Supporting Information

The Critical Role of Oxygen-Evolution Kinetics in Electrochemical Stability of Oxide Superionic Conductors

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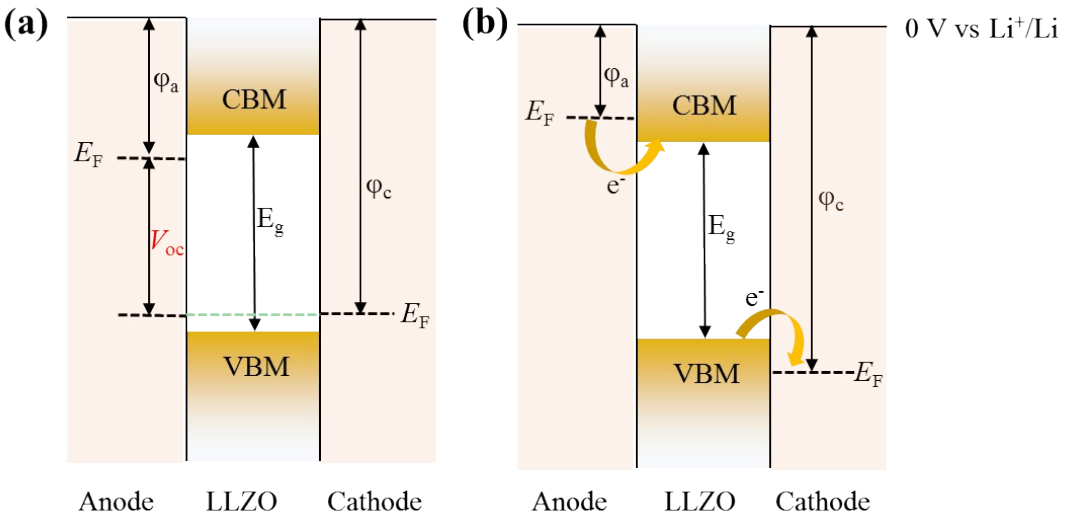


Figure S1. (a) Electrodes electrochemical potentials versus the electrochemical window and bandgap of the LLZO electrolyte; (b)The process of electron-transfer between electrodes and LLZO electrolyte.

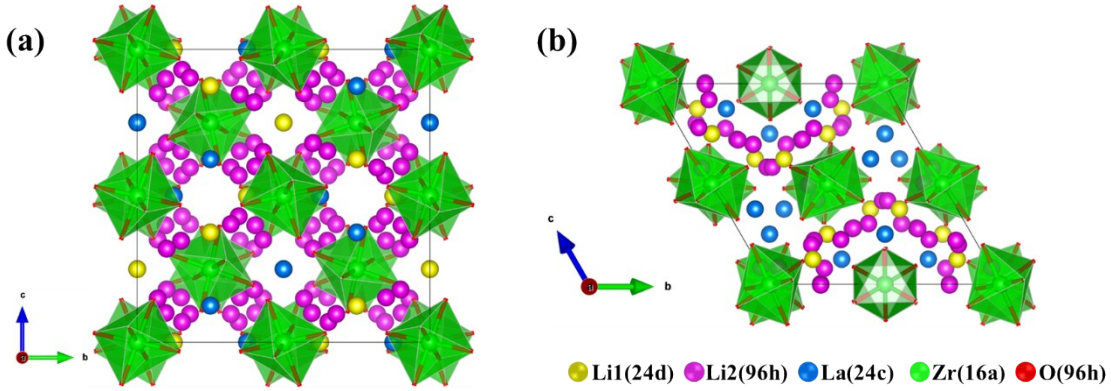


Figure S2 The unit cell (a) and primitive cell (b) of LLZO with full Li ions occupation.

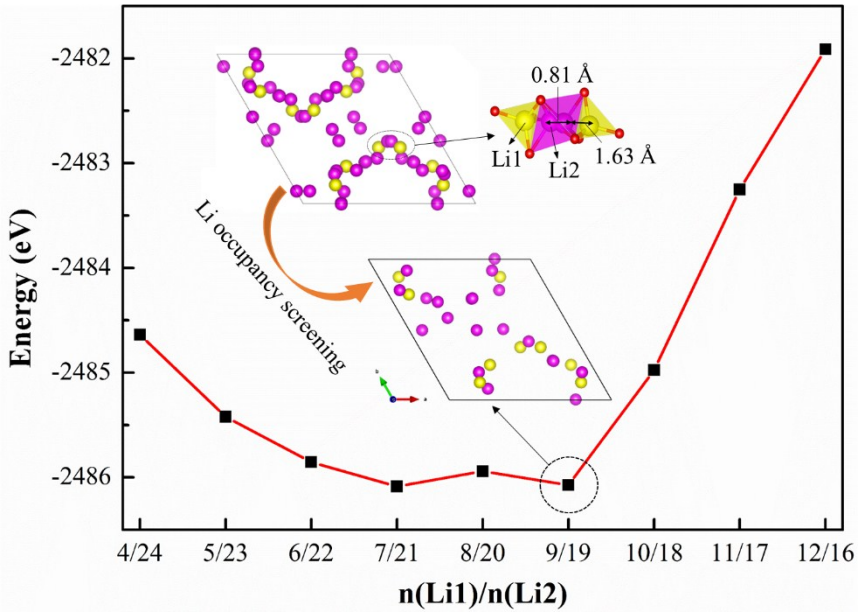
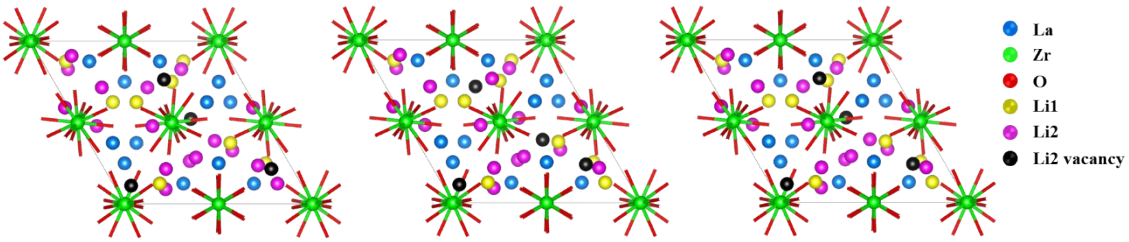


Figure S3 The energy of each Li1/Li2 ratio in the primitive cell obtained by supercell program.



(a) (b) (c)

Figure S4. The first three structures with the lowest free energy of LLZO primitive cells screened by supercell.

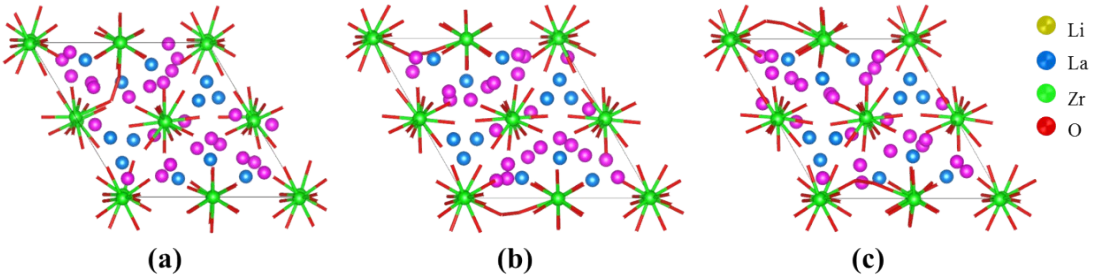


Figure S5. The most three stable LLZO with 4 lithium ions removed structures of all the generations produced by META. The O-O bond is formed by O1 and O2. (a) The first stable structure, (b) the second stable structure, (c) the third stable structure.

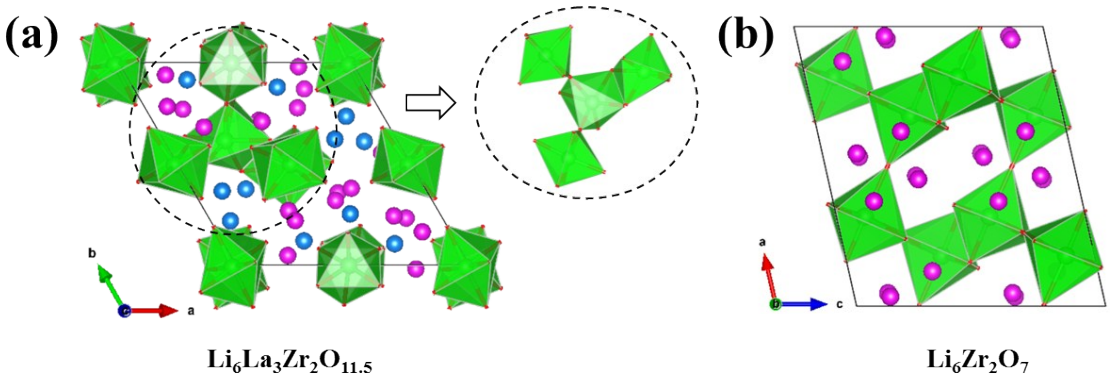


Figure S6. (a)The most stable LLZO with 4 Li ions, O1 and O2 removed structure produced by META. The local structure change is showed in the dashed black circle. (b)The structure of one of the decomposed phases $Li_6Zr_2O_7$.

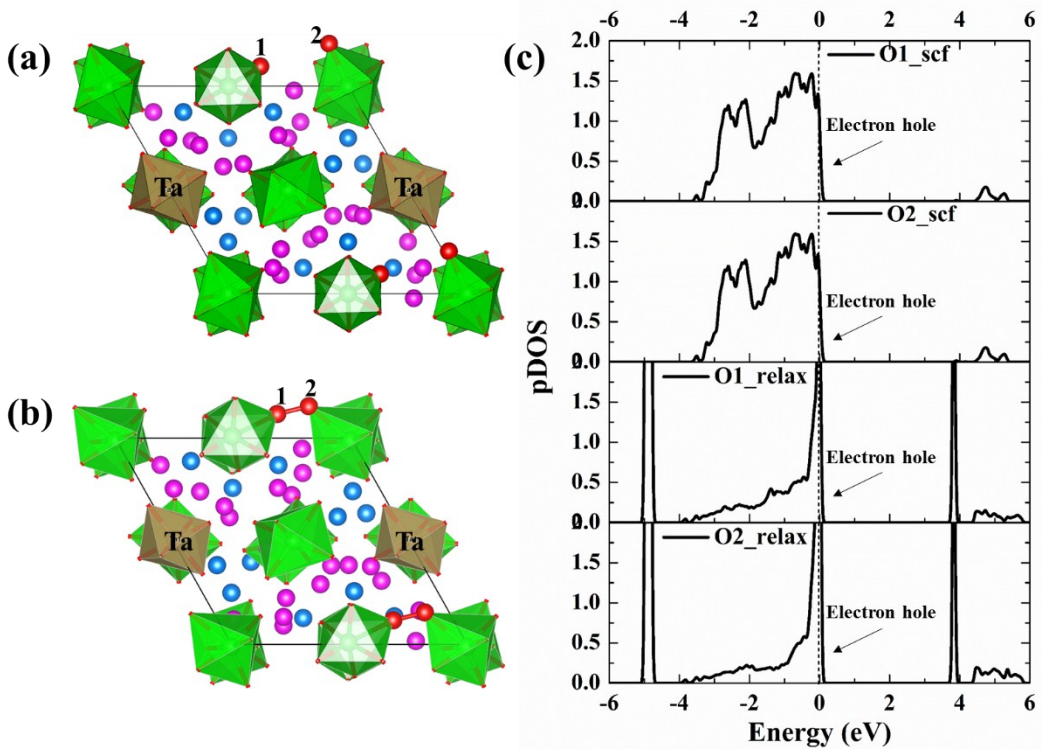


Figure S7. (a)The crystal structure of LLZO_Ta with four Li removed but the crystal lattice isn't relaxed. (b) The crystal structure of LLZO_Ta with four Li removed and the crystal lattice is relaxed by Meta. (c) The local electronic structure of O1 and O2 before (scf) and after (relax) Meta_dynamics.

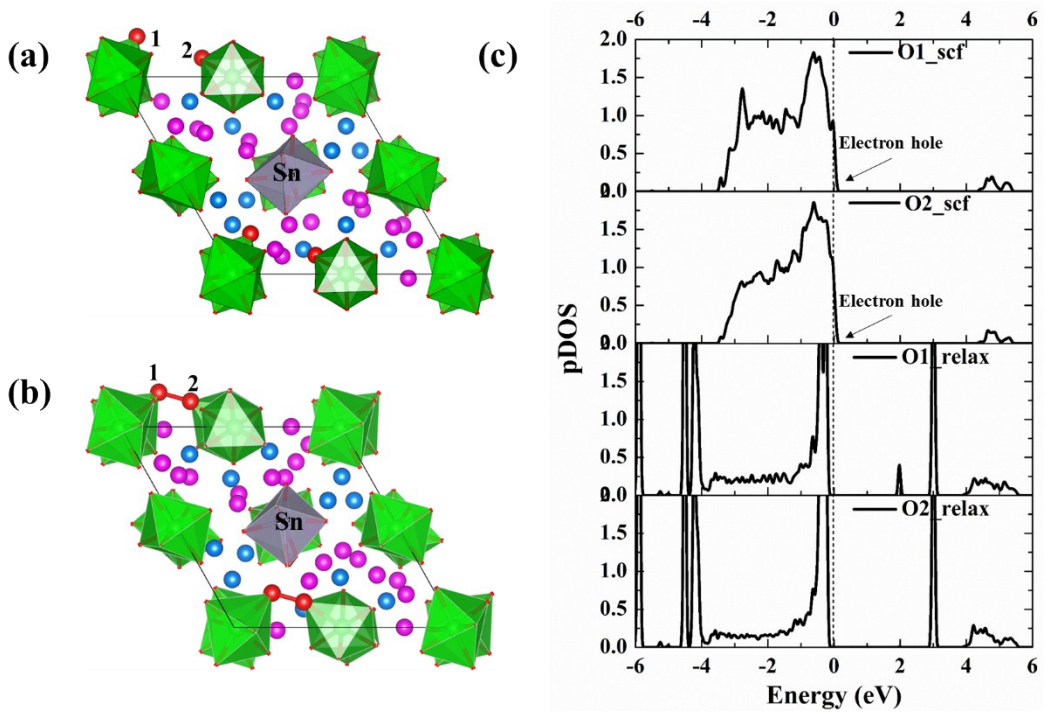


Figure S8. (a)The crystal structure of LLZO_Sn with four Li removed but the crystal lattice isn't relaxed. (b) The crystal structure of LLZO_Sn with four Li removed and the crystal lattice is relaxed by Meta. (c) The local electronic structure of O1 and O2 before (scf) and after (relax) Meta_dynamics.

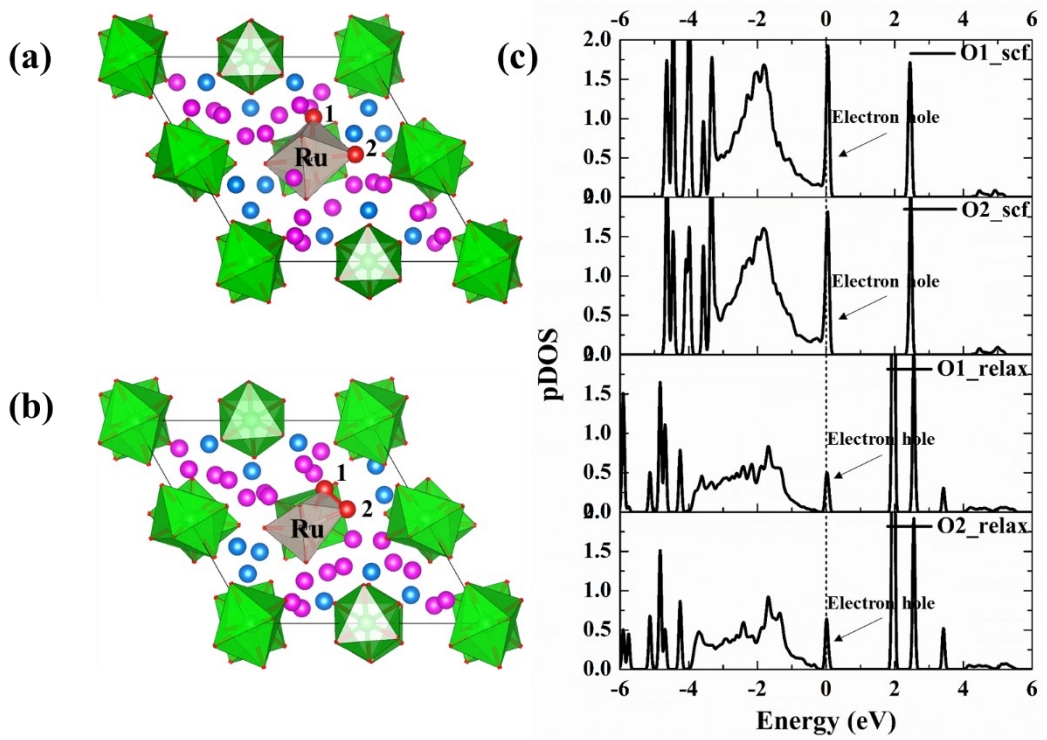


Figure S9. (a)The crystal structure of LLZO_Ru with four Li removed but the crystal lattice isn't relaxed. (b) The crystal structure of LLZO_Ru with four Li removed and the crystal lattice is relaxed by Meta. (c) The local electronic structure of O1 and O2 before (scf) and after (relax) Meta_dynamics.

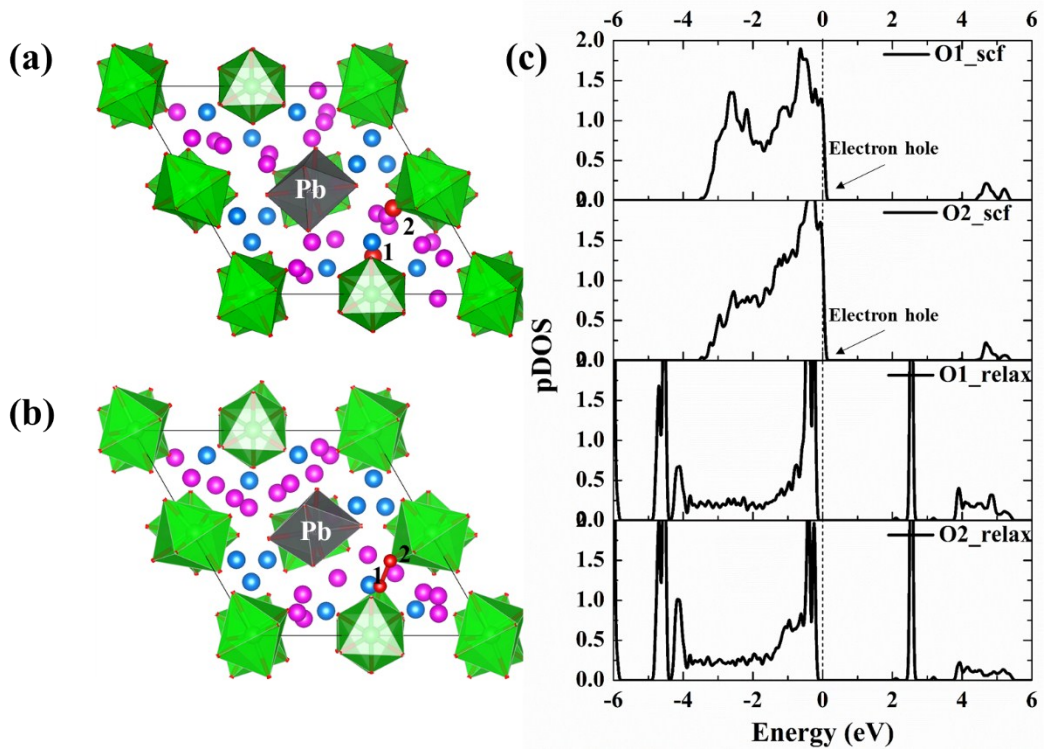


Figure S10. (a)The crystal structure of LLZO_Pb with four Li removed but the crystal lattice isn't relaxed. (b) The crystal structure of LLZO_Pb with four Li removed and the crystal lattice is relaxed by Meta. (c) The local electronic structure of O1 and O2 before (scf) and after (relax) Meta_dynamics.

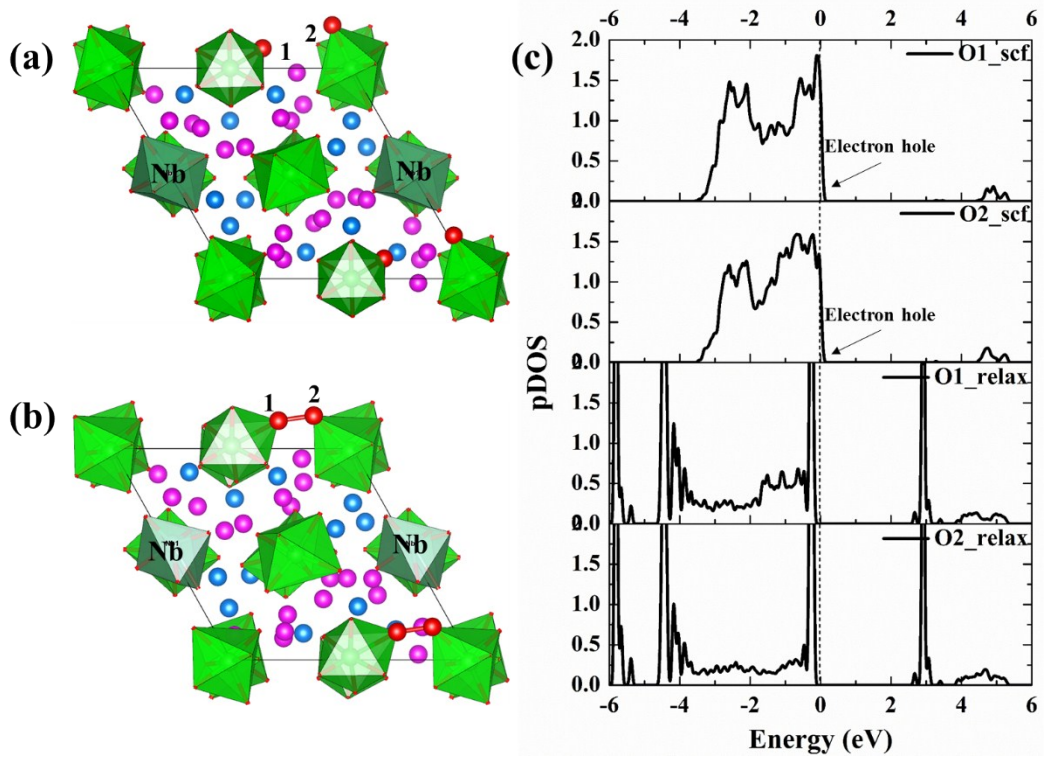


Figure S11. (a)The crystal structure of LLZO_Nb with four Li removed but the crystal lattice isn't relaxed. (b) The crystal structure of LLZO_Nb with four Li removed and the crystal lattice is relaxed by Meta. (c) The local electronic structure of O1 and O2 before (scf) and after (relax) Meta_dynamics.

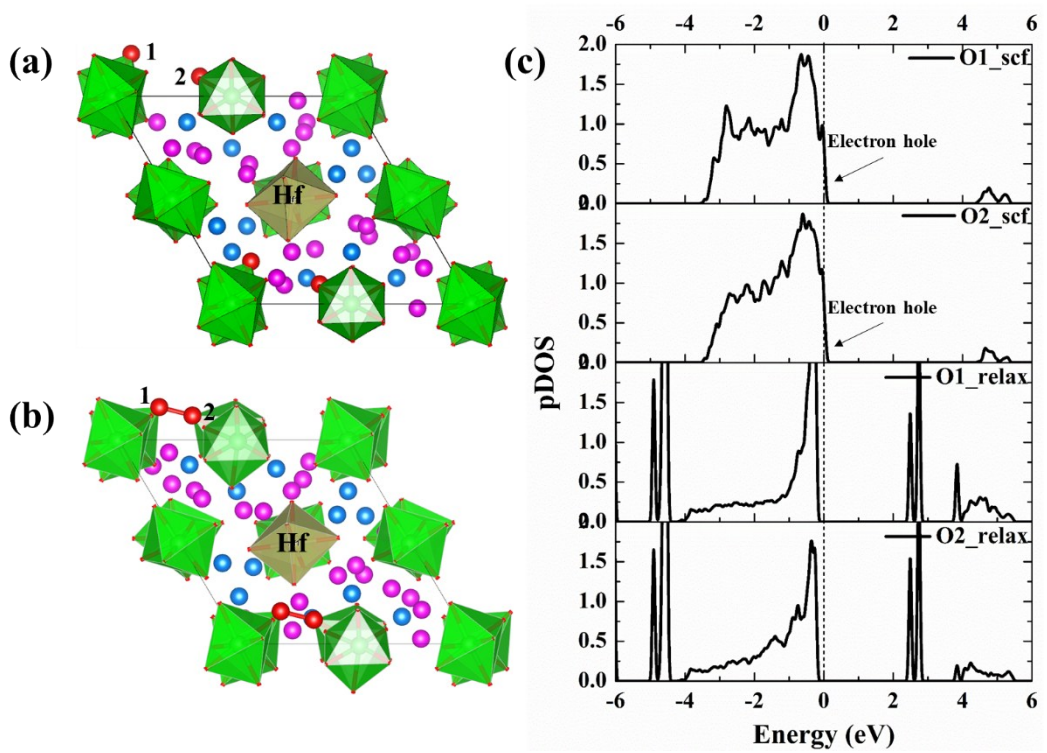


Figure S12. Figure S11. (a)The crystal structure of LLZO_Hf with four Li removed but the crystal lattice isn't relaxed. (b) The crystal structure of LLZO_Hf with four Li removed and the crystal lattice is relaxed by Meta. (c) The local electronic structure of O1 and O2 before (scf) and after (relax) Meta_dynamics.

Table S1 Bader charge analysis of O1 and O2 for each NEB image

	0	**1**	**2**	**3**
O1	**-1.11**	**-0.94**	**-0.64**	**-0.49**
O2	**-1.31**	**-1.12**	**-0.76**	**-0.65**

Table S2 Relevant parameters for fitting function $V=6.71-0.27q/r^3$.

Element	Valence	Crystal Radii (Å)	Voltage (V)
Ru	+5	0.71	2.85
Ta	+5	0.78	4.057
Nb	+5	0.82	4.34
Sn	+4	0.83	4.859
Zr	+4	0.86	4.94
Hf	+4	0.85	4.99
Pb	+4	0.92	5.286

Table S3 Relevant parameters used for voltage prediction.

Element	Valence	Crystal Radii (Å)	Voltage (V)
Ru	+4	0.680	3.306
Cr	+4	0.690	3.452
V	+4	0.720	3.843
Hf	+4	0.720	3.843
Nb	+5	0.780	3.891
Ta	+5	0.780	3.891
Rh	+4	0.740	4.070
Ti	+4	0.745	4.122
Pd	+4	0.755	4.224
Ir	+4	0.765	4.320
Re	+4	0.770	4.367
Tc	+4	0.785	4.499
Mo	+4	0.790	4.540
W	+4	0.800	4.621
Sn	+4	0.830	4.840
Bi	+5	0.900	4.876
Ga	+3	0.760	4.883
Pa	+5	0.920	4.993
Zr	+4	0.860	5.029
Tb	+4	0.900	5.244
Pb	+4	0.915	5.315
Sc	+3	0.885	5.554
Pr	+4	0.990	5.609
Sb	+3	0.900	5.611
In	+3	0.940	5.746
Th	+4	1.080	5.863
Lu	+3	1.001	5.912
Zn	+2	0.880	5.927
Yb	+3	1.008	5.929
Te	+4	1.110	5.930
Tm	+3	1.020	5.956
Er	+3	1.030	5.978
Y	+3	1.040	5.999
Ho	+3	1.041	6.001
Gd	+3	1.078	6.072
Eu	+3	1.087	6.087
Po	+4	1.200	6.093
Sm	+3	1.098	6.106
Dy	+3	1.105	6.118
Pm	+3	1.110	6.126
Nd	+3	1.123	6.146