Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

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First principles study on Li metallic phase nucleation at grain boundaries in lithium lanthanum titanium oxide (LLTO) solid electrolyte

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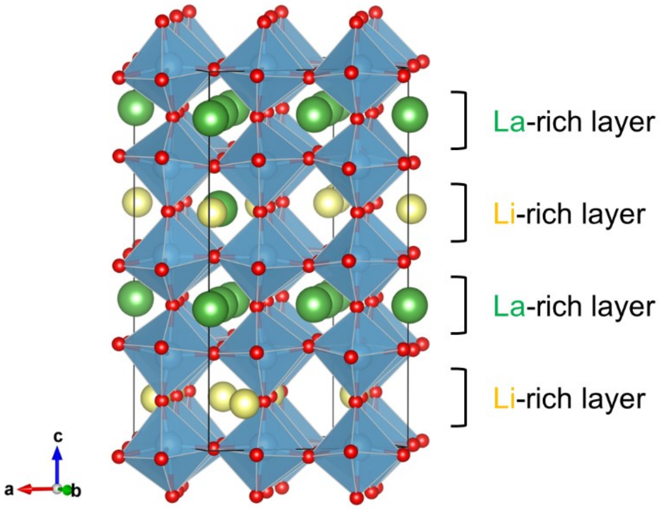

Figure S1. Atomic structure of LLTO where Li-rich and La-rich layers are alternating.

Grain boundary types	Grain boundary formation energy (J m^{-2})
∑3(111)	0.584
∑5(210)	1.613
∑5(001)	1.364

Table S1. Grain boundary formation energy of LLTO (x = 0.1167) with different orientations.

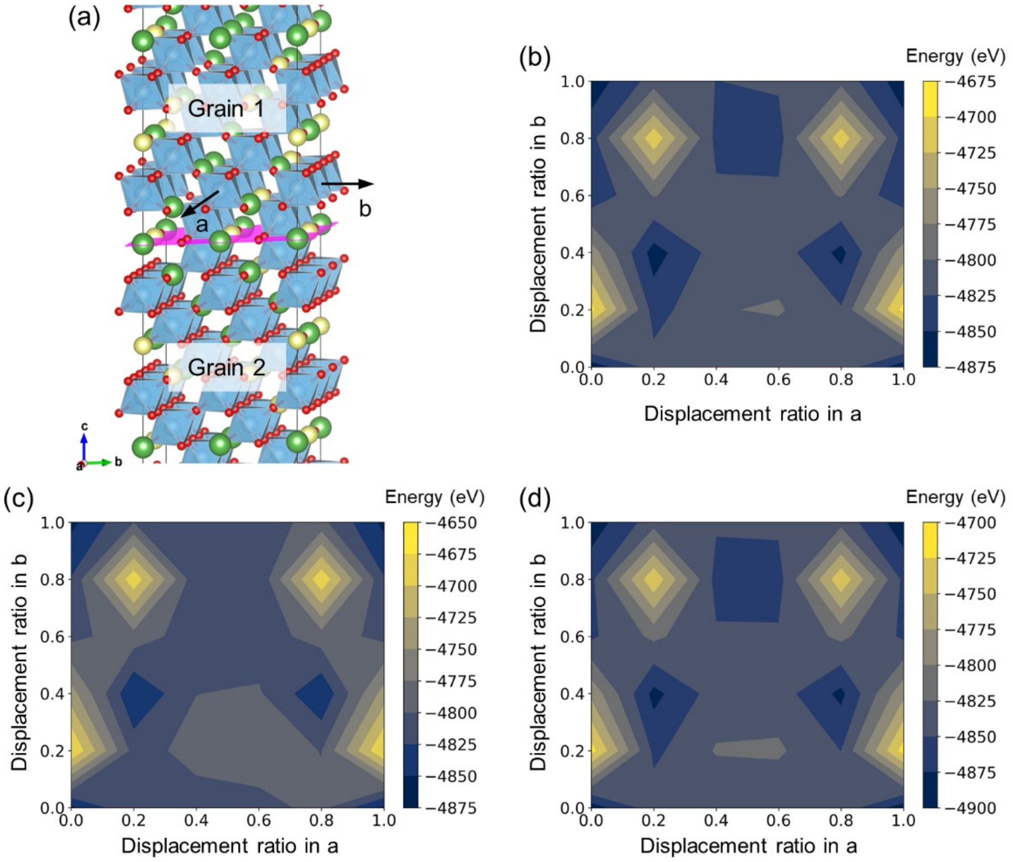

Figure S2. (a) Schematic of rigid-body translation between two different grains. The potential energy surfaces of LLTO ∑3(111) GB at (b) x = 0.1167, (c) 0.0417, and (d) 0.1667. Navy regions identify energetically stable regions.

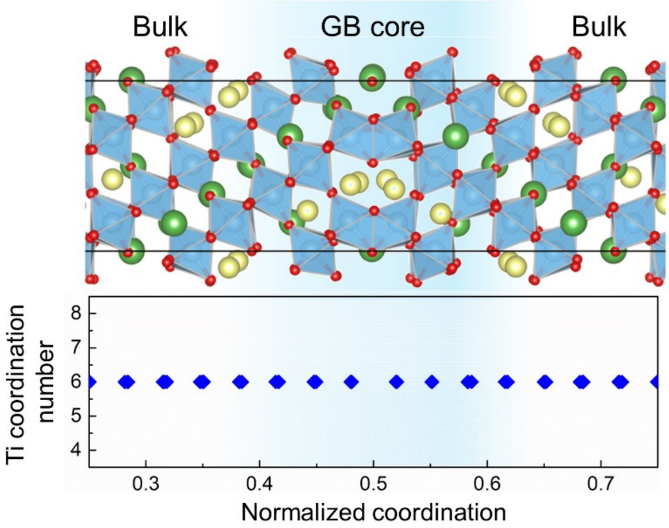

Figure S3. Ti coordination number for ∑3(111) boundary at x = 0.1167 as a function of normalized coordination normal to the GB plane.

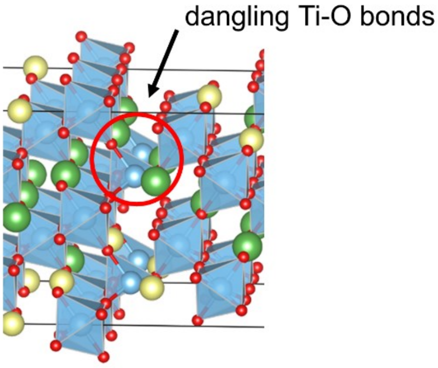

Figure S4. The dangling Ti-O bonds in the GB core of ∑3(111) boundary at x = 0.1167.

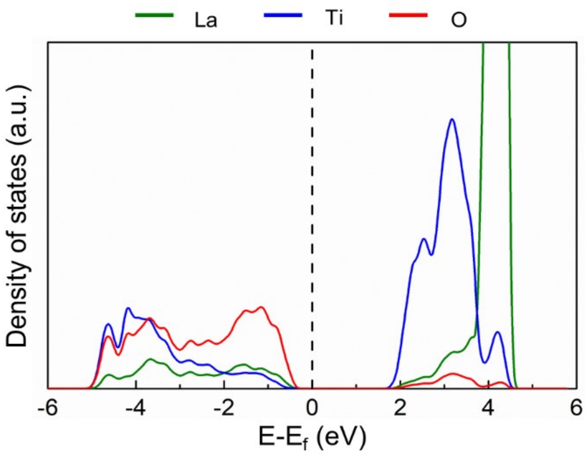

Figure S5. Combined graphs of partial density of states of La 5d-electron (green), Ti 3d-electron (blue), and O 2p-electron (red) for bulk LLTO.

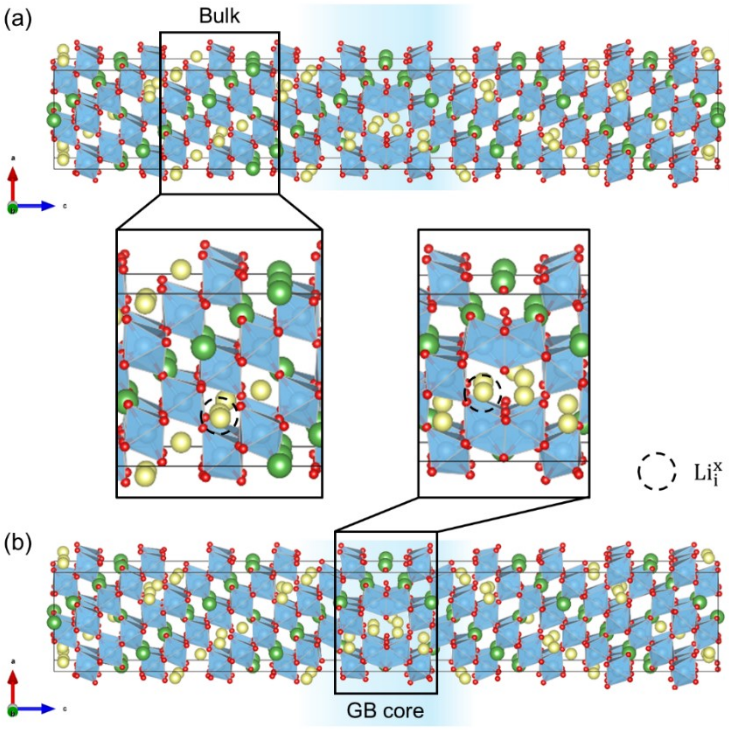

Figure S6. Li interstitial defect in (a) bulk-like and (b) GB core regions of stoichiometric GB.

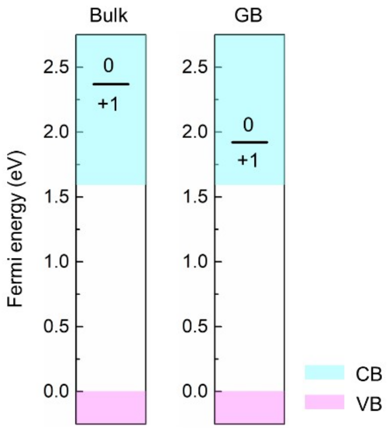

Figure S7. The charge transition levels are depicted for the Li interstitial defect in bulk-like (left) and GB core regions (right) of stoichiometric GB. The valence band (VB) and conduction band (CB) edges are shown in shaded areas.

In the LIBs, there is an externally applied potential that affects the chemical potential of Li.[1] Indeed, the chemical potential of Li differs depending on the internal location of the LIB, the electrochemical property of SE would also vary depending on the internal location of LIBs.[2]

To evaluate the effects of externally applied potential for the charge carrier properties of LLTO, the chemical potential of Li in the cathode ($\mu^{Cathode}_{Li}$) is eV$_{cell}$ lower than that in the anode (μ^{Anode}_{Li}), $\mu^{Cathode}_{Li} = \mu^{Anode}_{Li} - eV_{cell}$, where e and V$_{cell}$ are the electron charge and the open-circuit voltage, respectively. Here, we applied the averaged open-circuit voltage of $LiCoO_2$ cathode (~4.2 V) relative to the Li metal.[3] Owing to the space-charge layer, SE near the electrode has a similar chemical potential as the Li chemical potential of the anode or cathode and converges to the Li chemical potential of the bulk SE as it moves away from the electrode.[1,2] Accordingly, the near anode and cathode Li chemical potential, corresponding to the upper and lower limit, respectively, were considered for examining the charge carrier feature of LLTO.

	Near anode (μ_{Li} = -1.91 eV)		Near cathode (μ_{Li} = -6.11 eV)	
	neutral	+1	neutral	+1
Bulk	-1.56	-3.93	2.64	0.27
GB	-1.58	-3.50	2.62	0.70

Table S2. The Li interstitial defect formation energy in two different charge states (neutral and +1) for bulk-like and GB core regions in the stoichiometric GB structure of LLTO. The defect formation energy computed based on the near anode and cathode Li chemical potential is corresponding to the upper and lower limit, respectively, of defect formation energy.

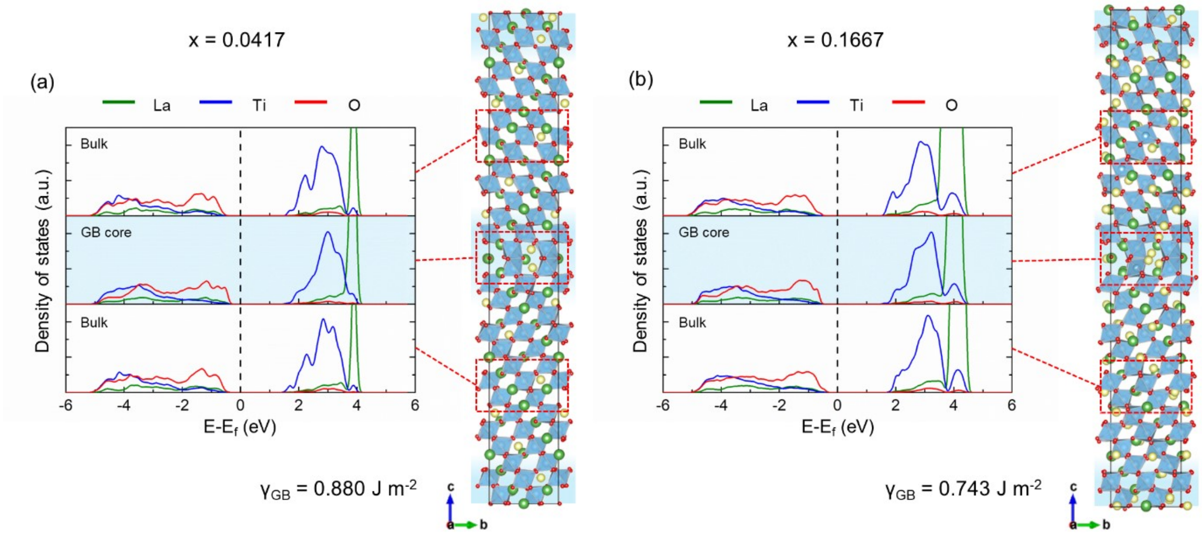

Figure S8. Combined graphs of regional-decomposed partial density of states of La 5d-electron (green), Ti 3d-electron (blue), and O 2p-electron (red) in each bulk-like (upper and lower) and the GB core (middle) region for (a) x = 0.0417 and (b) 0.1667 of LLTO; (red dashed rectangle on right panel) corresponding regions in the stoichiometric GB structure.

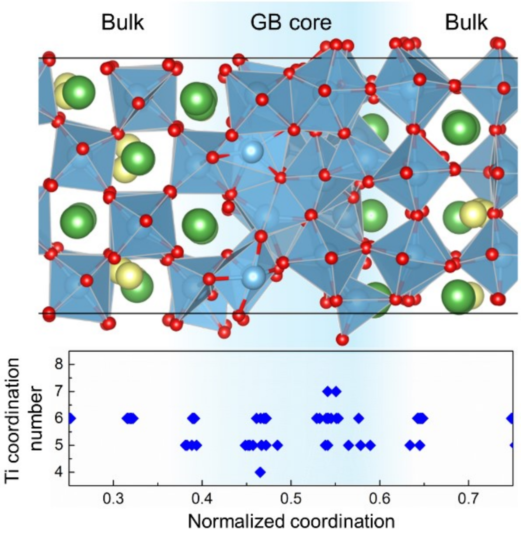

Figure S9. Ti coordination number for GB in-complex as a function of normalized coordination normal to the GB plane.

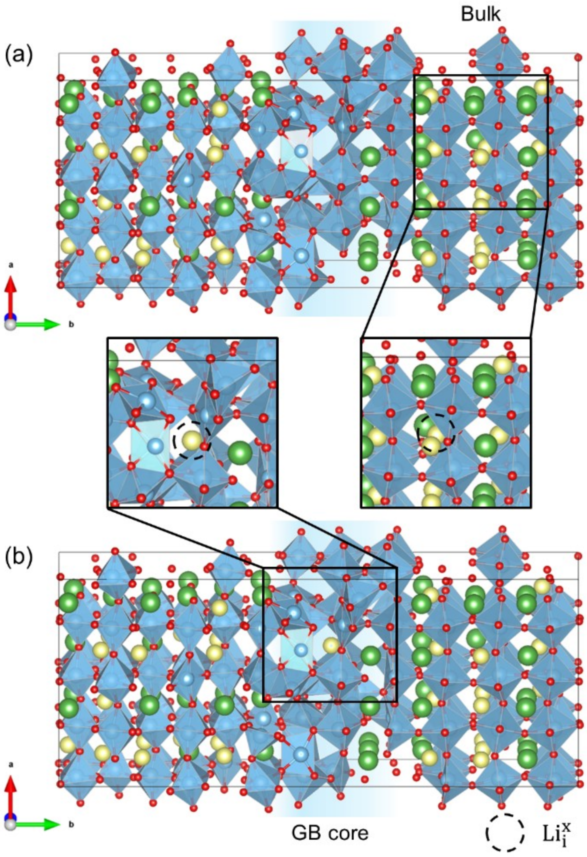

Figure S10. Li interstitial defect in (a) bulk-like and (b) GB core regions of A-site deficient GB.

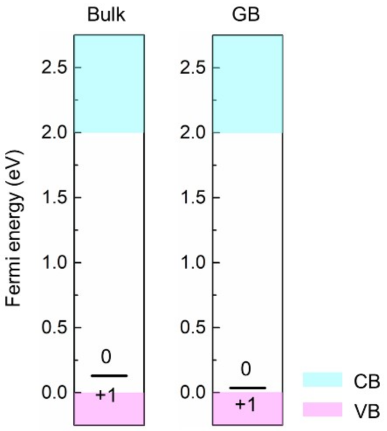

Figure S11. The charge transition levels are depicted for the Li interstitial defect in bulk-like (left) and GB core regions (right) of A-site deficient GB. The valence band (VB) and conduction band (CB) edges are shown in shaded areas.

	Near anode (μ_{Li} = -1.91 eV)		Near cathode (μ_{Li} = -6.11 eV)	
	neutral	+1	neutral	+1
Bulk	-4.43	-4.56	-0.23	-0.36
GB	-3.40	-3.44	0.80	0.76

Table S3. The Li interstitial defect formation energy in two different charge states (neutral and +1) for bulk-like and GB core regions in the A-site deficient GB structure of LLTO. The defect formation energy computed based on the near anode and cathode Li chemical potential is corresponding to the upper and lower limit, respectively, of defect formation energy.

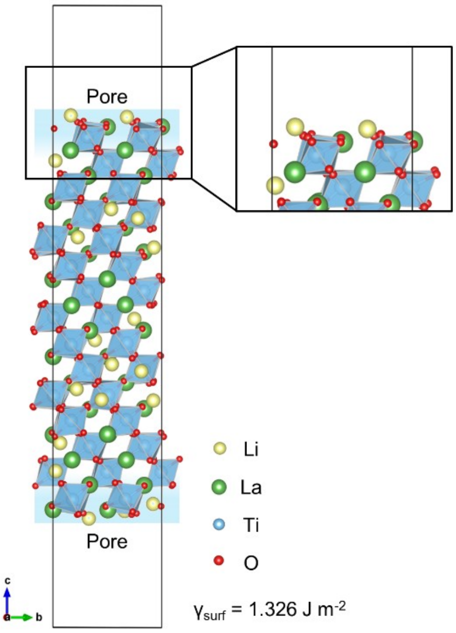

Figure S12. The atomic structure and surface energy of intergranular pore space ((111) surface) for LLTO. The pore region is highlighted as the blue shaded region. The Li, La, Ti, and O atoms are shown in yellow, green, blue, and red sphere, respectively.

To define the chemical potentials of the element in LLTO, four equations relating the DFT total energies with the four chemical potentials (μ_{Li}, μ_{La}, μ_{Ti}, and μ_{O}) are needed.[4] To reflect the oxidizing and experimental synthesis conditions of LLTO, we consider the composition of LLTO, La_2O_3, Li_2O, and O_2. Table S2 shows the chemical potentials of each element which is used in calculating the surface energy of the nonstoichiometric surface (Figure S12).

Elements	μ_i (eV)
Li	-4.949
La	-14.405
Ti	-18.658
O	-4.364

Table S4. Chemical potentials of Li, La, Ti, and O in oxidizing condition.

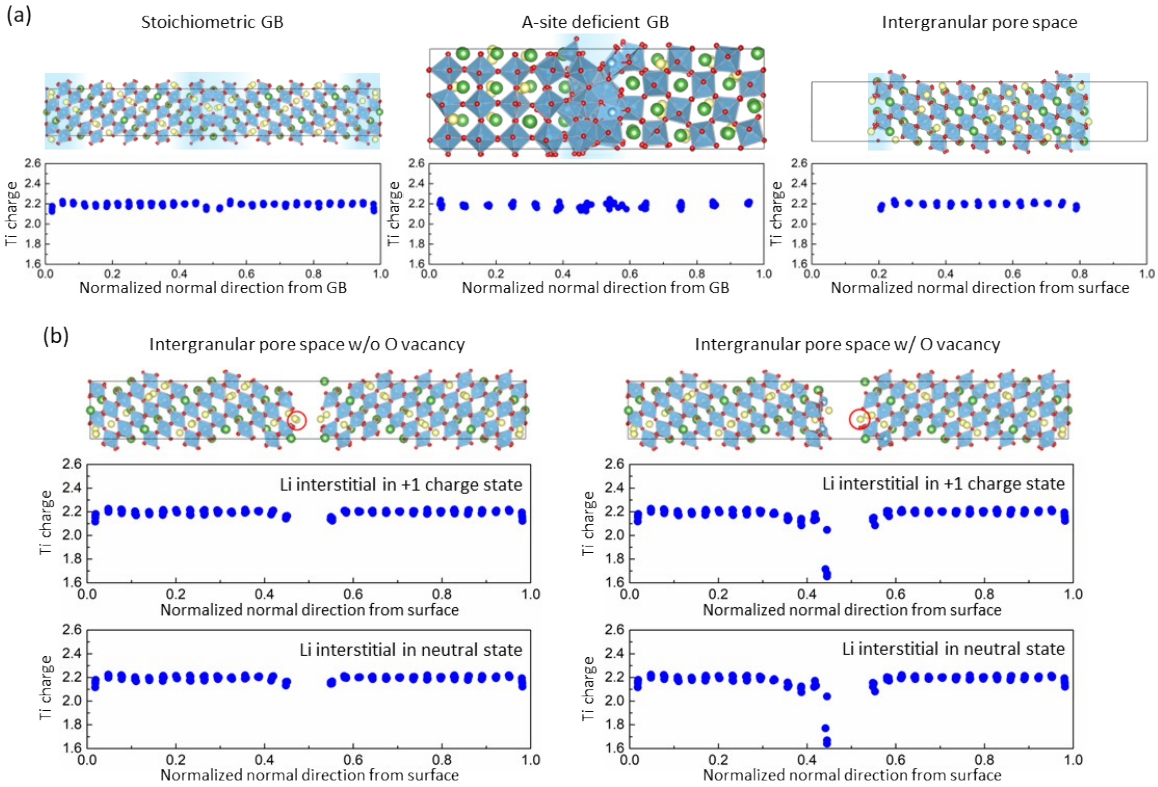

Figure S13. (a) Ti charge state for three representative intergranular microstructures (left: stoichiometric GB, middle: A-site deficient GB, and right: intergranular pore space). (b) Ti charge state when the interstitial Li-ion is in a neutral (lower) and +1 (upper) charge state in two different systems (left: intergranular pore space without O vacancy and right: intergranular pore space with O vacancy).

Reference

1. A. C. Luntz, J. Voss and K. Reuter, *Chem. Mater.*, 2015, **6**, 4599-4604.
2. S. Stegmaier, J. Voss, K. Reuter and A. C. Luntz, *Chem. Mater.*, 2017, **29**, 4330-4340.
3. K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, 1980, **15**, 783-789.
4. P. Canepa, J. A. Dawson, G. S. Gautam, J. M. Statham, S. C. Parker and M. S. Islam, *Chem. Mater.*, 2018, **30**, 3019-3027.