—Supporting Information—

H_2O and CO_2 surface contamination of the lithium garnet $Li_7La_3Zr_2O_{12}$ solid electrolyte

Yuheng Li,[†] Asmee M. Prabhu,[‡] Tej S. Choksi,[*,‡] and Pieremanuele Canepa[*,†,¶]

†*Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, 117575, Singapore*

‡*School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore*

¶*Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, 117585, Singapore*

E-mail: tej.choksi@ntu.edu.sg; pcanepa@nus.edu.sg

Contents

S1   Benchmark Tests on Dispersion Corrections

Table S1: Benchmark tests for dispersion corrections. Experimental and calculated lattice parameters a and c (in Å) for bulk tetragonal $Li_7La_3Zr_2O_{12}$. Mean absolute error (MAE, in Å) of the calculated lattice parameters. Surface energy (γ, in J m^{-2}) for stoichiometric Zr-terminated (110) surface, calculated using slab models re-scaled with the bulk lattice parameters.

Method	a	c	MAE	γ
Experiment[a]	13.134	12.663	—	—
PBE[b]	13.204	12.704	0.060	1.52
PBE	13.228	12.708	0.078	1.46
PBE+D3	13.107	12.587	0.043	1.91
PBE+D3-BJ	13.082	12.586	0.060	1.96

[a] Data from Awaka et al. [1]
[b] Data from Canepa et al. [2]

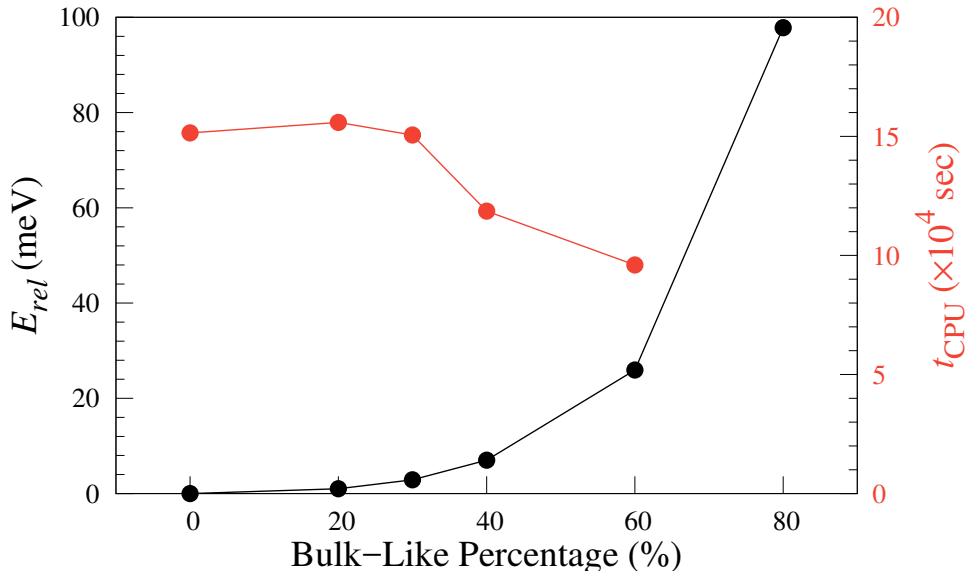# S2   Convergence Tests on Bulk-Like Percentage in Slab

Figure S1: Change of total energy for the slab model and CPU time as functions of bulk-like percentage. Total energy for the slab calculated with zero percent bulk-like region (all atomic positions were relaxed) is used as reference. The CPU time parameter is used to identify reasonable consumption of computational resources for the large 248-atom system.
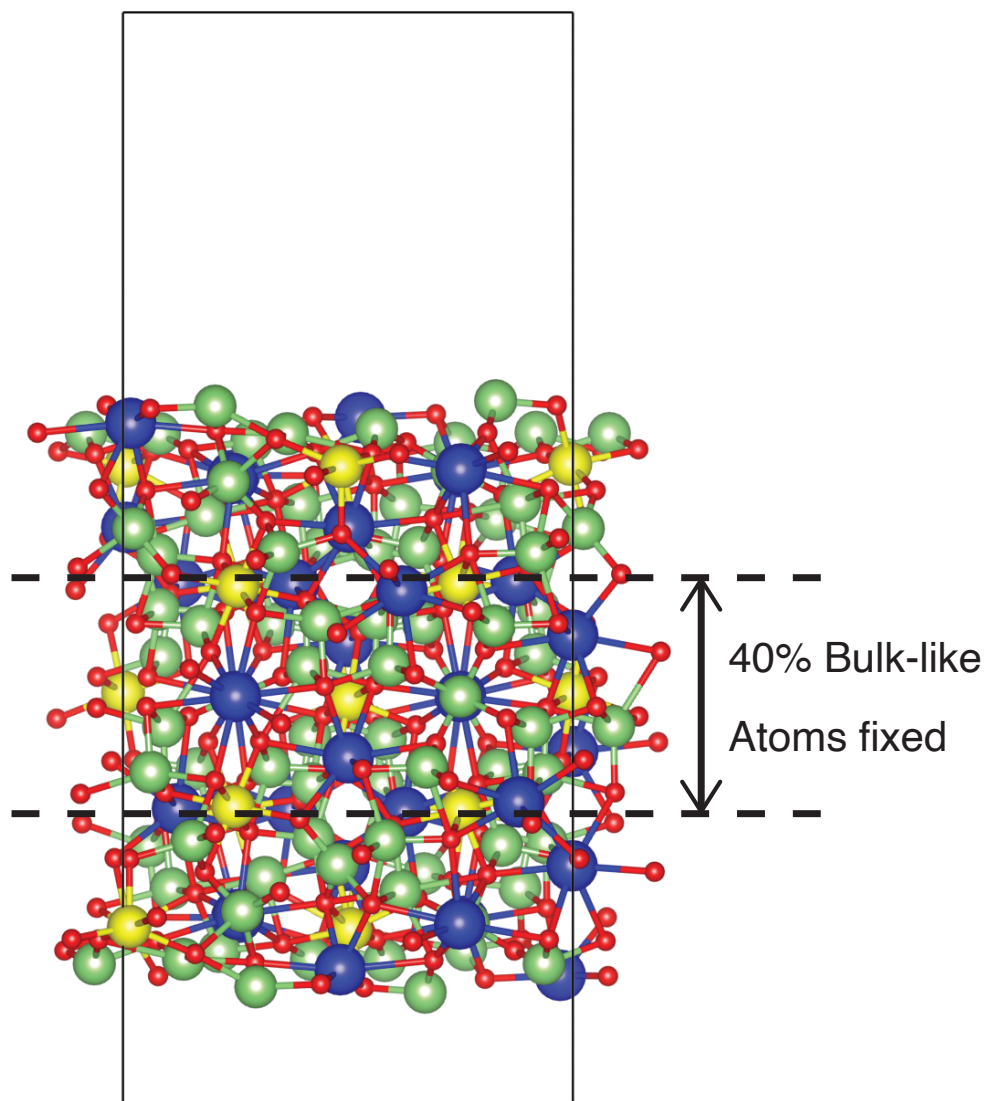
S3   Unit Cell of Slab Model

Figure S2: Side view of the complete slab unit cell for the (010) Li-terminated off-stochiometry surface of $Li_7La_3Zr_2O_{12}$. The dashed lines and double-headed arrow show the center bulk-like region (40%), where the atomic positions are fixed during structural optimization.

S4   Tests on Single-Point Energy Cutoff

Table S2: Adsorption energy (ΔE_{ads}, in eV) from PBE (without D3-BJ) calculations, where optimizations were done with an energy cutoff of 440 eV, and single-point calculations were done with different energy cutoffs of 440 eV and 520 eV.

No./Molecule	Model Name	ΔE_{ads} @ 440 eV	ΔE_{ads} @ 520 eV
single H_2O	Li[3O]	−1.02	−1.02
	Li[2O]	−0.97	−0.96
multiple H_2O	2/5 ML	−0.99	−0.99
	3/5 ML	−0.91	−0.90
	4/5 ML	−0.93	−0.93
	5/5 ML	−0.93	−0.93
	6/5 ML	−0.91	−0.91
single CO_2	O[LiLaZr]	−1.87	−1.86

S5   Metal Sites' Local Environment and H_2O Dissociation

Table S3: Distance (in Å) between water adsorption sites and their neighboring O atoms. Site is the adsorption site listed in the order of adsorption energy from more negative to more positive. ΔE_{ads} informs adsorption energy for the site. LiOH indicates whether the adsorbed H_2O molecule dissociates and promotes LiOH formation. Distance lists O–Site distance before adsorption for all O atoms bonded to the site. ∗ denotes the surface O atom that forms bond with the dissociated proton from H_2O.

Site	ΔE_{ads}	LiOH	Distance
Li[3O]	−1.21	Yes	1.91, 1.92*, 2.11
Li[2O]	−1.14	No	1.83, 1.84
La[5O]	−0.85	No	2.20, 2.30, 2.32, 2.47, 2.74
La[6O]	−0.80	No	2.34, 2.38, 2.41, 2.47, 2.49, 2.73
Li[3O]	−0.65	No	1.97, 2.01, 2.08

S6 Forced Dissociation of H$_2$O at High Coverage

Table S4: Water adsorption energy (in eV/molecule) at increasing number of molecules (ML). Site is the adsorption site. $\delta\Delta E_{ads}$ informs the change of ΔE_{ads} upon the addition of a H$_2$O molecule. All water molecules were forced to dissociate before relaxation. In parallel to Table 1 in the main text, the number of dissociated water molecule (H$_2$O) after relaxation is indicated, and LiOH indicates whether the addition of a new H$_2$O molecule promotes LiOH formation. * denotes that a previously dissociated H$_2$O has become intact.

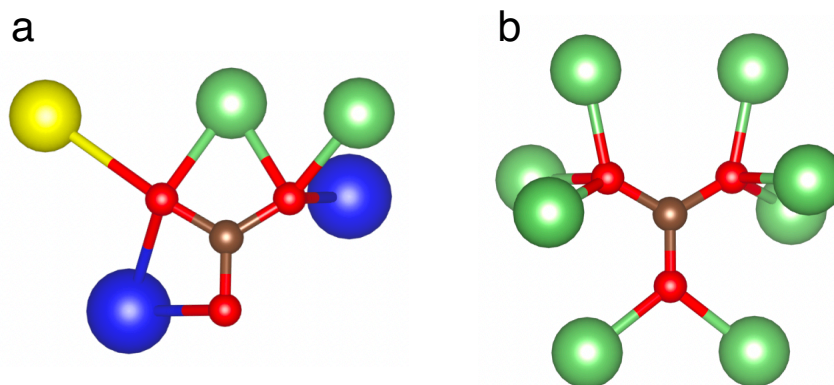| ML	Site	ΔE_{ads}	$\delta\Delta E_{ads}$	H$_2$O	LiOH
1/5	Li[3O]	−1.21	—	1	Yes
2/5	Li[2O]	−1.24	−0.03	2	Yes
3/5	La[5O]	−1.13	+0.11	2	No
4/5	La[6O]	−1.06	+0.07	2*	Yes
5/5	Li[3O]	−1.10	−0.04	3	Yes
6/5	Li[3O]	−1.13	−0.03	3*	Yes

S7 Geometry of Surface Carbonates

Figure S3: Structure unit of CO$_3^{2-}$ and bonded metal ions for (a) carbonate formed on the most favorable O[LiLaZr] site upon CO$_2$ adsorption and (b) bulk Li$_2$CO$_3$ from Ref. 3 (ICSD 66941).
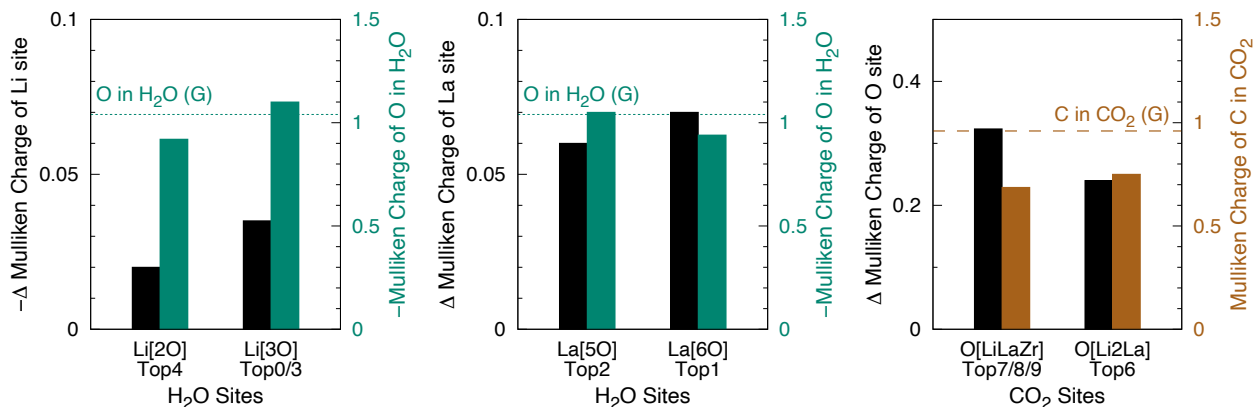
S8 Post-Adsorption Mulliken Charge

Figure S4: Change of Mulliken charge for all adsorption sites and Mulliken charge of O in H₂O and C in CO₂ after adsorption. The horizontal dashed lines mark Mulliken charge of gas-phase H₂O and CO₂.

References

(1) Awaka, J.; Kijima, N.; Hayakawa, H.; Akimoto, J. Synthesis and Structure Analysis of Tetragonal $Li_7La_3Zr_2O_{12}$ with the Garnet-Related Type Structure. *Journal of Solid State Chemistry* **2009**, *182*, 2046–2052.

(2) Canepa, P.; Dawson, J. A.; Sai Gautam, G.; Statham, J. M.; Parker, S. C.; Islam, M. S. Particle Morphology and Lithium Segregation to Surfaces of the $Li_7La_3Zr_2O_{12}$ Solid Electrolyte. *Chem. Mater.* **2018**, *30*, 3019–3027.

(3) Idemoto, Y.; Richardson, J. W.; Koura, N.; Kohara, S.; Loong, C.-K. Crystal Structure of $(Li_xK_{(1-x)}2CO_3$ (x = 0, 0.43, 0.5, 0.62, 1) by Neutron Powder Diffraction Analysis. *Journal of Physics and Chemistry of Solids* **1998**, *59*, 363–376.