Electronic Supplementary Information of "Tritium Diffusion in Li_2TiO_3 Crystal Terminated with (001) Surface from First-Principles Calculations"

Jin-Yang Su,[a] Wen Yang,[b,*] Jia-Hong Zhu,[c] Wei-Hua Wang,[d] Kun Li,[a] Shu-Ping Liu,[a] Yong-Tang Li [b]

[a] School of Applied Science, Taiyuan University of Science and Technology, Taiyuan 030024, Shanxi, P. R. China

[b] Shanxi Key Laboratory of Metal Forming Theory and Technology, School of Material Science and Engineering, Taiyuan University of Science and Technology, Taiyuan 030024, Shanxi, P. R. China

[c] Department of Mechanical Engineering, Tennessee Technological University, Cookeville, TN, USA

[d] Department of Electronic Science and Engineering, Key Laboratory of Photo-Electronic Thin Film Device and Technology of Tianjin, Nankai University, Tianjin 300350, P. R. China

Section I Surface formation energy of four types of slab models

The surface formation energy of four different off-stoichiometric surface slab models was calculated according to Eq. (1) of the paper. The corresponding slab models of pure-O surface ($Li_{48}Ti_{24}O_{84}$), Li-Ti surface ($Li_{52}Ti_{32}O_{72}$), pure-Li surface ($Li_{60}Ti_{24}O_{72}$) and 1/3-Li surface ($Li_{52}Ti_{24}O_{72}$) were plotted in Fig. S1, respectively. For off-stoichiometric surfaces, their ground state mixed phases were determined by the Open Quantum Materials Database (OQMD) and the mixing ratio were calculated and presented in Table S1.

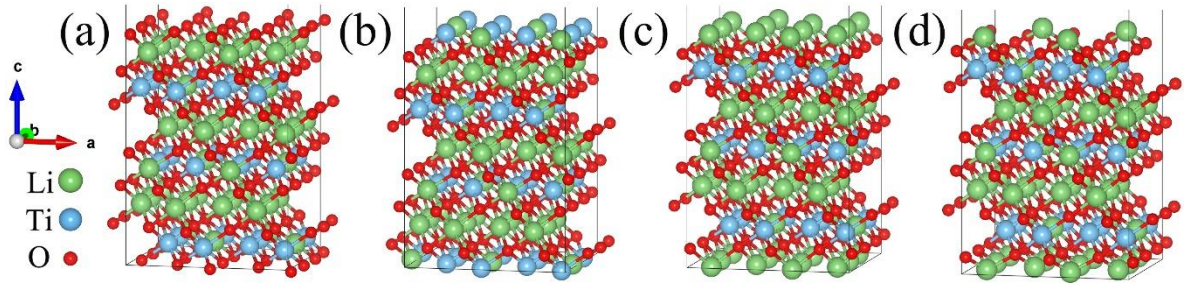

Fig. S1 Slab models of four types of off-stoichiometric surfaces (a) Pure-O Surface ($Li_{48}Ti_{24}O_{84}$) (b) Li-Ti Surface ($Li_{52}Ti_{32}O_{72}$) (c) Pure-Li Surface ($Li_{60}Ti_{24}O_{72}$) (d) 1/3-Li Surface ($Li_{52}Ti_{24}O_{72}$)

Table S1 Ground state mixed phases and surface formation energy of different slab models.

Slab model	Chemical formula	Phase mixtures	E_f(eV/Å^2)
Pure O Surface	$Li_{48}Ti_{24}O_{84}$	20 Li_2TiO_3+4.8 LiO_3+0.8 $Li_4Ti_5O_{12}$	0.242
Li-Ti Surface	$Li_{52}Ti_{32}O_{72}$	16.8 $LiTiO_2$+8.8 Li_4TiO_4+3.2 Ti_2O	0.210
Pure Li Surface	$Li_{60}Ti_{24}O_{72}$	12 Li_4TiO_4+12 $LiTiO_2$	0.088
1/3-Li Surface	$Li_{52}Ti_{24}O_{72}$	16 Li_2TiO_3+4 Li_4TiO_4+4 $LiTiO_2$	0.083

The total energy of the ground state phases including LiO_3, Li_4TiO_4, Li_2TiO_3, $LiTiO_2$, $Li_4Ti_5O_{12}$ and Ti_2O was calculated with the parameters identical to those in section 2 of the paper. And the obtained total energy of this work was compared with the results in the Open Quantum Materials Database, as was shown in Table S2. It is clear that the error is less than 0.5 %, which further confirms our calculation method.

According to our obtained total energy of different ground state phases, the surface formation energy was calculated by Eq. (1), which is 0.242 eV/Å^2 for pure-O surface, 0.210 eV/Å^2 for Li-Ti surface, 0.088 eV/Å^2 for pure-Li surface, and 0.083 eV/Å^2 for 1/3-Li surface, respectively.

Table S2 Total energy of ground state phases of this work in comparison with that of Open Quantum Materials Database (OQMD).

Ground state phase	Total energy (eV/atom) (Open Quantum Materials Database)	Total energy (eV/atom) (This work)	Error (%)
LiO_3	-4.808	-4.803	0.10
Li_4TiO_4	-6.273	-6.297	0.39
Li_2TiO_3	-7.024	-7.017	0.10
$LiTiO_2$	-7.497	-7.514	0.22
$Li_4Ti_5O_{12}$	-7.810	-7.807	0.04
Ti_2O	-8.626	-8.591	0.41

Section II Detailed data of PES for tritium adsorption on 1/3-Li (001) surface

All data plotted in Figure 3 (b) of PES was presented in the following Table S3 and Table S4. There were totally 1215 (27×45) sets of data in Table S3. The number labelled green were coordinates of the uniform grid with spacing of 0.2 Å in x and y direction of top layer of 1/3-Li (001) surface. It was noted that the grid was only made in half area of the surface slab due to its symmetric property. During simulations, we found that some optimizations were not converged when tritium atom was placed too close to a neighboring Li atom. For such cases, we frozen the neighboring Li atom and optimized the system again to calculate the tritium adsorption energy. Such 136 sets of data were labelled red in Table S3.

Besides, there were still possible inevitably missed data although the spacing of 0.2 Å was already fine. Thus, the sites with lowest adsorption energy were obtained furthermore and presented in Table S4. Because of the symmetric property, the results of adsorption sites of A3/A4/B3/B4/C3/C4 were identical to those of A1/A2/B1/B2/C1/C2, respectively.

Table S3 Adsorption energy of tritium at different grid positions on 1/3-Li (001) surface

X(Å) / Y(Å) E(eV)	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2
0.0	-1.376	-1.431	-0.770	2.958	2.956	2.951	2.946	2.943	2.941	2.942	2.944	2.947	-1.303	-1.807	-1.892	-1.924	-1.891	-1.811	-1.975	-2.066	-2.095	-2.072	-2.011	-1.924	-1.820	-1.376	-1.069
0.2	-1.248	-0.836	-0.367	2.951	2.948	2.943	2.939	2.937	2.936	2.938	2.942	2.950	2.960	2.969	-1.778	-1.794	-1.754	-1.880	-2.042	-2.127	-2.144	-2.105	-2.030	-1.934	-1.556	-1.248	-0.837
0.4	-1.138	-0.569	2.933	2.945	2.942	2.937	2.933	2.932	2.931	2.934	2.939	2.947	2.959	2.973	2.989	-1.601	-1.657	-1.907	-2.072	-2.154	-2.166	-2.121	-2.039	-1.942	-1.503	-1.138	-0.570
0.6	-1.073	-0.403	2.927	2.941	2.938	2.934	2.930	2.929	2.929	2.931	2.937	2.945	2.958	2.973	2.989	-1.348	-1.658	-1.912	-2.079	-2.163	-2.173	-2.126	-2.043	-1.946	-1.471	-1.073	-0.403
0.8	-1.063	-0.388	2.927	2.940	2.938	2.934	2.930	2.928	2.928	2.931	2.937	2.946	2.957	2.972	2.989	-1.215	-1.657	-1.912	-2.080	-2.164	-2.174	-2.127	-2.044	-1.947	-1.466	-1.063	-0.388
1.0	-1.108	-0.463	2.925	2.942	2.940	2.936	2.932	2.930	2.930	2.933	2.938	2.947	2.958	2.972	2.989	-1.493	-1.658	-1.910	-2.076	-2.159	-2.170	-2.123	-2.041	-1.944	-1.488	-1.108	-0.463
1.2	-1.203	-0.731	-0.365	2.947	2.945	2.941	2.937	2.934	2.935	2.936	2.941	2.949	2.959	2.973	-1.709	-1.713	-1.666	-1.895	-2.059	-2.142	-2.156	-2.113	-2.034	-1.937	-1.534	-1.203	-1.461
1.4	-1.329	-0.990	-0.705	2.954	2.952	2.947	2.943	2.939	2.939	2.941	2.944	2.950	2.958	-1.774	-1.848	-1.871	-1.833	-1.847	-2.011	-2.099	-2.121	-2.089	-2.020	-1.928	-1.596	-1.329	-0.990
1.6	-1.433	-1.156	-0.846	2.961	2.961	2.955	2.950	2.946	2.944	2.943	2.949	-1.144	-1.339	-1.839	-1.933	-1.969	-1.938	-1.846	-1.920	-2.017	-2.053	-2.041	-1.991	-1.912	-1.810	-1.394	-1.156
1.8	-1.647	-1.504	-0.878	-0.575	2.967	2.962	2.955	2.946	2.946	-1.073	-0.979	-1.080	-1.737	-1.866	-1.973	-2.018	-1.990	-1.896	-1.778	-1.888	-1.944	-1.957	-1.930	-1.867	-1.771	-1.647	-1.504
2.0	-1.551	-1.397	-1.229	-0.665	-1.268	-1.386	-1.462	-0.696	-0.566	-0.819	-0.977	-1.779	-1.846	-1.918	-1.996	-2.035	-2.004	-1.905	-1.741	-1.713	-1.790	-1.826	-1.820	-1.770	-1.679	-1.550	-1.397
2.2	-1.578	-1.250	-1.274	-1.287	-1.468	-1.592	-1.672	-1.726	-1.773	-1.822	-0.772	-1.911	-1.952	-1.993	-2.032	-2.047	-2.000	-1.888	-1.714	-1.885	-1.946	-1.966	-1.943	-1.871	-1.747	-1.578	-1.250
2.4	-1.777	-1.603	-1.407	-1.457	-1.640	-1.766	-1.181	-1.897	-1.935	-1.969	-1.998	-2.021	-2.039	-2.055	-2.066	-2.052	-1.985	-1.854	-1.947	-2.032	-2.083	-2.100	-2.081	-2.022	-1.919	-1.777	-1.603
2.6	-1.931	-1.796	-1.643	-1.594	-1.776	-1.901	-1.982	-2.031	-2.062	-2.085	-2.098	-2.103	-2.099	-2.088	-2.070	-2.029	-1.939	-1.932	-2.045	-2.119	-2.162	-2.179	-2.166	-2.121	-2.041	-1.931	-1.796
2.8	-2.037	-1.942	-1.831	-1.688	-1.869	-1.994	-2.075	-2.124	-2.151	-2.165	-2.165	-2.150	-2.122	-2.082	-2.032	-1.960	-1.847	-1.975	-2.082	-2.148	-2.187	-2.204	-2.199	-2.170	-2.115	-2.037	-1.941
3.0	-2.095	-2.036	-1.963	-1.861	-1.911	-2.037	-2.120	-2.172	-2.199	-2.206	-2.192	-2.157	-2.102	-2.029	-1.942	-1.838	-1.804	-1.958	-2.061	-2.124	-2.161	-2.180	-2.185	-2.172	-2.141	-2.095	-2.036
3.2	-2.106	-2.080	-2.042	-1.967	-1.893	-2.023	-2.112	-2.169	-2.198	-2.201	-2.175	-2.120	-2.036	-1.929	-1.802	-1.659	-1.731	-1.886	-1.990	-2.051	-2.089	-2.113	-2.128	-2.131	-2.123	-2.106	-2.080

3.4	-2.075	-2.078	-2.070	-2.021	-1.912	-1.947	-2.046	-2.110	-2.145	-2.145	-2.109	-2.035	-1.924	-1.781	-1.613	-1.400	-1.612	-1.769	-1.873	-1.934	-1.975	-2.008	-2.035	-2.054	-2.067	-2.075	-2.079
3.6	-2.012	-2.042	-2.060	-2.037	-1.948	-1.795	-1.918	-1.994	-2.036	-2.036	-1.992	-1.901	-1.766	-1.588	-1.380	-1.247	-1.456	-1.613	-1.715	-1.777	-1.824	-1.868	-1.910	-1.947	-1.982	-2.012	-2.042
3.8	-1.927	-1.987	-2.036	-2.035	-1.964	-1.824	-1.625	-1.815	-1.865	-1.869	-1.733	-1.665	-1.554	-1.409	-1.242	-0.613	-1.270	-1.423	-1.522	-1.584	-1.639	-1.697	-1.755	-1.813	-1.870	-1.927	-1.987
4.0	-1.835	-1.941	-2.017	-2.026	-1.964	-1.833	-1.759	-1.850	-1.894	-1.898	-1.863	-1.787	-1.676	-1.537	-1.379	-0.702	-0.569	2.962	-1.297	2.940	-0.391	-0.062	-0.323	-1.938	-1.744	-1.833	-1.941
4.2	-1.783	-1.914	-1.985	-1.993	-1.933	-1.785	-1.919	-1.991	-2.012	-1.993	-1.938	-1.852	-1.741	-1.326	-1.035	-0.724	2.967	2.962	2.956	2.951	2.946	2.942	2.940	-1.045	-1.613	-1.783	-1.914
4.4	-1.747	-1.857	-1.915	-1.915	-1.855	-1.261	-2.030	-2.087	-2.088	-2.045	-1.969	-1.873	-2.098	-1.229	-0.918	2.953	2.959	2.954	2.949	2.945	2.942	2.941	2.943	2.947	-1.594	-1.746	-1.858
4.6	2.965	-1.753	-1.790	-1.781	-1.768	-1.971	-2.094	-2.142	-2.130	-2.070	-1.983	-1.882	-1.421	-1.045	-0.714	2.954	2.950	2.946	2.941	2.938	2.937	2.937	2.940	2.945	2.954	2.965	-1.753
4.8	2.965	2.980	-1.607	-1.583	-1.793	-2.000	-2.123	-2.168	-2.148	-2.082	-1.991	-1.635	-1.347	-0.880	-0.164	2.951	2.944	2.940	2.936	2.932	2.932	2.932	2.937	2.944	2.952	2.966	2.980
5.0	2.965	2.981	2.997	-1.323	-1.797	-2.006	-2.132	-2.176	-2.155	-2.087	-1.996	-1.613	-1.302	-0.790	-0.351	2.936	2.941	2.937	2.933	2.930	2.928	2.930	2.934	2.942	2.952	2.966	2.981
5.2	2.964	2.981	2.996	-1.497	-1.796	-2.007	-2.132	-2.177	-2.155	-2.087	-1.996	-1.609	-1.295	-0.777	-0.317	2.935	2.940	2.936	2.932	2.929	2.928	2.929	2.933	2.941	2.951	2.964	2.981
5.4	2.966	2.981	2.995	-1.470	-1.796	-2.004	-2.128	-2.172	-2.151	-2.084	-1.993	-1.625	-1.327	-1.403	-0.367	2.936	2.942	2.938	2.934	2.930	2.930	2.931	2.935	2.942	2.952	2.966	2.981
5.6	2.966	2.980	-1.715	-1.696	-1.781	-1.987	-2.111	-2.157	-2.140	-2.075	-1.986	-1.657	-1.391	-1.470	-0.631	2.934	2.948	2.943	2.939	2.935	2.934	2.935	2.938	2.944	2.954	2.967	2.981
5.8	-1.721	-1.819	-1.865	-1.859	-1.795	-1.939	-2.064	-2.117	-2.111	-2.058	-1.975	-1.876	-1.477	-1.488	-0.847	2.954	2.955	2.951	2.945	2.942	2.939	2.940	2.942	2.947	2.955	2.956	-1.819
6.0	-1.771	-1.894	-1.958	-1.286	-1.900	-1.845	-1.977	-2.042	-2.053	-2.020	-1.954	-1.863	-1.752	-1.304	-1.006	-0.699	2.963	2.958	2.954	2.948	2.945	2.943	2.944	2.939	-1.893	-1.771	-1.894
6.2	-1.798	-1.928	-2.004	-2.012	-1.952	-1.825	-1.840	-1.922	-1.955	-1.948	-1.903	-1.823	-1.712	-1.578	-1.038	-0.725	2.962	2.965	2.959	2.951	2.945	-0.367	0.010	-1.003	-1.687	-1.797	-1.929
6.4	-1.883	-1.960	-2.023	-2.028	-1.963	-1.830	-1.657	-1.757	-1.814	-1.828	-1.801	-1.729	-1.619	-1.477	-1.315	-1.141	-0.757	-1.334	-1.429	-0.773	-0.586	-0.626	-0.877	-1.954	-1.814	-1.883	-1.960
6.6	-1.973	-2.014	-2.045	-2.032	-1.953	-1.808	-1.840	-1.919	-1.961	-1.961	-1.912	-1.815	-1.669	-1.328	-1.170	-1.180	-1.384	-1.537	-1.638	-1.700	-1.750	-1.798	-1.845	-1.891	-1.932	-1.973	-2.014
6.8	-2.047	-2.061	-2.063	-2.026	-1.928	-1.892	-1.993	-2.061	-2.097	-2.097	-2.055	-1.974	-1.852	-1.694	-1.507	-1.346	-1.555	-1.710	-1.812	-1.874	-1.916	-1.952	-1.983	-2.009	-2.030	-2.047	-2.061
7.0	-2.093	-2.080	-2.054	-1.991	-1.872	-1.993	-2.085	-2.144	-2.176	-2.178	-2.147	-2.084	-1.988	-1.865	-1.721	-1.561	-1.692	-1.846	-1.948	-2.009	-2.046	-2.073	-2.091	-2.100	-2.101	-2.093	-2.080

7.2	-2.103	-2.058	-2.000	-1.911	-1.905	-2.033	-2.118	-2.171	-2.200	-2.206	-2.188	-2.145	-2.077	-1.990	-1.887	-1.766	-1.785	-1.939	-2.041	-2.102	-2.138	-2.158	-2.165	-2.159	-2.137	-2.102	-2.058
7.4	-2.068	-1.988	-1.895	-1.775	-1.888	-2.014	-2.096	-2.146	-2.174	-2.186	-2.181	-2.159	-2.121	-2.068	-2.002	-1.916	-1.828	-1.981	-2.085	-2.149	-2.186	-2.203	-2.201	-2.177	-2.132	-2.068	-1.988
7.6	-1.987	-1.868	-1.734	-1.633	-1.817	-1.942	-2.024	-2.073	-2.104	-2.123	-2.132	-2.130	-2.117	-2.095	-2.065	-2.010	-1.908	-1.964	-2.074	-2.145	-2.185	-2.201	-2.191	-2.152	-2.083	-1.986	-1.869
7.8	-1.856	-1.699	-1.521	-1.513	-1.698	-1.826	-1.907	-1.958	-1.994	-2.023	-2.046	-2.063	-2.072	-2.078	-2.078	-2.052	-1.974	-1.834	-2.002	-2.083	-2.131	-2.148	-2.132	-2.078	-1.985	-1.856	-1.699
8.0	-1.682	-1.487	-1.126	-1.357	-1.542	-1.668	-1.750	-1.802	-1.847	-1.889	-1.929	-1.964	-1.997	-2.026	-2.055	-2.057	-2.001	-1.879	-1.868	-1.962	-2.020	-2.040	-2.021	-1.954	-1.840	-1.681	-1.488
8.2	-1.485	-1.327	-1.153	-1.175	-1.354	-1.477	-1.555	-1.280	-1.666	-1.725	-1.784	-1.841	-1.897	-1.955	-2.015	-2.045	-2.007	-1.902	-1.732	-1.776	-1.847	-1.872	-1.750	-1.705	-1.615	-1.485	-1.327
8.4	-1.609	-1.459	-0.856	-0.553	-0.615	-1.858	-1.330	-1.745	-1.831	-0.903	-0.529	-1.942	-1.787	-1.887	-1.986	-2.031	-2.003	-1.907	-1.745	-1.810	-1.876	-1.902	-1.886	-1.831	-1.737	-1.610	-1.459
8.6	-1.678	-1.182	-0.874	2.966	2.965	2.959	2.953	2.948	2.944	-1.840	-0.387	-1.910	-1.330	-1.856	-1.956	-1.999	-1.970	-1.879	-1.861	-1.962	-2.007	-2.008	-1.969	-1.899	-1.800	-1.678	-1.183
8.8	-1.375	-1.067	-0.768	2.958	2.956	2.951	2.946	2.943	2.942	2.942	2.945	2.947	-1.301	-1.807	-1.892	-1.924	-1.892	-1.811	-1.975	-2.066	-2.094	-2.072	-2.011	-1.924	-1.820	-1.376	-1.070

Table S4 Lowest tritium adsorption energy E_a at different adsorption sites on 1/3-Li (001) surface

Sites	E_a (eV)	X (Å)	Y (Å)
A1	-2.178	1.439	5.115
A2	-2.178	3.956	0.728
B1	-2.210	1.748	3.063
B2	-2.209	4.273	7.441
C1	-2.206	1.790	7.184
C2	-2.205	4.322	2.803