Computational Understanding of Delithiation, Overlithiation, and Transport Properties in Disordered Cubic Rock-Salt Type Li_2TiS_3. Supplementary Materials

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Table S1. Number of possible configurations based on the number of Lithium atoms removed from the structure. Calculated with CRYSTAL code.

Delithiation (%)	Li atoms removed	Configurations
100	18	1
94.44	17	18
88.89	16	153
83.33	15	816
77.78	14	3060
72.22	13	8568
66.67	12	18564
61.11	11	31824
55.56	10	43758
50	9	48620
44.44	8	43758
38.89	7	31824
33.33	6	18564
27.78	5	8568
22.22	4	3060
16.67	3	816
11.11	2	153
5.56	1	18
0	0	1

Table S2. Relative stability of three configurations each delithiation state. The most stable structure is considered for the energy-delta calculation.

x	Relative stability (eV)	x	Relative stability (eV)
2	0.000	**9**	0.000
	0.080		1.111
	0.142		3.538
3	0.000	**10**	0.000
	1.274		0.078
	1.561		0.210
4	0.000	**11**	0.000
	0.135		2.791
	1.229		3.630
5	0.000	**12**	0.000
	1.940		0.215
	2.285		1.594
6	0.000	**13**	0.000
	0.173		1.181
	0.883		2.653
7	0.000	**14**	0.000
	1.100		0.119

	1.503		0.154
8	0.000	**15**	0.000
	0.218		1.803
	0.939		3.102

Table S3. Reaction energy for the most stable structure for each delithiation state, x is the number of Li atoms removed. Also reported the required energy for a single lithium extraction.

x	**$\Delta E_{Reaction}$ (eV)**	**$\Delta E_{Li\ removal}$ (eV)**
1	4.18	4.18
2	6.31	2.14
3	10.22	3.90
4	12.63	2.41
5	16.29	3.66
6	18.30	2.01
7	22.18	3.00
8	24.35	2.17
9	27.21	2.86
10	30.33	3.12
11	32.75	2.42
12	34.87	2.12
13	37.80	2.93
14	41.34	3.54
15	43.93	2.60

Table S4. Band gap evolution as a function of delithiation for structures with even vacancies.

x	**Band Gap (eV)**
0	2.46
2	2.35
4	2.39
6	2.31
8	2.23
10	2.13
12	2.27
14	2.15

Table S5. State of charge and open circuit voltage for the LTS system.

SOC (%)	**OCV (V)**
0	
5.88	1.42
11.76	1.51
17.64	2.43
23.52	2.33

29.41	2.64
35.29	2.61
41.17	2.83
47.05	2.77
52.94	2.80
58.82	2.73
64.70	2.74
70.58	2.78
76.47	2.75
82.35	2.70
88.23	2.72
94.11	2.77
100	2.76

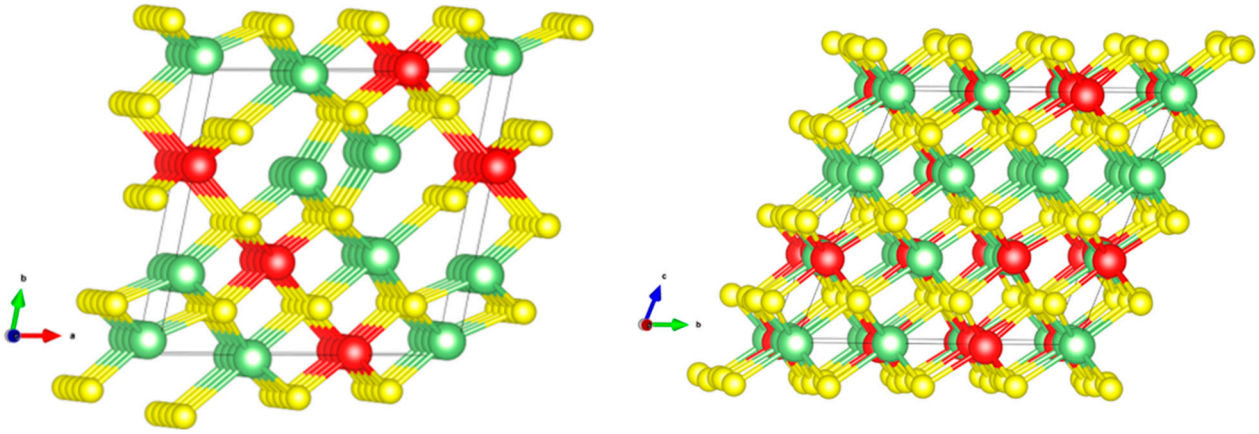

Figure S1. An example of ordered (left) and dispersed (right) structures.

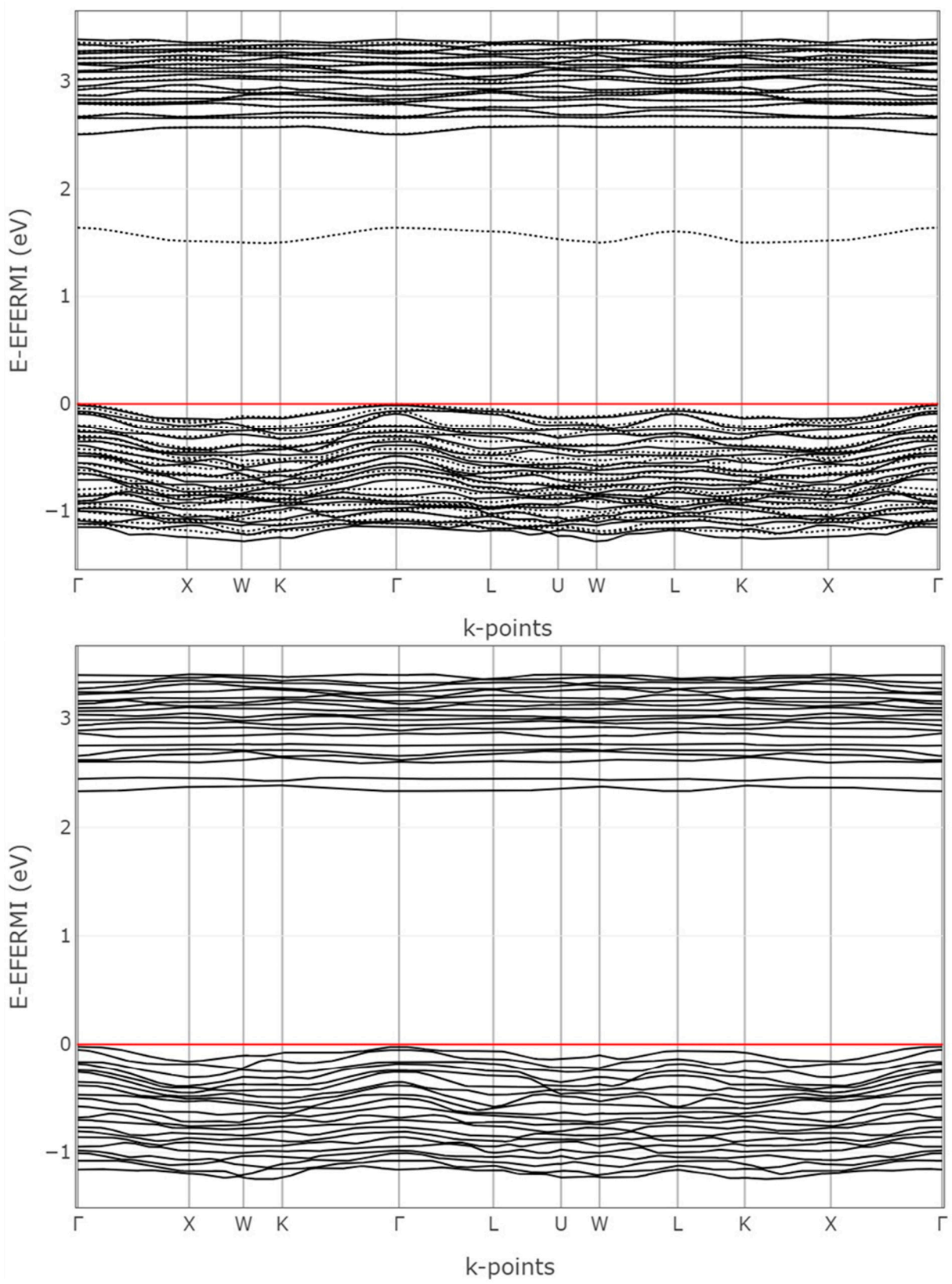

Figure S2. Band structure for mono-delithiated (top) and double-delithiated (bottom) structures.

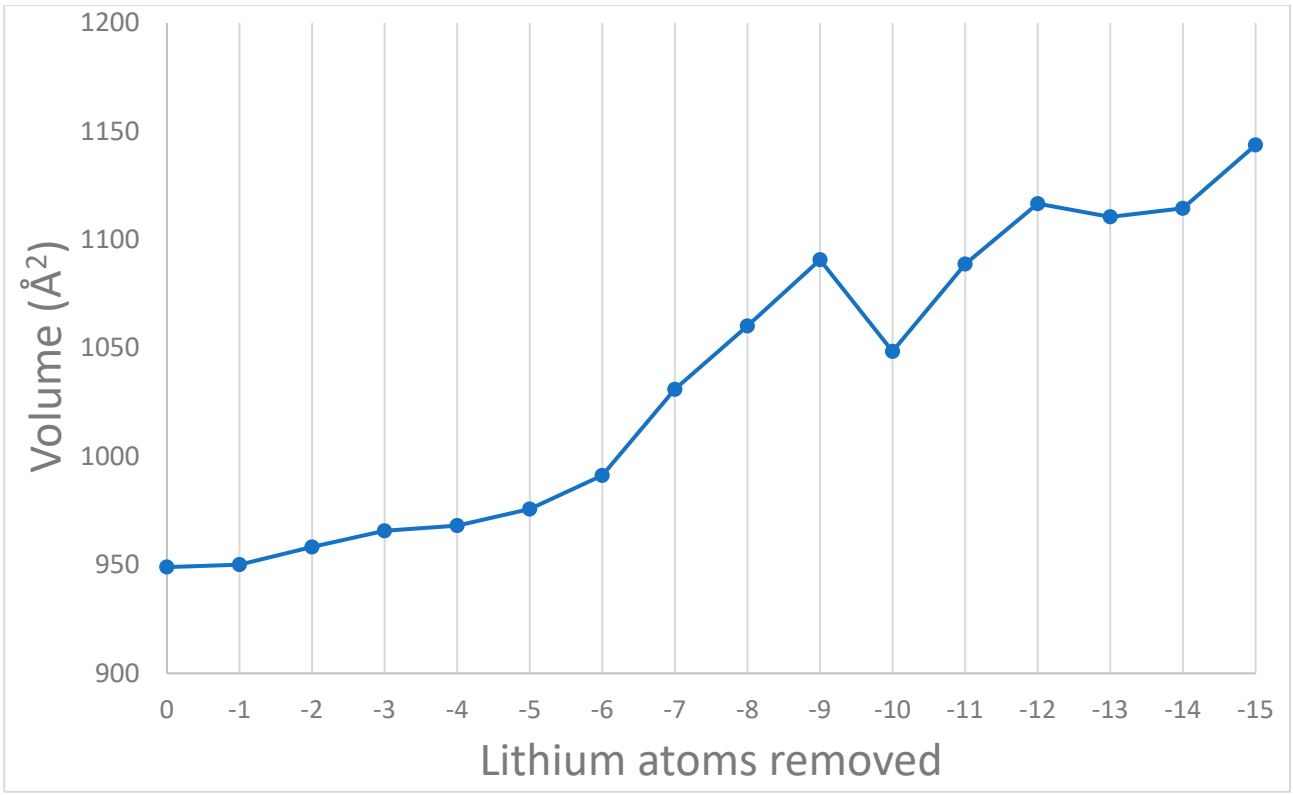

Figure S3. Volume variation during delithiation expressed in Å^2.

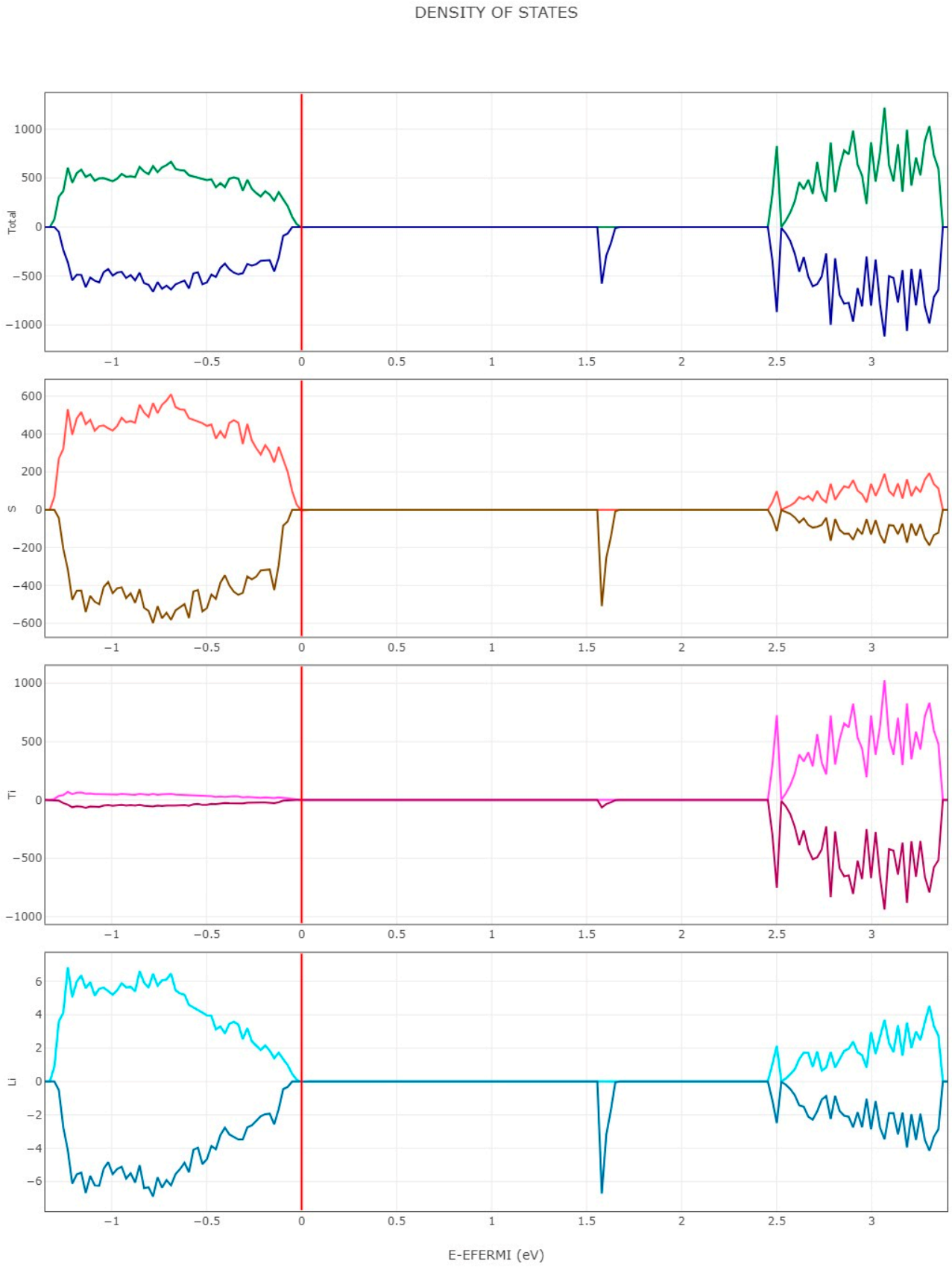

Figure S4. Density of states for mono-delithiated structure. Total DOS (top) and projections on atoms, from top to bottom: S, Ti, Li.