method, and the Hubbard U for Mn was set as 3.9 eV<sup>[7]</sup>. The spin polarization is involved in the calculations. The plane-wave cut-off energy was set to

400 eV, and the k-point was set to  $3 \times 1 \times 3$  Monkhorst-Pack mesh for geometry optimization and  $5 \times 3 \times 5$  for density of states (DOS) to sample values in the Brillouin zone. In the process of geometric optimization, atomic positions and lattice parameters were completely relaxed, the convergence condition was that energy, force, stress and displacement are less than  $5.0 \times 10^{-5}$  eV/atom, 0.1 eV/Å, 0.2 Gpa and 0.005 Å respectively.

**Material characterizations:** X-ray diffraction (XRD) patterns were collected using a Bruker diffractometer equipped with a Cu K $\alpha$  radiation source ( $\lambda = 1.5406$  Å). All samples were recorded in the range of  $2\theta = 10^{\circ}-90^{\circ}$  with an increment of 0.01° and a constant counting time of 0.8 s/step. Rietveld refinements of XRD were performed using the Topas software. The in-situ XRD test was operated with the range of  $2\theta = 16^{\circ}-$ 45.5° with a charge-discharge current of 0.5 C. The lattice morphology and SAED patterns were probed by HRTEM (JEM-2100F). Chemical oxidation valence and coordination environment were measured by XPS (Physical Electronics PHI model 5700).

**Electrochemical measurements:** The working electrodes were prepared by mixing active materials, Super P and polyvinylidene fluoride with a mass ratio of 8:1:1. The slurries were uniformly coated on an Al foil and dried in a vacuum at 120 °C, then they were punched into 14-mm diameter disks to assemble CR2025 coin cells in an argon-filled glovebox (<0.1 ppm of H<sub>2</sub>O and O<sub>2</sub>). the negative electrode is a Li foil and the separator is a polypropylene sheet. The mass loading of the active materials on the working electrodes is about 2-3 mg/cm<sup>2</sup>. 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate:

dimethyl carbonate (DMC) in a 1:1 ratio was used as the electrolyte. Galvanostatic charge/discharge tests with the voltage range of 2.0-4.8 V were performed on NEWARE battery tester at room temperature. Except for specific voltage labels, EIS tests were performed at 4.2 V using a Chenhua electrochemical analyzer (CHI660e) with a range of frequency from 0.01 Hz to 100 kHz.

## References

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