Supplementary Materials for

Crystalline Grain Interior Configuration Affects Lithium Migration Kinetics in Li-rich Layered Oxide

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Section I: Materials and Methods Material preparation

LLOs were prepared via solid-state reaction technology. In a typical synthesis, the required amounts of the transition metal acetates Mn(CH₃COO)₂ 4H₂O (Wako), Ni(CH₃COO)₂ 4H₂O (Wako) and Co(CH₃COO)₂ 4H₂O (Wako) were first mixed thoroughly. Second, the stoichiometric LiOH H₂O (Wako) (5% excess) was mixed with the transition metal mixture and then calcined in a furnace at 500 $^{\circ}$ C for 5 h. Then, the powder was pressed into pellets and calcined in a furnace at 900°C for 15 h. Finally, Li12Mn0.567Ni0166Co0.067O2 (0.5 Li2MnO3-0.5 LiMn_{0.42}Ni_{0.42}Co_{0.16}O₂) LLOs were prepared. The X-ray diffraction pattern and composition analysis can be found in ref. 1.

CSTTs-LLO preparation

CSTTs-LLOs were prepared by the ArIS method, which based on a shadowing technique. During the process of specimen preparation, a low-energy, low-angle Ar ion beam irradiates the specimen, while a thin shield belt allows low-angle irradiation of the Ar ion beam, thereby drastically reducing ion-beam irradiation damage to the specimen. Thus, the ArIS method can lead to highquality, homogenous, damage-free, and large electron-transparent areas of up to $100 \times 200 \ \mu m^2$ (20000 $\ \mu m^2$), even for complex poly-phase specimens. This allows detailed and statistically significant study of features and grain boundaries in poly-phase materials.

HAADF/ABF STEM observations and simulation

ED patterns and BF- and DF-TEM images were taken with a 200-kV JEM-2010HC electron microscope (JEOL), and the possible number of overlapping ED figures was calculated. Atomicresolution HAADF/ABF STEM images were taken with a 200-kV ARM-200CF electron microscope (JEOL) equipped with a spherical aberration corrector and a cold field-emission gun^{2, 3}. The microscope conditions for the atomic-scale analysis were as follows: the probe-forming aperture semiangle was 24 mrad, and the semiangles of the ABF and HAADF detectors were 12-24 and 90-370 mrad, respectively. The HAADF/ABF STEM image simulations were performed using the xHREM software package (HREM Research, Inc.)⁴.

First-principles calculation

Spin-polarized first-principles calculations were performed using the projector augmented wave method⁵ and the generalized gradient approximation (GGA), as implemented in the VASP software package. The basis sets were composed of plane waves up to 500 eV. The valence electron configurations of the potentials were taken to be $1s^2 2s^1$ for Li, $3p^6 3d^5 4s^2$ for Mn. $3p^6 3d^8 4s^2$ for Ni, and $2s^2 2p^4$ for O. The radial cutoffs of the PAW potentials of Li, Mn, Ni and O were 1.70, 2.30, 2.00 and 1.52 Å, respectively. The strong correlation effect of 3d electrons was taken into account using the GGA+U method. The values of U for Mn and Ni were set to 4.2 and 6 eV, respectively ⁶. First, a unit cell of Li₂MnO₃ was fully optimized until all residual forces acting on each atom became less than 0.02 eV/Å with a Γ centered k-mesh sampling of $3 \times 2 \times 3$. Li₂MnO₃

had site mixing of cations ⁷. In our calculations, the occupancies of the Li atoms at the 2b and 4h sites and of the Mn atoms at the 4g site were set to unity. DB models were constructed based on optimized Li_2MnO_3 (more detailed explanations are presented in the Supplementary Materials). For the DB models, the cell sizes of the model

were fixed, and the interior atomic positions were relaxed under the same conditions as mentioned for the unit cell. Only the Γ point was chosen for the *k*-point sampling of the domain boundary models. The energy profiles of Li⁺ migration via vacancy were evaluated using the nudged elastic band method ⁸.



Figure S1. Large and smooth CSTTs-LLOs for (S)TEM investigation. (a) Conventional TEM observation of LLOs.

A rhombohedral LiTMO₂ structure with a R^{3m} space group and a monoclinic Li₂MnO₃-like type structure with a C2/m space group are shown in (a). (b) Current (S)TEM observation of the large and smooth CSTTs-LLOs prepared by the ArIS method. (c and d) BF-TEM images of the as-synthesized nanoparticles with different magnification factors. (e and f) BF-TEM images of the sliced nanoparticles with different magnification factors.

Section II: ED simulation of the whole crystal particle

Pattern A in Figure 1b is chosen from the spot circled with red dotted lines in Figure S2b. This spot can only be reflected from the monoclinic Li_2MnO_3 -like structure projected along $[\overline{110}]_{mon}$ direction. Therefore, all of the regions with bright contrasts in domain A correspond to the monoclinic Li₂MnO₃-like structure projected along $[\overline{1}\overline{1}0]_{mon}$ direction. It is obvious that both the ED patterns associated with atomic structures presented in Figure S2a and Figure S2c can be expected if the monoclinic Li₂MnO₃-like structure projected along $[\overline{1}\overline{1}0]_{mon}$ direction is rotated in a clockwise or counter clockwise direction by 120° around the $[103]_{mon}$ -axis. Furthermore, the experimental spotted-streaks ED patterns in Figure 1b are similar to the simulative ones marked with

blue arrows in Figure S2e, resulting from the accumulated ED patterns marked with blue arrows in Figure S2a, Figure S2b and Figure S2c. Thus, the existence of staking faults with monoclinic Li₂MnO₃-like structure along [103]_{mon}-axis inside the studied ETTF-LLOs can be confirmed based on the ED experiments and simulations. In addition, it is also obvious that all of the ED patterns along yellow arrows in Figure S2a, Figure S2b, Figure S2c and Figure S2d are located in the same position, and can be overlapped and presented in Figure S2e. This proves the stacking faults existence of monoclinic Li2MnO3-like structure again and indicates that the rhombohedral LiTMO₂ structure projected along $[1\overline{1}0]_{rh}$ also probably exist inside the domain A, which will be confirmed and discussed by the HAADF/ABF STEM investigation in atomic resolution.



Figure S2. ED patterns and relative atomic structures of the monoclinic Li_2MnO_3 -like structure projected along (a), $[100]_{mon}$, (b), $[\overline{110}]_{mon}$ and (c), $[\overline{110}]_{mon}$ directions. (d) ED patterns and relative atomic structures of the rhombohedral LiTMO₂ structure projected along $[1\overline{10}]_{rh}$ direction. (e) Overlapped ED patterns by both ED patterns in (a), (b), (c) and (d). The ED pattern marked with red dotted line is located with the same site as A pattern in Figure 1b. The relationship between the atomic structures and corresponding ED patterns of (a), (b) and (c) are described with a rotation of 120° with each other. Blue arrows in (a), (b), and (c) show the characteristic ED patterns of Li_2MnO_3 -like structure projected along $[100]_{mon}$, $[\overline{110}]_{mon}$ and $[\overline{110}]_{mon}$ directions. Blue arrows in (e) show spotted-streaks ED patterns, which are resulted from the ED patterns in (a), (b), and (c), indicating the stacking faults existence in domain A. Yellow arrows in (e) show the overlapped ED patterns from both ED patterns of Li_2MnO_3 -like structure in (d).

The spot circled with red dotted lines in Figure S3a is located in the same place as Pattern B in Figure 1b. This pattern is originated from the ED patterns from the monoclinic Li₂MnO₃-like structure projected along $[011]_{mon}$ direction. The spot circled with red dotted lines in Figure S4a is located in the same place as Pattern C in Figure 1b, and this pattern corresponds to the ED patterns from the monoclinic Li₂MnO₃-like structure projected along $[0\overline{1}1]_{mon}$ direction. Thus, all of the regions with bright contrasts in B and C domains in Figure 1e and f correspond to the monoclinic Li₂MnO₃-like structure projected along $[011]_{mon}$ and $[0\overline{1}1]_{mon}$ directions, respectively. The regions with relative faint contrasts in B and C domains are most probably attributed from the other coexisted rhombohedral LiTMO₂ structure or some stacking faults of the monoclinic Li₂MnO₃like structure inside these domains. It is also obvious that pattern B and C have the relationship with rotation the monoclinic Li₂MnO₃-like structure projected along $[011]_{mon}$ direction about 180° toward the reader, presenting symmetrical feature of B and C domains in Figure 1i. In addition, obviously, all of the ED patterns along the yellow arrows in Figure S3a, Figure S3b, Figure S3c and Figure S3d are located in the same position, and can be overlapped and presented in Similar phenomena can be also Figure S3e. observed in Figure S4, the simulative Figure S4e can be originated from the ED patterns overlapping from Figure S4a, Figure S4b, Figure S4c and Figure S4d. Therefore, based on ED patterns simulation, both the stacking faults in monoclinic Li₂MnO₃-like structure and the rhombohedral LiTMO₂ structure probably exist inside the B and C domains, which will be confirmed and discussed by the HAADF/ABF STEM investigation in atomic resolution.



Figure S3. ED patterns and relative atomic structures of the monoclinic Li₂MnO₃-like structure projected along (a), $[011]_{mon}$, (b), $[\bar{3}\bar{2}3]_{mon}$ and (c), $[6\bar{1}3]_{mon}$ directions. ED patterns and relative atomic structures of the rhombohedral LiTMO₂ structure projected along (d), $[8\ 10\ 1]_{rh}$ directions. (e) Overlapped ED patterns by both the ED patterns in (a), (b), (c) and (d). The ED patterns circled with the red dotted lines are associated with the experimental B pattern in Figure 1b. Blue arrows in (a) and (e) show the characteristic ED patterns of Li₂MnO₃-like structure projected along $[011]_{mon}$, directions. Yellow arrows in e show the overlapped ED patterns from both ED patterns of Li₂MnO₃-like structure in (a),

(b), (c) and of LiTMO₂ structure in (d).



Figure S4. ED patterns and relative atomic structures of the monoclinic Li₂MnO₃-like structure projected along (**a**), $[0\overline{1} \ 1]_{mon}$, (**b**), $[613]_{mon}$ and (**c**), $[\overline{3}23]_{mon}$ directions. ED patterns and relative atomic structures of the rhombohedral LiTMO₂ structure projected along (**d**), $[\overline{108} \ 1]_{rh}$ direction. (**e**) Overlapped ED patterns by both the ED patterns in (**a**), (**b**), (**c**) and (**d**). The ED patterns circled with the red dotted lines are associated with the experimental C pattern in Figure 1b. Blue arrows in (**a**) and (**e**) show the characteristic ED patterns of Li₂MnO₃-like structure projected along $[0\overline{11}]_{mon}$ direction. Yellow arrows in (**e**) show the overlapped ED patterns from both ED patterns of Li₂MnO₃-like structure in (**a**), (**b**), (**c**) and of LiTMO₂ structure in (**d**).

The spot circled by red dotted lines in Figure S5 located in the same position as Pattern D in Figure 1b. It is obvious that this pattern is not only presented in the ED patterns from monoclinic LiTMO₂ Li₂MnO₃-like and rhombohedral structures, but also exist in the ED patterns from the possible existed spinel $LiMn_2O_4$ -like structure. However, except for the ED patterns marked along yellow arrows in Figure S5a, there are no ED patterns in the same position of Figure S5b, Figure S5c, Figure S5d and Figure S5e. This means the pattern D associated with the bright-contrasts regions in D domain (Figure 1g) is major contributed from the monoclinic Li₂MnO₃-like structure projected along $[00\overline{1}]_{mon}$ direction. The monoclinic Li₂MnO₃-like structure projected along $[\overline{3}1\overline{6}]_{mon}$ or $[\overline{3}\overline{1}\overline{6}]_{mon}$ directions, and LiTMO₂ structure projected along $[1\overline{1}\overline{1}]_{rh}$ direction also possibly exist and locate in the relative faint-

contrast regions inside this domain.

In previous studies, a little of spinel LiMn₂O₄-like structure is also found in these LLOs by the ED patterns along red arrows in Figure S5e, especially when these LLOs are investigated at the electrochemical delithiated states ⁹⁻¹¹. In this study, for the pristine ETTFs-LLOs, spinel LiMn₂O₄-like structure also probably exists, but the quantity may be extremely little and can be neglected. One of the reasons is that the ED patterns circled with yellow dotted lines have faint contrasts compared to their neighbor ones along the $[103]_{mon}$ -axis in Figure 1b, while the simulative ED patterns along red arrows of spinel LiMn₂O₄-like structure show the same contrast. In fact, there is no any bright contrast regions in the DF-TEM images if we chose the faint ED patterns, and also no spinel structures have been detected based on the synchrotron X-ray diffraction

research results on the same pristine material before 1,12,13 . Thus, for pristine ETTF-LLOs materials without electrochemical delithiation reaction, the spinel LiMn₂O₄-like structure observed by Boulineau et al in the discharged Li_{1.2}Mn_{0.61}Ni_{0.18}Mg_{0.01}O₂ material is extremely little in the ETTF-LLOs ⁹. Thus, the extra ED

patterns circled with yellow dotted lines in Figure 1b are probably attributed to the multiple reflections of monoclinic Li₂MnO₃-like or rhombohedral LiTMO₂ structures, which are often found in ED observation experiments, especially when there is much stacking faults.



Figure S5. ED patterns and relative atomic structures of the monoclinic Li_2MnO_3 -like structure projected along (a), $[00\overline{1}]_{mon}$, (b), $[\overline{3}1\overline{6}]_{mon}$ and (c), $[\overline{3}1\overline{6}]_{mon}$ directions. ED patterns and relative atomic structures of the rhombohedral LiTMO₂ structure projected along (d), $[1\overline{1}\overline{1}]_{rh}$ direction. ED patterns and relative atomic structures of the spinel LiMn₂O₄-like structure projected along (e), $[112]_s$ direction. (f) Overlapped ED patterns by both the ED patterns in (a), (b) and (c) of the Li₂MnO₃-like structure and (d) of the LiTMO₂ structure. The ED patterns circled with the red dotted lines are associated with the experimental B pattern in Figure 1b. Green arrows in (a) and (f) show the overlapped ED patterns from both ED patterns of Li₂MnO₃-like structure in (a), (b), (c) and of LiTMO₂ structure in (d). Red arrows in (e) show the characteristic ED patterns of spinel LiMn₂O₄-like structure projected along [112]_s direction.

Section III: Two structures distinguish and separation

Many researchers have noticed that the structure of these LLOs is complex, and the possible rhombohedral LiTMO₂ or monoclinic Li₂MnO₃ structures inside these materials are extremely difficult to be distinguished and separated^{9, 14-22}. Most of previous researches report that the LLOs are structured with the rhombohedral LiTMO₂ structure with $R\bar{3}m$ space group by average

structure investigation¹⁵⁻¹⁷. Some researchers think that these materials should be considered to be monoclinic Li_2MnO_3 structure with C2/m space group based on the local structure studies ²⁸. Until now, the debates on structure of these pristine LLOs have been lasted for more than 10 years ²³. The possible reasons and methods to distinguish these two structures unambiguously are described as follows.

(1) Rhombohedral LiTMO₂ and monoclinic Li₂MnO₃ structures have similar structures, both of them can be considered to be α -NaFeO₂ structure, because Li₂MnO₃ structure can also be described as Li[Li_{1/3}Mn_{2/3}]O₂ molecular formula (about 1/3 lithium and 2/3 manganese ions occupy the Fe-site in α -NaFeO₂ structure) ^{23, 26-28}. Thus, almost all of the x-ray diffraction peaks except for some weak peaks around 20°---25° of these two structures overlapped together. The structure of these LLOs can be explained with the Li₂MnO₃ structure, and

also the LiTMO₂ structure except for the few weak peaks around 20°---25°. In fact, two-structure coexistence models can also explain well the synchrotron X-ray diffraction of these LLOs ⁴. Therefore, the structure investigation on these LLOs is ambiguous if only the average structure analysis technique is used.

Local structure investigation on these (2)LLOs must be employed on distinguishing their actual structures. However, there are many challenges for local structure observation on these LLOs. The most important one is that the distances between TM layers and LiMn₂ layers in both LiTMO₂ and Li₂MnO₃ structures are extremely close to each other (~ 4.7 Å) 14 . That means two structures inside these LLOs cannot be distinguished the conventional TEM for observation techniques with relative low resolution on investigating local structure.



Figure S6. The characteristic atomic structures of (A), monoclinic Li₂MnO₃-like structure projected along (B), [100]_{mon},
(C), [110]_{mon}, (D), [110]_{mon}, (E), [110]_{mon} and (F), [110]_{mon} direction.



S7. The characteristic atomic structures of (a), rhombohedral LiTMO₂ structure projected along (b), $[1\overline{1}0]_{rh}$, and (c), $[\overline{1}10]_{rh}$ direction.

Based on more than four year ED, BF/DF-TEM and HAADF/ABF-STEM observation and computer simulation experiments, we found that the atomic-resolution images of Li₂MnO₃ structure projected along $[100]_{mon}$, $[\bar{1}\bar{1}0]_{mon}$, $[\bar{1}10]_{mon}$, $[110]_{mon}$ and $[1\bar{1}0]_{mon}$ directions can present its characteristic periodic atoms arrangement of transitional metal layer (Li-TM-TM type, Figure S6), while the atomic-resolution images of LiTMO₂ structure projected along $[1\bar{1}0]_{rh}$, and $[\bar{1}10]_{rh}$ directions show its characteristic atoms arrangement of transitional metal layer (TM-TM type Figure S7). Thus, two-structure coexistence essence can be definitely confirmed and separated if the characteristic atoms arrangements of rhombohedral LiTMO₂ structure and monoclinic Li₂MnO₃ structure both exist in the same crystal particle, especially for thin specimen. The characteristic atoms arrangements of two structures are concluded and described in Figure S8 with atomic structure models, simulative HAADF/ABF STEM images and line intensity profiles observation, respectively.



Figure S8. The characteristic difference between the rhombohedral LiTMO₂ structure and monoclinic Li₂MnO₃-like structure: (a) atomic structures models; (b) simulated HAADF/ABF STEM images based on fast-Fourier-transform multislice algorithm; (c) Line intensity profiles of the blue and red lines in Figure S8b, respectively. The green arrows and black lines in (a) show the major periodic difference of atomic arrangement between rhombohedral LiTMO₂ structure and monoclinic Li₂MnO₃-like structure. The distance between TM atoms in rhombohedral LiTMO₂ structure shows 0.14 nm, while the distance between TM atoms in monoclinic Li₂MnO₃-like structure show 0.14 nm and 0.28 nm, respectively.

Section IV: HAADF/ABF STEM simulation



Figure S9. Simulated HAADF/ABF STEM images and corresponding atomic structure models of the Li₂MnO₃-like structure projected along (a), $[011]_{mon}$, (b), $[6\overline{1}3]_{mon}$, (c), $[\overline{3}\overline{2}3]_{mon}$ crystallographic directions, and rhombohedral LiTMO₂ structure projected along (d), $[8\ 10\ 1]_{rh}$ crystallographic direction. (e), Overlapped simulative HAADF/ABF STEM images in (a), (b) and (c).



Figure S10. Simulated HAADF/ABF STEM images and corresponding atomic structure models of the Li₂MnO₃-like structure projected along (a), $[00\bar{1}]_{mon}$, (b), $[\bar{3}1\bar{6}]_{mon}$, (c), $[\bar{3}\bar{1}\bar{6}]_{mon}$ crystallographic directions, and rhombohedral LiTMO₂ structure projected along (d), $[1\bar{1}\bar{1}]_{rh}$ crystallographic direction. (e), Overlapped simulative HAADF/ABF STEM images in (a), (b) and (c).



Figure S11. (a), Simulated HAADF/ABF STEM images and (b), corresponding atomic structure models of spinel $LiMn_2O_4$ -like structure projected along [112]_s direction.

Section V: Domain boundary models of Li₂MnO₃-like structure.

The boundary models formed between domain A and D in Figure 3h is introduced firstly in this Domain boundary (DB) models are work. constructed by connecting two models of Li₂MnO₃ bulk with crystallographic orientation relationship observed by STEM. Figure S12 shows the orientation relationship of bulk-like models of the domain A and D used in this first-principle calculation. For the model of domain A, [103]_{mon}, $[\overline{1}10]_{mon}$ and $[\overline{3}\overline{1}0]_{mon}$ are selected as three lattice vectors (Figure S12 a-c). Lattice vectors of the domain D model are $[\overline{3}0\overline{1}]_{mon}$, $[00\overline{1}]_{mon}$ and $[0\overline{1}0]_{mon}$ (Figure S12 d-f). The lattice models of domain A and D are composed of 288 and 72 atoms, respectively. Table S1 summarizes geometry of the domain A and D lattice models, which are summarized together with lattice constants of Li₂MnO₃ obtained by our calculation and from the literature data of Ref. 7. Optimized lattice constants are overestimated with differences of about 1% in comparison with experimental data. This is within usual accuracy of GGA-type calculations. As shown in Table S1, there are

mismatches of lattice shapes between the domain A and D models. In order to merge two domain models into one DB model, the lattice shapes of the domain models need to be modified. First, all angles of the lattices are set to be at 90°. With regard to domain D, a supercell including $1 \times 2 \times$ 2, 288 atoms, cells are constructed. Lattice vector lengths of the domain D supercell in the b- and caxes are 10.128 and 17.254 Å, respectively. A structure model of DB is formed by connecting the unit cell of the domain A and the supercell of the domain D by the *ab*-planes. Totally, 576 atoms are contained in the DB model. We have constructed coherent DB models in the present study. For that purpose, the lengths of the *a*- and *b*-axes of the domain A (or D) model need to be matched with those of the domain D (or A) model. Before searching an optimal DB structure, we confirm which strained domain model is more favorable. The domain A (or D) model is deformed to have the same sizes of the a- and b-axes as the other domain model with keeping a constant cell volume. In addition to this deformation, a length of the *c*-axis is changed to find an optimal length Only atomic positions in the of the *c*-axis. deformed models are relaxed.



Figure S12. Crystallographic directions of domain A and D models. Lattice vectors of (a) the *a*-axis and (b) the *b*- and *c*-axes of the domain A model. (c) Projection of the domain A model from the *b*- and *c*-axes, respectively. Lattice vectors of (d) the *a*-axis and (e) the *b*- and *c*-axes of the domain D model. (f) Projection of the domain D model from the *b*- and *c*-axes, respectively.

	unit cell		domain A		domain D	
	Calc.	Exp.	domain A			
a (Å)	4.989	4.9292	14.326	([103] _{mon})	14.114	$([\overline{3}0\overline{1}]_{mon})$
b (Å)	8.627	8.5315	9.965	$([\overline{1}10]_{mon})$	5.064	$([00\overline{1}]_{mon})$
c (Å)	5.064	5.0251	17.275	$([\overline{3}\overline{1}0]_{mon})$	8.627	$([0\overline{1}0]_{mon})$
α (°)			89.918		90	
β (°)	109.439	109.337	89.768		90	
γ (°)			89.866		89.663	

Table S1. Lattice constants of the optimized Li₂MnO₃ unit cell and domain A and D models.

Figure S13 show excess strain energy ascribed to the deformation of a domain model. The strain energy is calculated by the equation (1).

(1) $\Delta E_{\text{strain}} = E_{\text{(strained domain)}} - E_{\text{(domain without strain)}}$ As shown in Figure S13, a combination of the strained domain A and the non-strained domain D models are more favorable than the opposite case. Coherent DB models are constructed on the basis of these results. According to STEM observation, DBs have transitional region. However, the transitional region is not taken into account in this work. The domain A and domain D models are directly connected with each other. In order to find an optimal DB structure, a termination plane to form a boundary, rigid translational shift parallel to the *ab*-plane (Δa and Δb) and a width of the DB (w) need to be determined other than crystallographic orientation relationship between two domain models. The values of Δa and Δb are fractional shifts normalized by the lattice constants of the DB model in the *a*- and *b*-axes, respectively. Regarding the domain A model, every atomic layer parallel to the *ab*-plane has stoichiometric content such as Li₂MnO₃ and is in a charge neutral state. In contrast, the domain D model has two possible termination planes parallel to the *ab*-plane. One is $(\text{LiO})^{-}$ plane and the other is $(\text{LiMnO}_2)^{+}$ plane. If one side of the domain D model is terminated by the $(\text{LiO})^{-}$ plane, the other side become the $(\text{LiMnO}_2)^{+}$ plane as shown in Figure S14a. In this case, two different boundaries coexist within a DB model. Moreover, a dipole moment in the domain model must affect electronic structures and energy states. In the case of termination by one of the $(\text{LiMnO}_2)^{+}$ plane as shown in Figure S14b, both sides of termination have the same configuration and a dipole moment in this model is canceled out. For simple simulations, this non-polar termination is applied to the domain D model.

We have constructed series of DB models with varying values of Δa , Δb and w, and DB energies (ΔE_{DB}) are evaluated to determine the most stable configuration. ΔE_{DB} is calculated by the following equation (2),

$$\Delta E_{\rm DB} = \{E_{\rm DB} - (E_{\rm domain\,A} + E_{\rm domain\,D})\} / 2S_{\rm DB}$$
(2)

where E_{DB} , $E_{\text{domain A}}$ and $E_{\text{domain D}}$ are calculated total energy of a DB model, a bulk-like domain A and D models, respectively. S_{DB} is a cross sectional area of the DB in the boundary model. ΔE_{DB} is defined as an excess energy to form DBs.



Figure S13. Dependence of strain energy of domain A and D models on changes in a lattice vector of the *c*-axis.



Figure S14 a polarized and b non-polarized termination of domain D model.

As shown in Figure 3, our STEM observation viewing from $[\bar{1}10]_{mon}$ of domain A or $[00\bar{1}]_{mon}$ of domain D has revealed that cation layers of domain A and D are aligned. Figure S15 shows atomic layers of the domain A and D models on the termination planes. Spacing between the cation

layers is a/6. The domain D model has iterative cation layers of Li and Mn in the direction of *a*axis. Both of the domain A and D model have a periodicity of b/2 in the direction of *b*-axis. Due to such periodicity, parameters of $\Delta a = 0$ or 1/6 and 0 $\leq \Delta b < 0.5$ as rigid translation shifts are enough to survey relative positions between domain A and D models parallel to the *ab*-palne. Figure S16 shows dependence of ΔE_{DB} of the DB models with $\Delta a = 0$ or 1/6 on the parameters of Δb and *w*. The series of calculations reveal that the DB models with parameters of (Δa , Δb , *w*) = (1/6, 0.3, 1.5) and (0, 0.2, 1.5) have the lowest ΔE_{DB} of 0.421 and 0.423 J/m², respectively. One cation layer shift in the *a*axis hardly affects the energy states of the DB models. It should be noted that structure optimization of the DB model with small shift of Δb from the most stable models results in similar configuration and energy states. For the further analysis of Li⁺ migration nearby the DB, we have adopted the configuration of (Δa , Δb , w) = (1/6, 0.3, 1.5). The DB model is illustrated in the Figure 4a of the main text.



Figure S15. An atomic layer parallel to the DB of (a) domain A model, (b) domain D model and (c) domain D model



Figure S16. Plots of the DB formation energy to translations of the *b*-axis. $(\Delta a, \Delta b, w) = (1/6, 0.3, 1.5)$ and (0, 0.2, 1.5)have the lowest ΔE_{DB} of 0.421 and 0.423 J/m²

Section VI: Li⁺ vacancy migration mechanism.

We have computationally investigated Li⁺ migration behavior via vacancy mechanism in Li₂MnO₃. As mentioned in the main text, we use the nudged elastic band (NEB) method. For a transition state search based on the NEB method, initial and final atomic configurations in a process of Li⁺ migration are needed as starting models for the search. In order to create an initial state of Li^+ migration, one Li atom, not only Li⁺ but also an electron, is removed from the perfect model. Therefore, the models including one Li⁺ vacancy still keep neutral charge states. This situation is similar to delithiation of Li₂MnO₃ cathode. After introduction of a vacancy in a model, all atomic positions are optimized under the same calculation conditions as the case of perfect models. A model of a final state of a migration process is separately prepared with the same manners. Details of the NEB method are found in Ref. 8.

We show energy profiles of long-range diffusion paths in Figure 4 and 5. In the case of $\text{Li} \perp \text{DB}$ in Figure 4c, the paths are composed of 3, 4, and 8 elementary processes of migration in the domain A, the domain D and the DB models, respectively. Each elementary process is separately determined by the NEB method. It should be noted that a migrating Li^+ ion is switched at every diffusion process in the case of the vacancy mechanism. We take the Li⁺ migration in the domain A model as an example and explain detail in Figure S17. At the initial state of the first process, an vacancy is located at Li(1) (Figure S17a). A Li⁺ ion at a neighboring Li(2) site to the Li(1) site moves to the vacancy position (Figure S17b). In the final states of the first process, the vacancy is situated at the Li(2) site (Figure S17c). In the second process, the positions of a Li⁺ ion and a vacancy are exchanged between the Li(2) and Li(3) sites (Figure S17d and e). Migrating distances of Li^+ ions in every process are summed up and energy profiles are indicated as shown in Figure S17e. Energy profiles of long-range diffusion of $Li \perp DB$ and Li//DB shown in Figure 4e, 4f, 5h and 5i are plotted by this manner.

From the NEB calculations for the bulk-like domain D model without strain, energy barriers against Li⁺ ion migration are 0.83 eV and 0.61 eV for paths of 4h \rightarrow 4h and 2e \rightarrow 4h, respectively. These results are comparable to the literature data, 0.84 eV and 0.61 eV ²⁹.



Figure S17. Continuous Li^+ migration processes by vacancy mechanism in bulk-like domain A model. (a) Initially a vacancy is located at the Li(1) sites. (b) The neighboring Li^+ ion at the Li(2) site migrates to the Li(1) site. (c) A final state of Li^+ migration from the Li(2) to Li(1) sites. (d) Subsequently, the Li^+ ion at Li(3) site migrates to the Li(2) site. (e) A final state of Li^+ migration from the Li(3) to Li(2) sites. (f) Energy profiles of the continuous the two processes of Li^+ migration.

Section VII: Ni-segregated domain boundary model.

Before analyses regarding influence by Ni segregation at the domain boundaries on Li^+ migration, the stable position of Ni in the monoclinic Li_2MnO_3 domains are determined.

Assumed that behavior of Ni substitution in Li_2MnO_3 is analogous to that in $LiNi_{0.42}Mn_{0.42}Co_{0.16}O_2$ layer-type cathode, we focus on Ni substitution for Li sites. We assume that a Li^+ vacancy is additionally formed to maintain a condition of charge neutrality in the

system when a Li⁺ ion is replaced by a Ni²⁺ ion. Firstly, formation energies of a defect pair of substituted Ni and Li vacancy represented as $(Ni_{Li}^{\bullet} + V'_{Li})^x$ by the Kröger-Vink notation are calculated in bulk Li₂MnO₃. A formation energy of $(Ni_{Li}^{\bullet} + V'_{Li})^x$ is calculate by the following equation (3) ³⁰,

$$\begin{split} \Delta E(\mathrm{Ni}_{Li}^{\bullet} + \mathrm{V}_{\mathrm{Li}}') \\ &= E_{\mathrm{defect}}(\mathrm{Ni}_{Li}^{\bullet} + \mathrm{V}_{\mathrm{Li}}') - E_{\mathrm{perfect}} + 2\mu_{\mathrm{Li}} - \mu_{\mathrm{Ni}} \\ (3) \end{split}$$

where E_{defect} (Ni[•]_{Li} + V'_{Li}) and $E_{perfect}$ are total energies of the defective model containing the defect pair of (Ni[•]_{Li} + V'_{Li})^x and the perfect model, respectively. μ_i is a chemical potentials of an element of *i*. The chemical potential is determined under a condition of phase equilibrium among coexisting compounds. In the present study, a phase equilibrium condition among Li₂MnO₃, Li₂O and NiO is taken into account. Under this condition, chemical potentials satisfy the following relationship,

$$E(\text{Li}_{2}\text{MnO}_{3}) = 2\mu_{\text{Li}} + \mu_{\text{Mn}} + 3\mu_{0}$$
$$E(\text{Li}_{2}\text{O}) = 2\mu_{\text{Li}} + \mu_{0}$$
$$E(\text{NiO}) = \mu_{\text{Ni}} + \mu_{0}$$

where E(X) is a total energy of a compound X calculated by a DFT calculation. For calculations of Li₂O and NiO primitive cells, we use k-point sampling meshes of $5 \times 5 \times 5$ and $7 \times 7 \times 7$, respectively. Other calculation conditions of structure optimization for Li2O and NiO are same as the case of Li₂MnO₃. A Ni ion is substituted for three types of Li sites, 2b in the LiMn₂-layers and 2c and 4h in the Li-layers. A vacancy is introduced at a neighboring Li site from the Ni position. Results of formation energies of $(Ni_{Li}^{\bullet} + V'_{Li})^x$ in the domain A model are summarized in Table S2. Ni_{Li}^{\bullet} prefers to be located at the 2b site. Li⁺ vacancy formation at the 2b sites in the Li-layer is energetically unfavorable.

Table S2. Calculated formation energies of in $(Ni_{Li}^{\bullet} + V'_{Li})^x$ in Li₂MnO₃. Plural data in a column are obtained from calculations with different configurations of Ni and Li vacancy

Sites		
Ni^ullet_{Li}	V'_{Li}	Formation energy (eV)
2b	2c	1.521
2b	4h	1.525
2c	2b	1.831
2c	4h	1.630, 1.632, 1.637
4h	2b	1.782
4h	2c	1.572, 1.606
4h	4h	1.567, 1.633

According to the energetical hierarchy of Ni substitution sites in the bulk model, Ni is substituted for the Li 2b sites in the LiMn₂-layer of the DB models. Simultaneously, a vacancy is introduced at Li site neighboring Ni in the Li-layer. Before investigating the influence of Ni substitution on Li^+ migration, Ni segregation near DB indicated in Figure 5a are studied using DFT calculations. Figure S17 illustrates DB models

with $(Ni_{Li}^{\bullet} + V_{Li}')^x$ in the domain interior and nearby the DB. Formation energies of $(Ni_{Li}^{\bullet} + V_{Li}')^x$ are calculated to be 1.479 eV and 0.653 eV in the domain interior and nearby the DB, respectively. Ni substitution energy nearby the DB is much easier rather than in the bulk region. This result support Ni segregation at domain boundaries observed by EDS-STEM.



Figure S18. Ni substitution accompanied by a Li vacancy (a) in the bulk-like region and (b) near the DB.

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