Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

"Supporting Information"

First-principles study on discharge electrochemical and catalytic performance of sulfur cathode host $Fe_{0.875}M_{0.125}S_2$ (M = Ti, V)

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Table S1. The lattice constant of Li_2FeS_2 with different space groups

Li_2FeS_2	*a* (Å)	*b*	*c*	*α* (°)	*ß*	*γ*
Ibam	5.87	10.03	5.08	90.00	90.00	90.00
Immm	3.39	4.66	11.04	90.00	90.00	90.00
*P*3*m*1	3.89	3.89	6.21	90.00	90.00	120.00
$P\bar{3}m1$	3.81	3.81	6.08	90.00	90.00	120.00
$P2_1/c$	6.71	6.38	8.12	90.00	92.83	90.00
*P*42*mcn*	5.77	5.77	5.69	90.00	90.00	90.00

Table S2. Chemical potentials for elements in $Li_2Fe_{0.875}M_{0.125}S_2$

μ_M	Ti	V	Fe	Li	S
DFT	-7.834	-8.988	-8.309	-1.875	-4.113
Ref	-7.770	-8.941	-8.308	-1.897	-4.114

Table S3. Formation energy of Fe in Li_2FeS_2 substituted by M atom (M = Ti, V)

Li_2FeS_2	*Ibam*	*Immm*	*P*3*m*1	$P\bar{3}m1$	$P2_1/c$	*P*42*mcn*
$Li_2Fe_{0.875}Ti_{0.125}S_2$	-2.57	-1.69	-0.76	-2.77	-2.34	-0.10
$Li_2Fe_{0.875}V_{0.125}S_2$	-3.49	-0.64	-0.81	-0.80	-1.23	-0.57

Figure S1. The structures of Li_2FeS_2 with different *Ibam* (a), *Immm* (b), *P*3*m*1 (c), $P\bar{3}m1$ (d), $P2_1/c$ (e) and *P*42*mcm* (f) space groups. (yellow, pink and green are for S, Fe and Li atoms.)

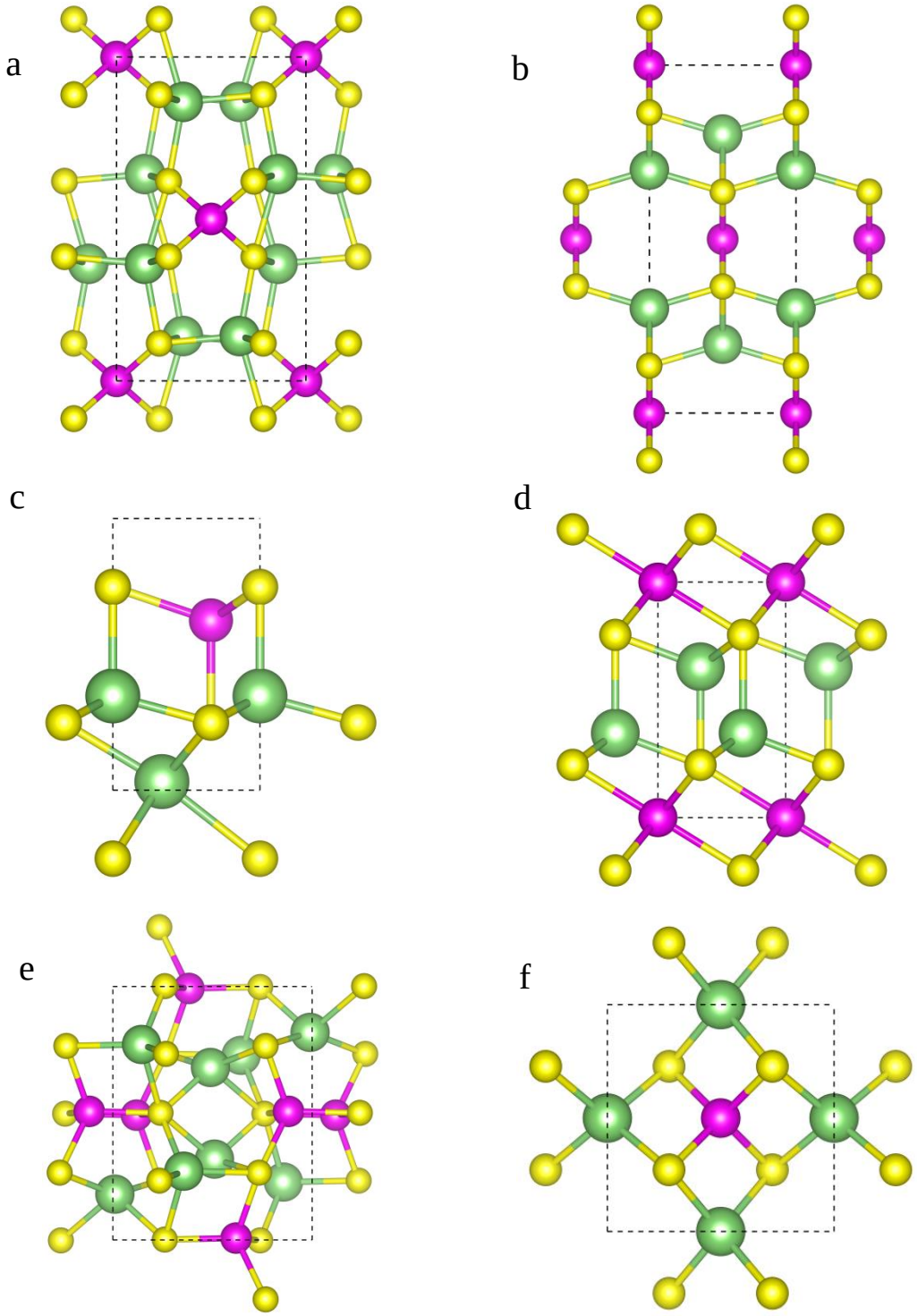
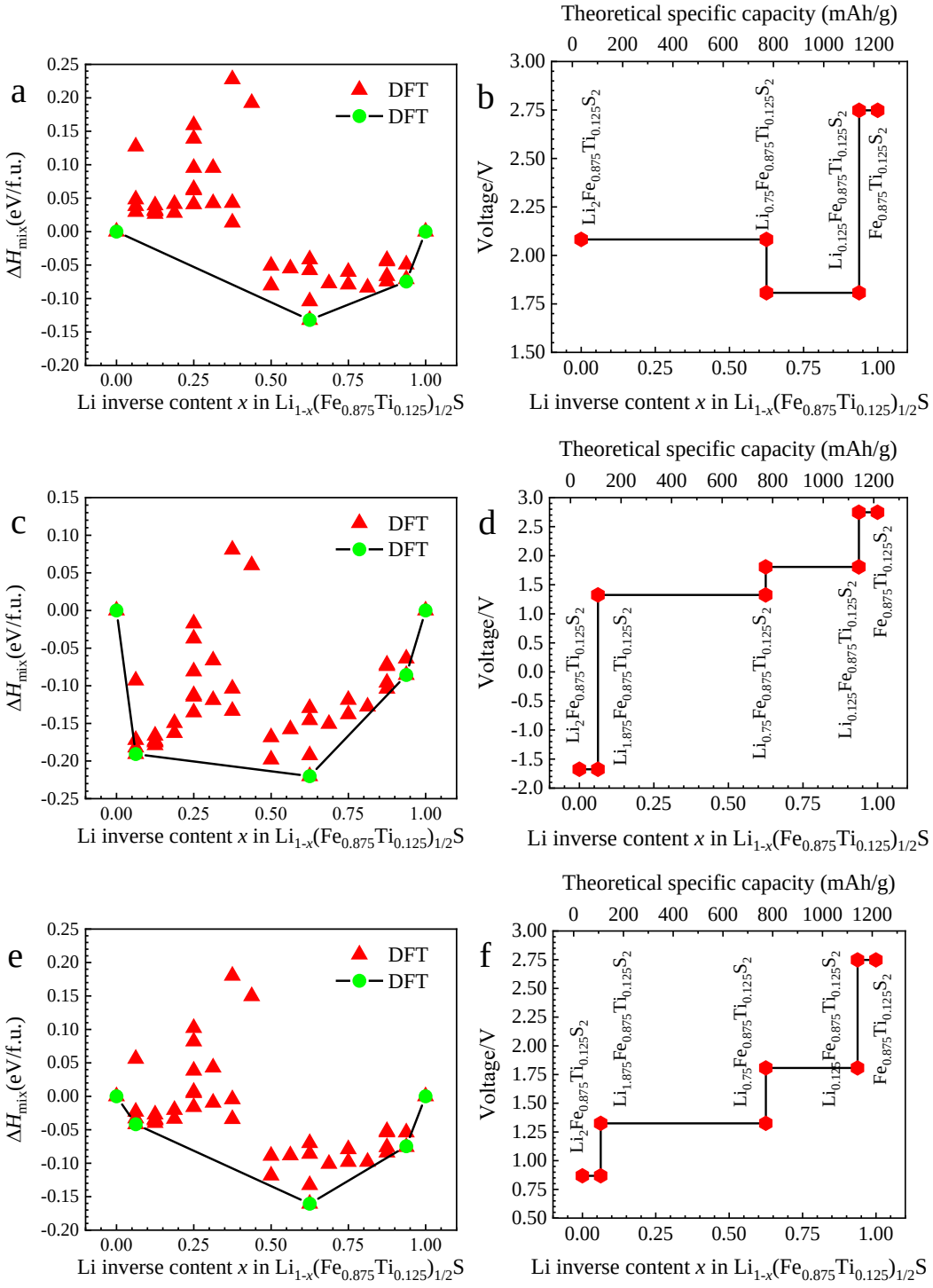


Figure S2. The formation energy of mixing enthalpy of $Li_{1-x}(Fe_{0.875}Ti_{0.125})_{1/2}S$ with different *Ibam* (a), *Immm* (c), *P*3*m*1 (e), $P\bar{3}m1$ (g), $P2_1/c$ (i) and *P*42*mcm* (m) is a function of Li concentration; the voltage of $Li_{1-x}(Fe_{0.875}Ti_{0.125})_{1/2}S$ with different *Ibam* (b), *Immm* (d), *P*3*m*1 (f), $P\bar{3}m1$ (h), $P2_1/c$ (j) and *P*42*mcm* (n) increases with the increase of theoretical capacity.



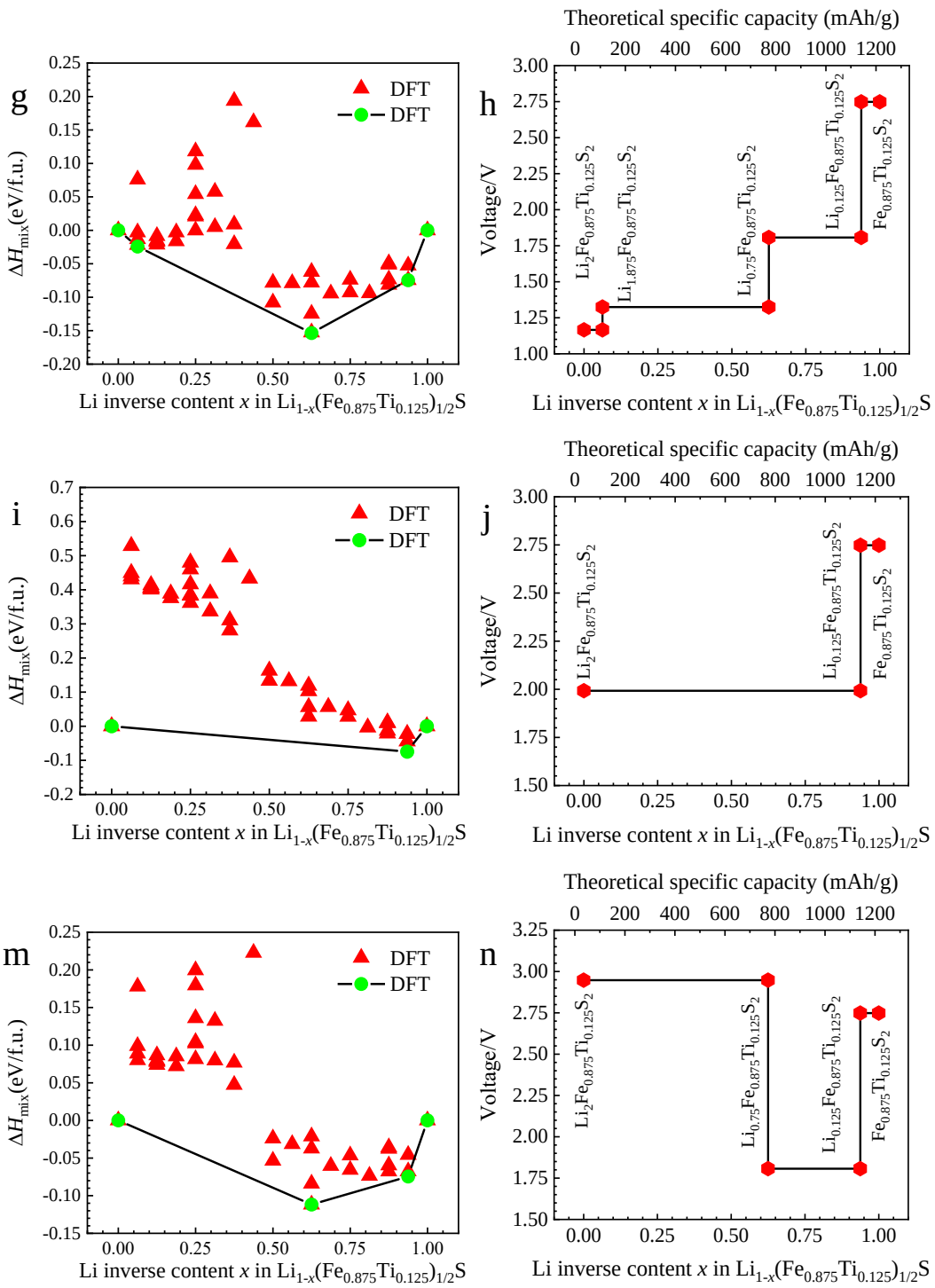
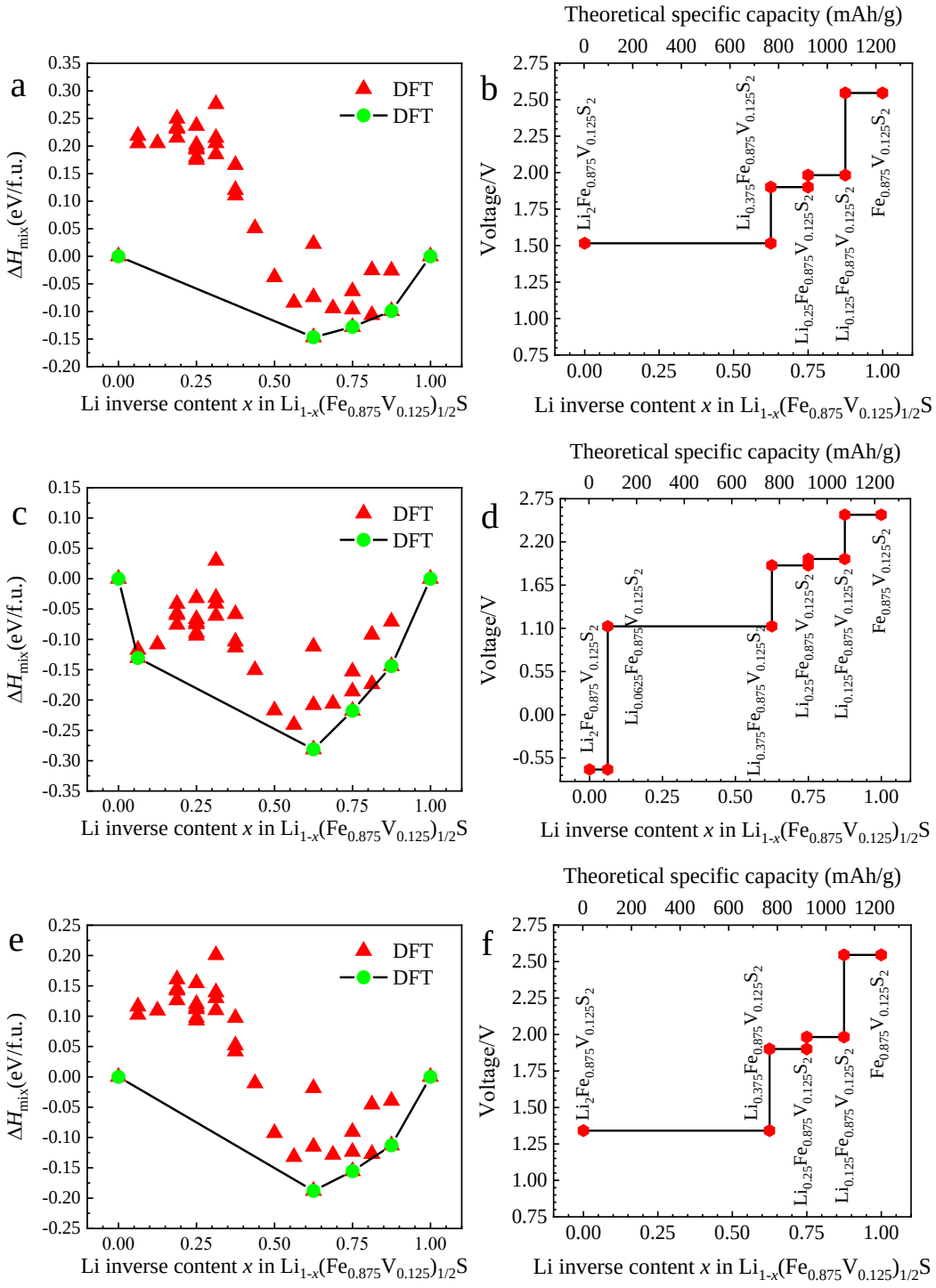

g
h
i
j
m
n
DFT
DFT
ΔH_{mix}(eV/f.u.)
Voltage/V
Theoretical specific capacity (mAh/g)
0 200 400 600 800 1000 1200
$Li_2Fe_{0.875}Ti_{0.125}S_2$
$Li_{1.875}Fe_{0.875}Ti_{0.125}S_2$
$Li_{0.75}Fe_{0.875}Ti_{0.125}S_2$
$Li_{0.125}Fe_{0.875}Ti_{0.125}S_2$
$Fe_{0.875}Ti_{0.125}S_2$
Li inverse content x in $Li_{1-x}(Fe_{0.875}Ti_{0.125})_{1/2}S$

Figure S3. The formation energy of mixing enthalpy of $Li_{1-x}(Fe_{0.875}V_{0.125})_{1/2}S$ with different *Ibam* (a), *Immm* (c), *P*3*m*1 (e), $P\bar{3}m1$ (g), $P2_1/c$ (i) and *P*42*mcm* (m) is a function of Li concentration; the voltage of $Li_{1-x}(Fe_{0.875}V_{0.125})_{1/2}S$ with different *Ibam* (b), *Immm* (d), *P*3*m*1 (f), $P\bar{3}m1$ (h), $P2_1/c$ (j) and *P*42*mcm* (n) increases with the increase of theoretical capacity.



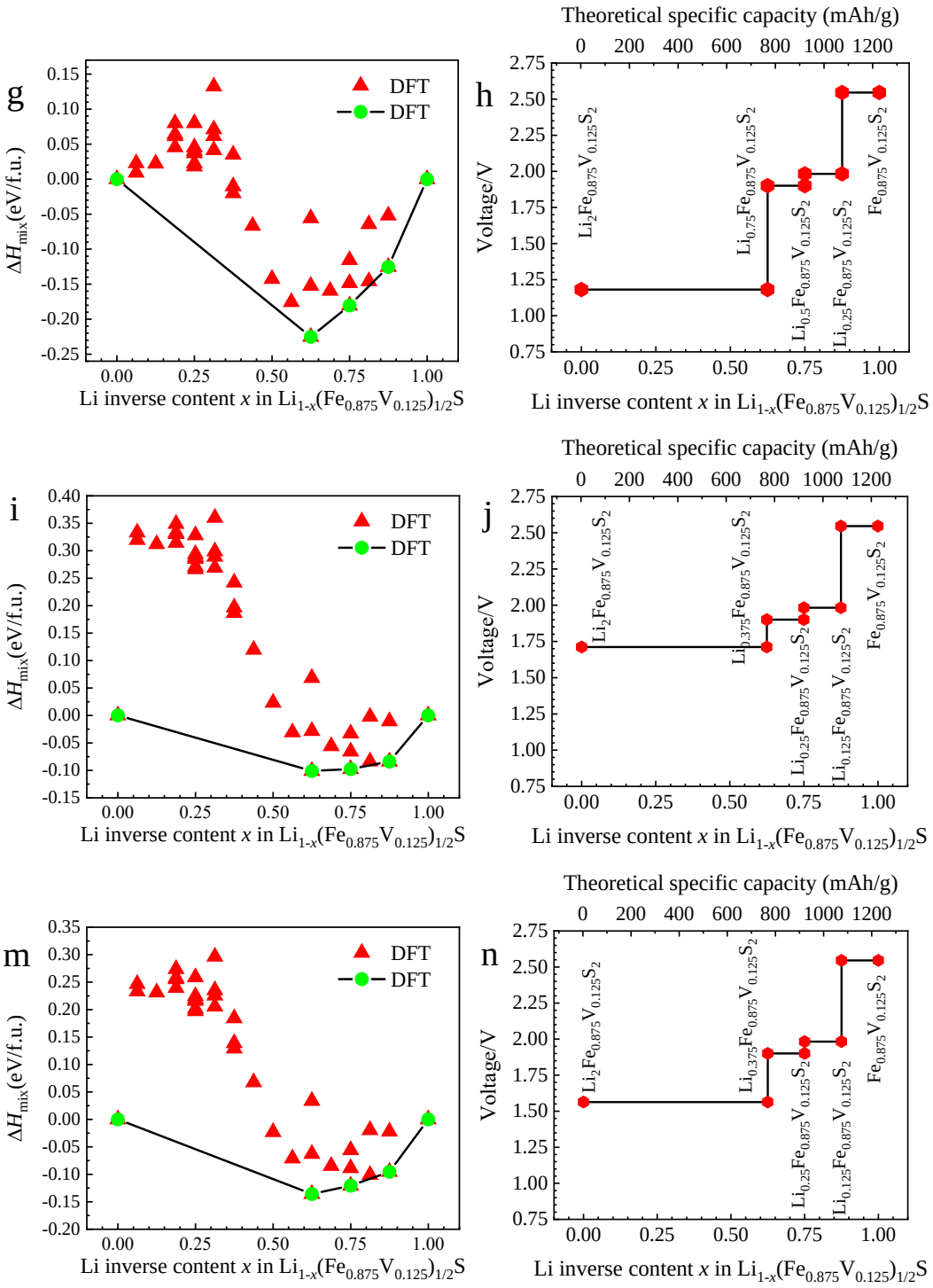

g
h
i
j
m
n
DFT
DFT
ΔH_{mix}(eV/f.u.)
Voltage/V
Theoretical specific capacity (mAh/g)
0 200 400 600 800 1000 1200
$Li_2Fe_{0.875}V_{0.125}S_2$
$Li_{0.75}Fe_{0.875}V_{0.125}S_2$
$Li_{0.5}Fe_{0.875}V_{0.125}S_2$
$Li_{0.25}Fe_{0.875}V_{0.125}S_2$
$Fe_{0.875}V_{0.125}S_2$
$Li_2Fe_{0.875}V_{0.125}S_2$
$Li_{0.375}Fe_{0.875}V_{0.125}S_2$
$Li_{0.25}Fe_{0.875}V_{0.125}S_2$
$Li_{0.125}Fe_{0.875}V_{0.125}S_2$
$Fe_{0.875}V_{0.125}S_2$
Li inverse content x in $Li_{1-x}(Fe_{0.875}V_{0.125})_{1/2}S$

Table S4. Lattice parameters and atomic position for $Li_{1-x}(Fe_{0.875}Ti_{0.125})_{1/2}S$

Space group	*a* (Å)	*b*	*c*	*α* (°)	*β*	*γ*
$P\bar{3}m1$	7.5359	7.5359	12.0754	90	90	120
	Atom position					
$Li_2Fe_{0.875}Ti_{0.125}S_2$	Fe1	0.500000000	0.500000000	0.000000000		
	Fe2	0.500000000	0.000000000	0.000000000		
	Fe3	0.000000000	0.500000000	0.000000000		
	Fe4	0.000000000	0.000000000	0.000000000		
	Fe5	0.500000000	0.500000000	0.500000000		
	Fe6	0.500000000	0.000000000	0.500000000		
	Fe7	0.000000000	0.500000000	0.500000000		
	Li1	0.834079981	0.668160021	0.178360000		
	Li2	0.165920019	0.331839979	0.821640015		
	Li3	0.331839979	0.165919960	0.178360000		
	Li4	0.668160021	0.834080040	0.821640015		
	Li5	0.834080040	0.165920019	0.178360000		
	Li6	0.165919960	0.834079981	0.821640015		
	Li7	0.660610020	0.830299973	0.315340012		
	Li8	0.339389980	0.169700027	0.684659958		
	Li9	0.169700027	0.830310047	0.315340012		
	Li10	0.830299973	0.169689953	0.684659958		
	Li11	0.169689953	0.339389980	0.315340012		
	Li12	0.830310047	0.660610020	0.684659958		
	Li13	0.333333373	0.666666687	0.179380000		
	Li14	0.666666627	0.333333313	0.820620000		
	Li15	0.666666687	0.333333373	0.321550012		
	Li16	0.333333313	0.666666627	0.678449988		
	S1	0.832710028	0.665409982	0.887520015		
	S2	0.167289972	0.334590018	0.112479985		
	S3	0.334590018	0.167300045	0.887520015		
	S4	0.665409982	0.832699955	0.112479985		
	S5	0.832699955	0.167289972	0.887520015		
	S6	0.167300045	0.832710028	0.112479985		
	S7	0.837019980	0.674040020	0.386209995		
	S8	0.162980020	0.325959980	0.613790035		
	S9	0.325959980	0.162979960	0.386209995		
	S10	0.674040020	0.837020040	0.613790035		
	S11	0.837020040	0.162980020	0.386209995		
	S12	0.162979960	0.837019980	0.613790035		
	S13	0.333333373	0.666666687	0.884909987		
	S14	0.666666627	0.333333313	0.115090013		
	S15	0.333333373	0.666666687	0.392439991		
	S16	0.666666627	0.333333313	0.607560039		
	Ti1	0.000000000	0.000000000	0.500000000		
Cm	7.49471	7.48775	12.17978	90.00340	90	120.03074
	Atom position					
$Li_{1.875}(Fe_{0.875}Ti_{0.125})_{1/2}S$	Fe1	0.006220	0.006531	0.000753		
	Fe2	0.999644	0.499288	0.996220		
	Fe3	0.500311	0.006531	0.000753		
	Fe4	0.495261	0.490521	0.001115		
	Fe5	0.938234	0.960219	0.503258		

		Fe6	0.999025	0.498051	0.497200	
		Fe7	0.521985	0.960219	0.503258	
		Li1	0.823272	0.676340	0.816541	
		Li2	0.817713	0.135426	0.808488	
		Li3	0.666772	0.327516	0.680880	
		Li4	0.353068	0.676340	0.816541	
		Li5	0.173978	0.847956	0.673712	
		Li6	0.336503	0.173008	0.815816	
		Li7	0.160743	0.327516	0.680880	
		Li8	0.845004	0.666962	0.312759	
		Li9	0.666385	0.832767	0.170354	
		Li10	0.838691	0.177383	0.321953	
		Li11	0.665229	0.334926	0.185383	
		Li12	0.321960	0.666962	0.312759	
		Li13	0.167718	0.835436	0.182589	
		Li14	0.331281	0.162562	0.327213	
		Li15	0.169698	0.334926	0.185383	
		S1	0.837595	0.664394	0.112354	
		S2	0.665921	0.831841	0.905290	
		S3	0.837191	0.174382	0.116607	
		S4	0.671797	0.332512	0.884906	
		S5	0.326800	0.664394	0.112354	
		S6	0.167448	0.834896	0.883324	
		S7	0.333502	0.167004	0.114647	
		S8	0.160714	0.332512	0.884906	
		S9	0.825891	0.667832	0.617553	
		S10	0.662228	0.824455	0.373286	
		S11	0.831237	0.162474	0.607702	
		S12	0.666455	0.342169	0.390339	
		S13	0.341943	0.667832	0.617553	
		S14	0.166273	0.832544	0.396835	
		S15	0.342485	0.184970	0.607964	
		S16	0.175714	0.342169	0.390339	
		Ti1	0.518415	0.536830	0.505578	
Cm	6.64332	6.72032	12.56177	90	78.21938	120.38419
			Atom position			
		Fe1	0.933420	0.972605	0.009684	
		Fe2	0.933420	0.460815	0.009684	
		Fe3	0.478210	0.989105	0.002973	
		Fe4	0.484065	0.492032	0.001250	
		Fe5	0.999532	0.987758	0.497122	
		Fe6	0.999532	0.511773	0.497122	
		Fe7	0.550615	0.025307	0.494937	
		Li1	0.103324	0.801661	0.734841	
$Li_{0.75}(Fe_{0.875}Ti_{0.125})_{1/2}S$		Li2	0.102895	0.301447	0.729379	
		Li3	0.017014	0.258507	0.244112	
		Li4	0.466682	0.725909	0.256293	
		Li5	0.012186	0.756092	0.244453	
		Li6	0.466681	0.240771	0.256293	
		S1	0.735724	0.617861	0.115573	
		S2	0.681681	0.843651	0.898259	
		S3	0.724080	0.112041	0.119190	
		S4	0.681680	0.338029	0.898259	

		S5	0.244583	0.620014	0.102603	
		S6	0.162257	0.831128	0.917398	
		S7	0.244582	0.124567	0.102603	
		S8	0.172243	0.336121	0.912581	
		S9	0.807151	0.653575	0.619333	
		S10	0.762204	0.890456	0.375879	
		S11	0.815875	0.157938	0.598778	
		S12	0.762203	0.371747	0.375879	
		S13	0.298212	0.660719	0.594793	
		S14	0.250610	0.875304	0.396509	
		S15	0.298211	0.137492	0.594793	
		S16	0.226145	0.363072	0.399310	
		Ti1	0.572867	0.536434	0.494838	
Cm	6.45880	6.31241	12.90679	90.33601	90	120.77020
			Atom position			
$Li_{0.125}(Fe_{0.875}Ti_{0.125})_{1/2}S$		Fe1	0.975268	0.952891	0.995568	
		Fe2	0.023410	0.546820	0.996876	
		Fe3	0.477623	0.952891	0.995568	
		Fe4	0.522435	0.544871	0.998691	
		Fe5	0.987341	0.015468	0.509253	
		Fe6	0.986926	0.473853	0.507206	
		Fe7	0.528127	0.015468	0.509253	
		Li1	0.313123	0.126245	0.269154	
		S1	0.833707	0.664660	0.109255	
		S2	0.666913	0.833825	0.884570	
		S3	0.833496	0.166992	0.081029	
		S4	0.667709	0.335125	0.910557	
		S5	0.330954	0.664660	0.109255	
		S6	0.168634	0.837266	0.883998	
		S7	0.332286	0.164572	0.081639	
		S8	0.167415	0.335125	0.910557	
		S9	0.850868	0.674518	0.612766	
		S10	0.677411	0.854820	0.393412	
		S11	0.834969	0.169940	0.621511	
		S12	0.674662	0.327274	0.392700	
		S13	0.323652	0.674518	0.612766	
		S14	0.170058	0.840115	0.418967	
		S15	0.327251	0.154503	0.612994	
		S16	0.152612	0.327274	0.392700	
		Ti1	0.503453	0.506906	0.505098	

Table S5. Lattice parameters and atomic position for $Li_{1-x}(Fe_{0.875}V_{0.125})_{1/2}S$

Space group	a	b	c	α	β	γ
$P\bar{3}m1$	7.5258	7.5258	12.0294	90	90	120
	Atom position					
$Li_2Fe_{0.875}V_{0.125}S_2$	Fe1	0.500000000	0.500000000	0.000000000		
	Fe2	0.500000000	0.000000000	0.000000000		
	Fe3	0.000000000	0.500000000	0.000000000		
	Fe4	0.500000000	0.500000000	0.500000000		
	Fe5	0.500000000	0.000000000	0.500000000		
	Fe6	0.000000000	0.500000000	0.500000000		
	Fe7	0.000000000	0.000000000	0.500000000		
	Li1	0.831239998	0.662479997	0.184000000		
	Li2	0.168760002	0.337520003	0.815999985		
	Li3	0.337520003	0.168760002	0.184000000		
	Li4	0.662479997	0.831239998	0.815999985		
	Li5	0.831239998	0.168760002	0.184000000		
	Li6	0.168760002	0.831239998	0.815999985		
	Li7	0.668760002	0.834380031	0.320719987		
	Li8	0.331239998	0.165619999	0.679280043		
	Li9	0.165619999	0.834380031	0.320719987		
	Li10	0.834380031	0.165619999	0.679280043		
	Li11	0.165619999	0.331239998	0.320719987		
	Li12	0.834380031	0.668760002	0.679280043		
	Li13	0.333333373	0.666666687	0.175760001		
	Li14	0.666666627	0.333333313	0.824239969		
	Li15	0.666666687	0.333333343	0.320239991		
	Li16	0.333333313	0.666666627	0.679759979		
	S1	0.838419974	0.676840007	0.888870001		
	S2	0.161580026	0.323159993	0.111129999		
	S3	0.323159993	0.161579967	0.888870001		
	S4	0.676840007	0.838420033	0.111129999		
	S5	0.838420033	0.161580026	0.888870001		
	S6	0.161579967	0.838419974	0.111129999		
	S7	0.832669973	0.665349960	0.387620002		
	S8	0.167330027	0.334650010	0.612380028		
	S9	0.334650010	0.167319983	0.387620002		
	S10	0.665349960	0.832679987	0.612380028		
	S11	0.832679987	0.167330027	0.387620002		
	S12	0.167319983	0.832669973	0.612380028		
	S13	0.333333373	0.666666687	0.891240001		
	S14	0.666666627	0.333333313	0.108759999		
	S15	0.333333373	0.666666687	0.383459985		
	S16	0.666666627	0.333333313	0.616540015		
	Ti1	0.000000000	0.000000000	0.000000000		
$C2$	6.70890	6.59793	11.77052	90.55140	90	120.55796
	Atom position					
$Li_{0.75}(Fe_{0.875}V_{0.125})_{1/2}S$	Fe1	0.013527	1.000000	0.000000		
	Fe2	0.477290	0.463676	0.006250		
	Fe3	0.013615	0.536324	0.993750		
	Fe4	0.995452	0.000000	0.500000		
	Fe5	0.468747	0.478895	0.501288		
	Fe6	0.989852	0.521105	0.498712		

		Fe7	0.463237	0.000000	0.500000	
		Li1	0.503136	0.004249	0.747193	
		Li2	0.961172	0.005961	0.748951	
		Li3	0.498424	0.507848	0.755684	
		Li4	0.498886	0.995752	0.252807	
		Li5	0.990576	0.492152	0.244316	
		Li6	0.955212	0.994039	0.251049	
		S1	0.308904	0.165561	0.127959	
		S2	0.143344	0.834440	0.872041	
		S3	0.818444	0.662501	0.100870	
		S4	0.667977	0.339879	0.892548	
		S5	0.328098	0.660122	0.107452	
		S6	0.155943	0.337499	0.899130	
		S7	0.829712	0.177810	0.094701	
		S8	0.651902	0.822190	0.905299	
		S9	0.310586	0.162655	0.616901	
		S10	0.147932	0.837346	0.383099	
		S11	0.805751	0.663925	0.602158	
		S12	0.653328	0.337056	0.396357	
		S13	0.316272	0.662945	0.603643	
		S14	0.141826	0.336075	0.397842	
		S15	0.815900	0.173118	0.594296	
		S16	0.642782	0.826882	0.405704	
		V1	0.435289	0.000000	0.000000	
*C*2	6.60466	6.42753	12.22412	90.36223	90	120.91589
			Atom position			
$Li_{0.5}(Fe_{0.875}V_{0.125})_{1/2}S$		Fe1	0.018225	1.000000	0.000000	
		Fe2	0.468200	0.451352	0.007567	
		Fe3	0.016848	0.548648	0.992433	
		Fe4	0.035706	1.000000	0.500000	
		Fe5	0.485387	0.456577	0.505667	
		Fe6	0.028810	0.543423	0.494333	
		Fe7	0.489539	0.000000	0.500000	
		Li1	0.990685	0.483494	0.743413	
		Li2	0.519300	0.526618	0.758429	
		Li3	0.992682	0.473382	0.241571	
		Li4	0.507191	0.516506	0.256587	
		S1	0.307986	0.148640	0.128285	
		S2	0.159347	0.851361	0.871715	
		S3	0.815669	0.659189	0.100574	
		S4	0.670252	0.342891	0.893170	
		S5	0.327362	0.657110	0.106830	
		S6	0.156480	0.340811	0.899426	
		S7	0.836514	0.182837	0.088357	
		S8	0.653676	0.817163	0.911643	
		S9	0.338018	0.149339	0.619331	
		S10	0.188679	0.850662	0.380669	
		S11	0.831029	0.661247	0.601051	
		S12	0.683287	0.338278	0.395804	
		S13	0.345009	0.661723	0.604196	
		S14	0.169782	0.338753	0.398949	
		S15	0.851194	0.178745	0.588058	
		S16	0.672449	0.821255	0.411942	

		V1	0.443810	0.000000	1.000000		
*C*2	6.49310	6.28227	13.03767	89.03111	90	121.11646	
	Atom position						
$Li_{0.25}(Fe_{0.875}V_{0.125})_{1/2}S$		Fe1	0.031964	1.000000	0.000000		
		Fe2	0.464327	0.438343	0.008413		
		Fe3	0.025984	0.561657	0.991587		
		Fe4	0.031452	1.000000	0.500000		
		Fe5	0.474333	0.445079	0.502826		
		Fe6	0.029254	0.554921	0.497174		
		Fe7	0.472053	0.000000	0.500000		
		Li1	0.697432	0.859633	0.734688		
		Li2	0.837799	0.140367	0.265312		
		S1	0.311177	0.140185	0.124265		
		S2	0.170992	0.859816	0.875735		
		S3	0.813727	0.649949	0.094979		
		S4	0.677148	0.352051	0.896957		
		S5	0.325097	0.647950	0.103044		
		S6	0.163778	0.350051	0.905021		
		S7	0.843402	0.181553	0.083070		
		S8	0.661849	0.818447	0.916930		
		S9	0.323680	0.143879	0.615007		
		S10	0.179802	0.856122	0.384993		
		S11	0.814872	0.652833	0.597355		
		S12	0.688232	0.346212	0.401902		
		S13	0.342019	0.653789	0.598098		
		S14	0.162039	0.347167	0.402645		
		S15	0.837294	0.171505	0.584562		
		S16	0.665789	0.828495	0.415438		
		V1	0.451188	0.000000	1.000000		

Figure S4. Partial density of states for $Li_2Fe_{0.875}Ti_{0.125}S_2$ (a), $Li_{1.875}Fe_{0.875}Ti_{0.125}S_2$ (b), $Li_{0.75}Fe_{0.875}Ti_{0.125}S_2$ (c), $Li_{0.125}Fe_{0.875}Ti_{0.125}S_2$ (d) and $Fe_{0.875}Ti_{0.125}S_2$ (e); charge distribution of Fe and Ti atoms (f).

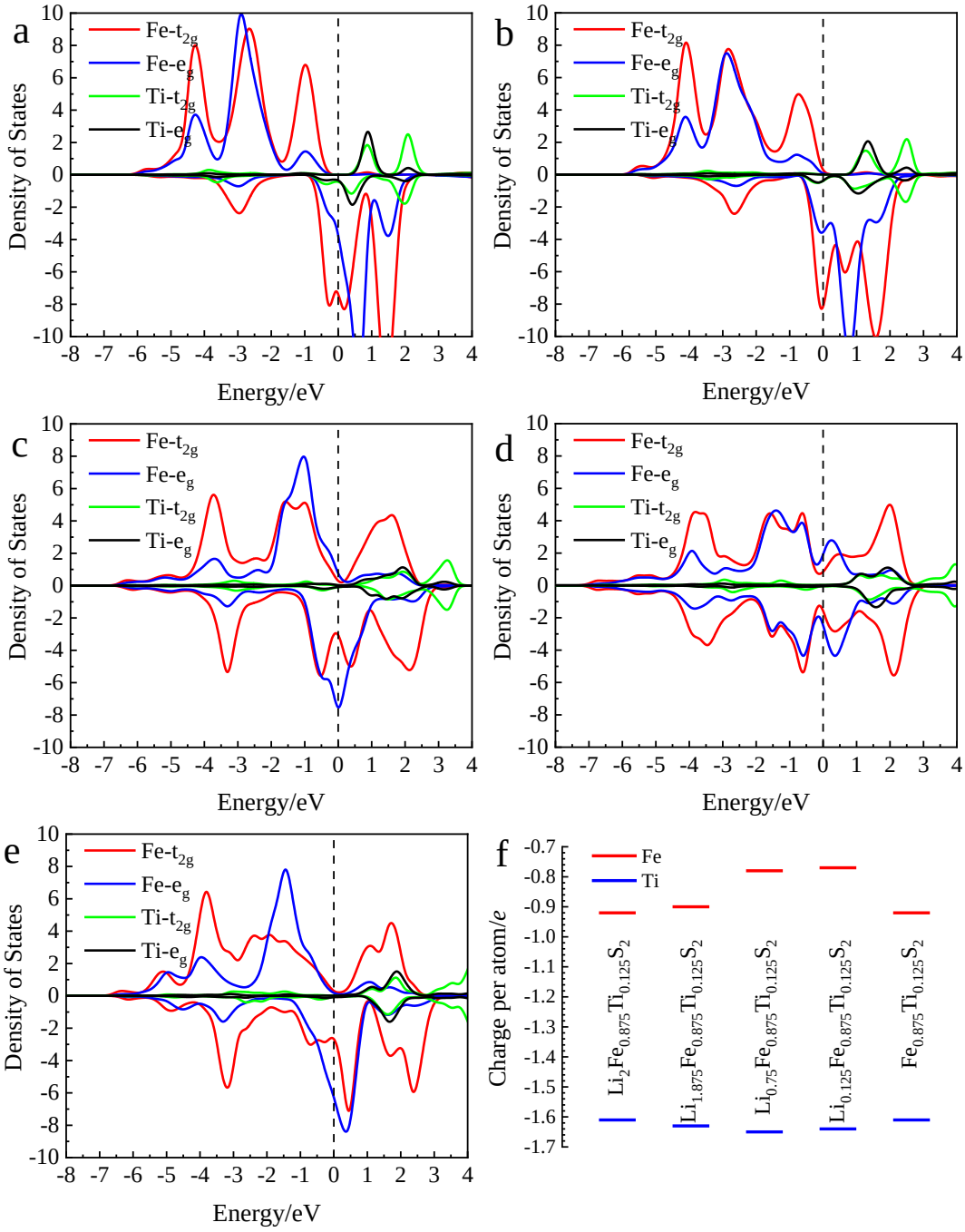


Figure S5. Partial density of states for $Li_2Fe_{0.875}V_{0.125}S_2$ (a), $Li_{0.75}Fe_{0.875}V_{0.125}S_2$ (b), $Li_{0.5}Fe_{0.875}V_{0.125}S_2$ (c), $Li_{0.25}Fe_{0.875}V_{0.125}S_2$ (d), and $Fe_{0.875}V_{0.125}S_2$ (e); charge distribution of Fe and V atoms (f).

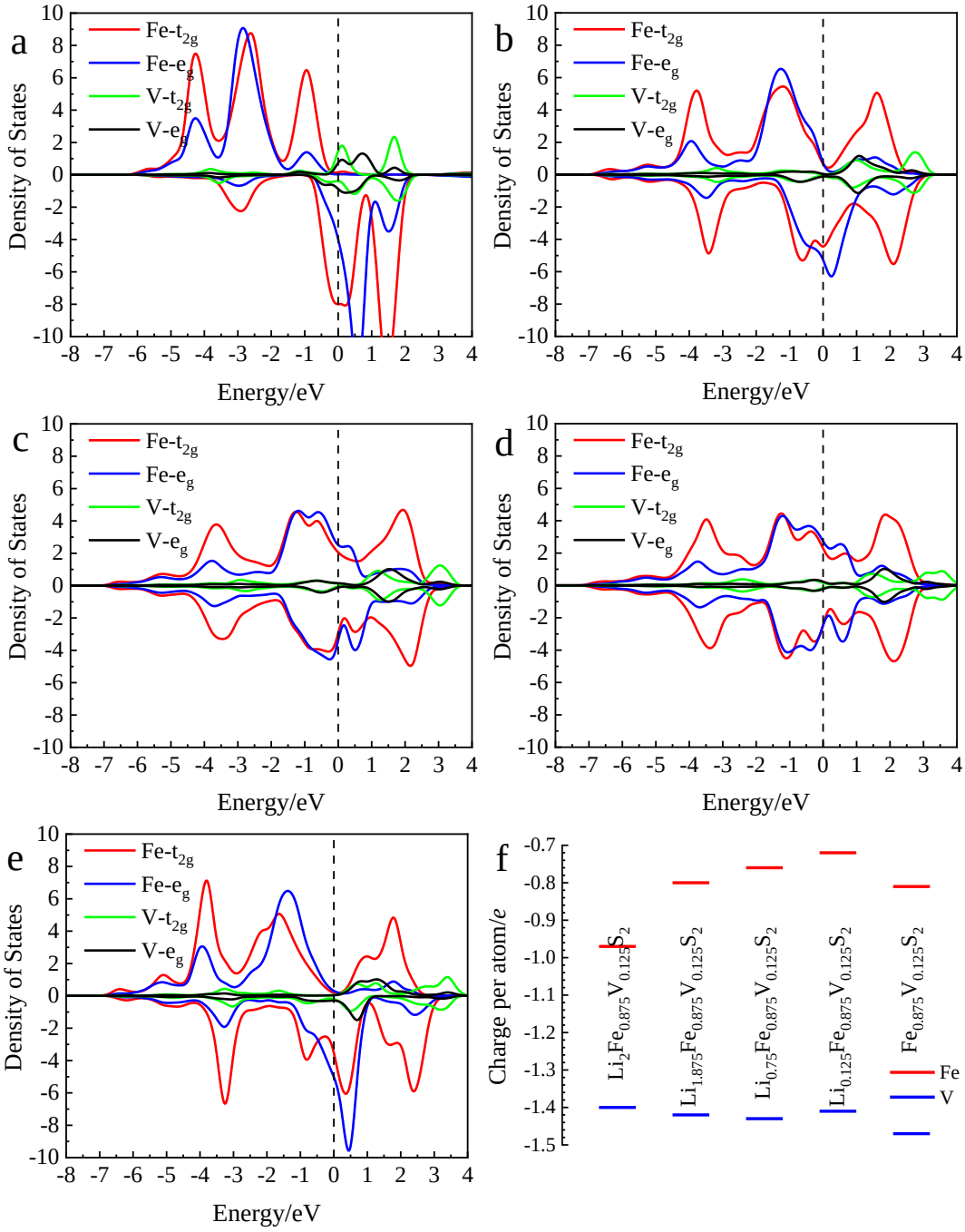


Figure S6. Li diffusion paths in $Li_2Fe_{0.875}Ti_{0.125}S_2$ (a) and $Li_2Fe_{0.875}V_{0.125}S_2$ (b) bulks (1-6 is for Li1-Li6.)

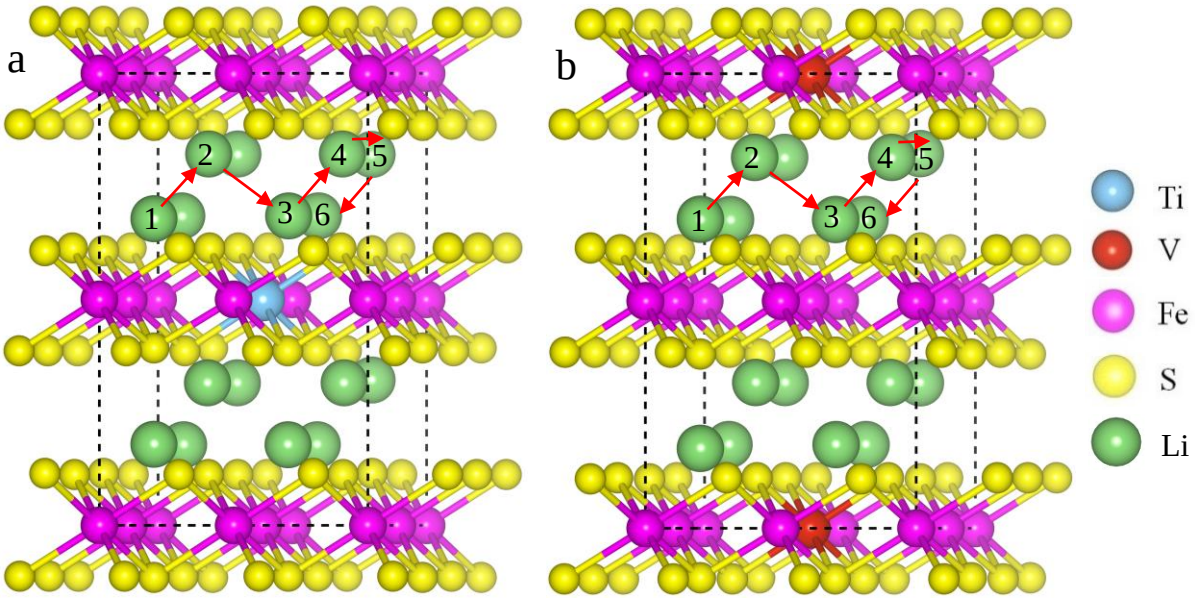


Figure S7. The structures for Li_2FeS_2(100) (a), Li_2FeS_2(110) (b), Li_2FeS_2(001) (c), Li_2FeS_2(002) (d), $Li_2Fe_{0.875}Ti_{0.125}S_2$(002) (e) and $Li_2Fe_{0.875}V_{0.125}S_2$(002) (f)

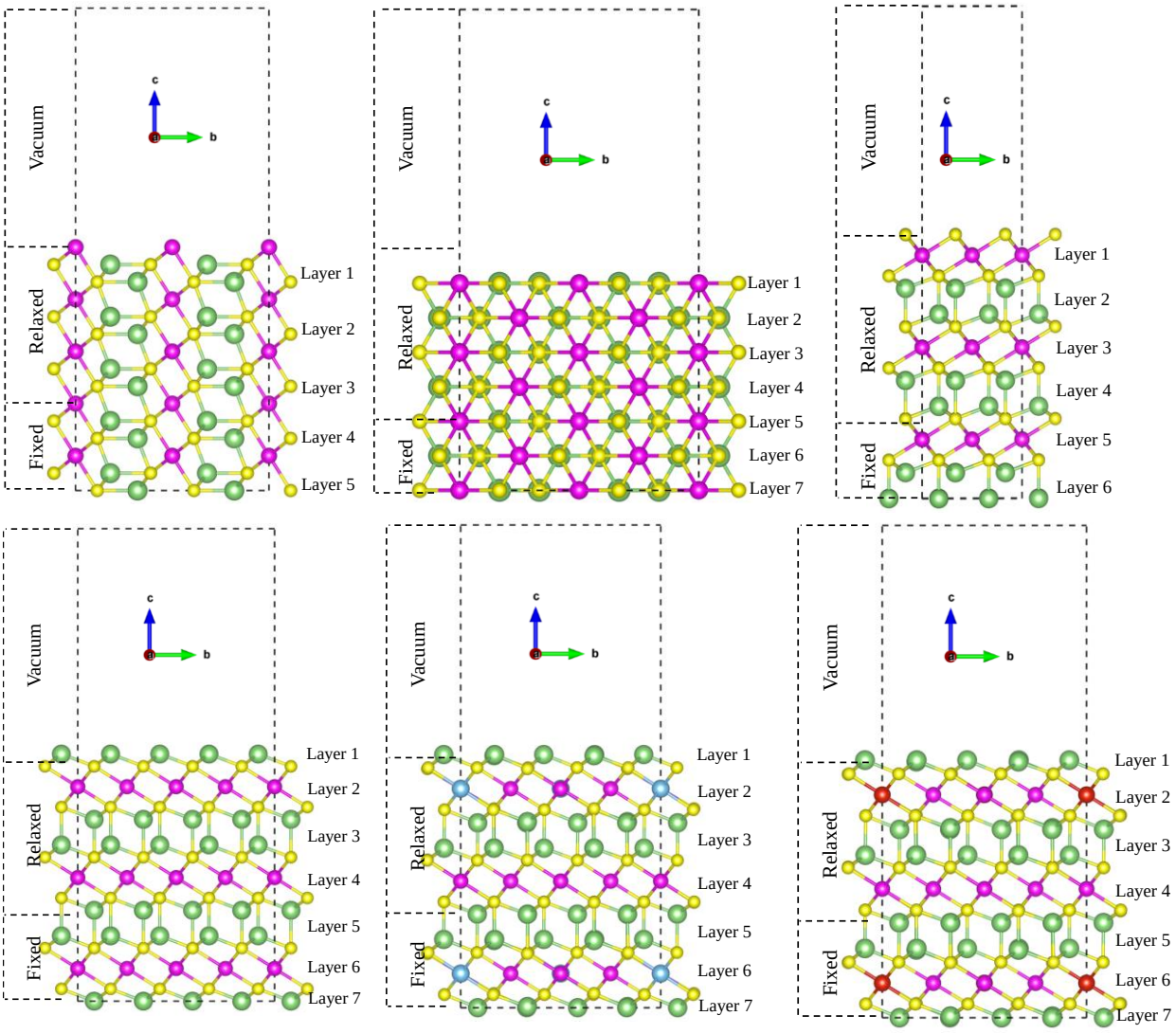


Figure S8. The structures for Li_2S_2-Li_2FeS_2(002) (a), Li_3S_2-Li_2FeS_2(002) (b), LiS-Li_2FeS_2(002) (c) and Li_2S-Li_2FeS_2(002) (d)

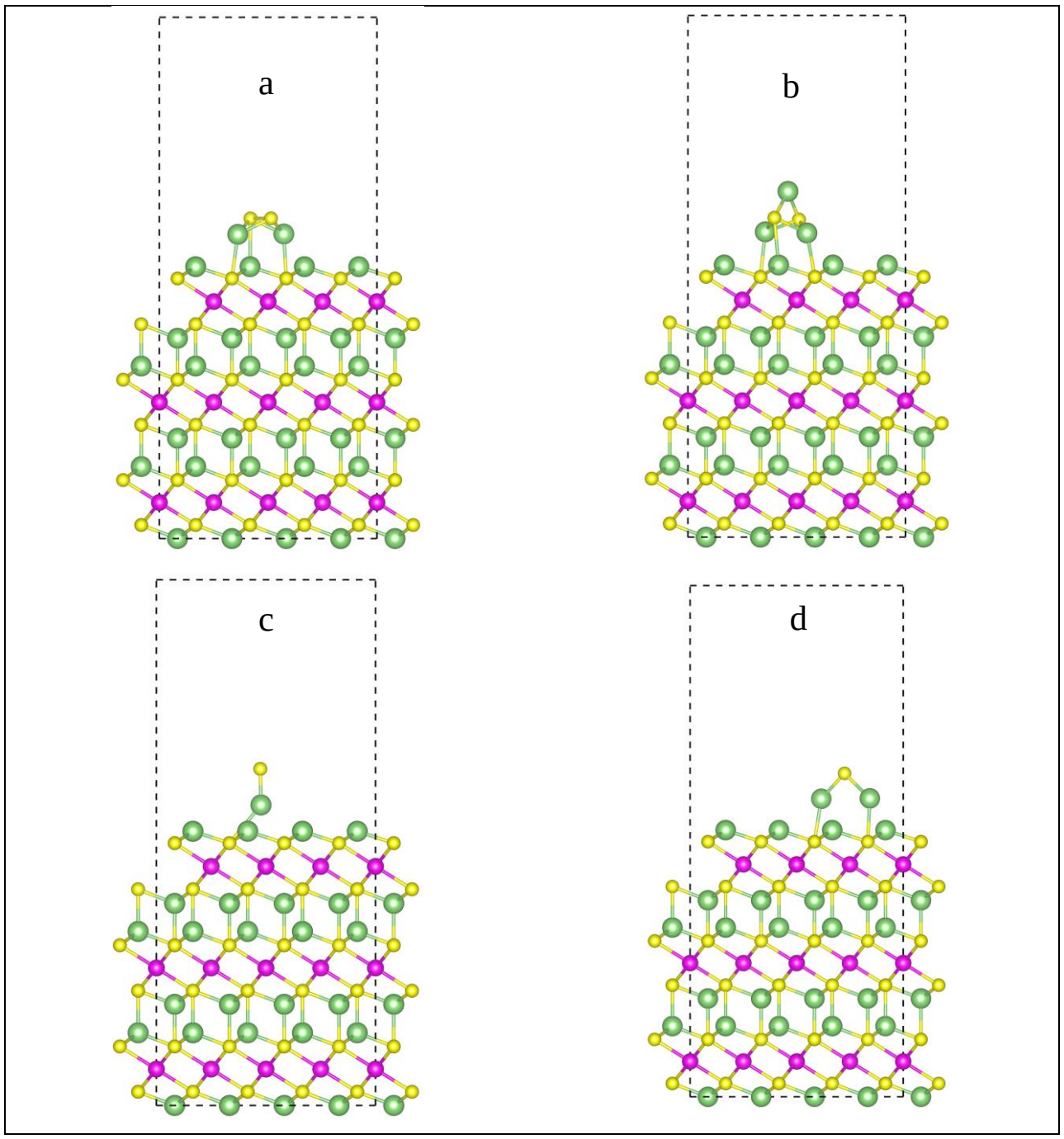


Figure S9. The structures for Li_2S_2-$Li_2Fe_{0.875}Ti_{0.125}S_2$(002) (a), Li_3S_2-$Li_2Fe_{0.875}Ti_{0.125}S_2$(002) (b), LiS-$Li_2Fe_{0.875}Ti_{0.125}S_2$(002) (c) and Li_2S-$Li_2Fe_{0.875}Ti_{0.125}S_2$(002) (d)

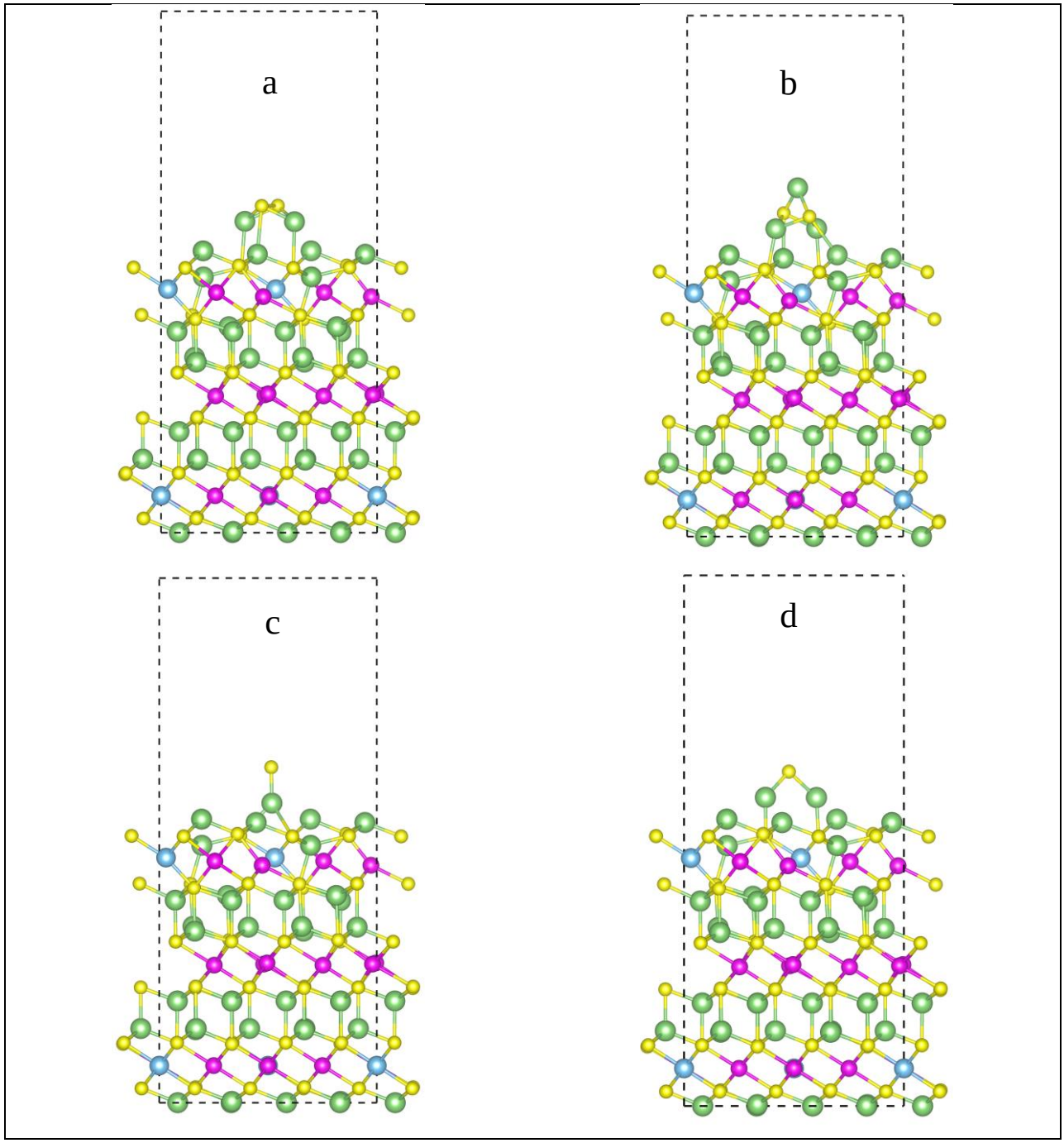


Figure S10. The structures for Li_2S_2-$Li_2Fe_{0.875}V_{0.125}S_2$(002) (a), Li_3S_2-$Li_2Fe_{0.875}V_{0.125}S_2$(002) (b), LiS-$Li_2Fe_{0.875}V_{0.125}S_2$(002) (c) and Li_2S-$Li_2Fe_{0.875}V_{0.125}S_2$(002) (d)

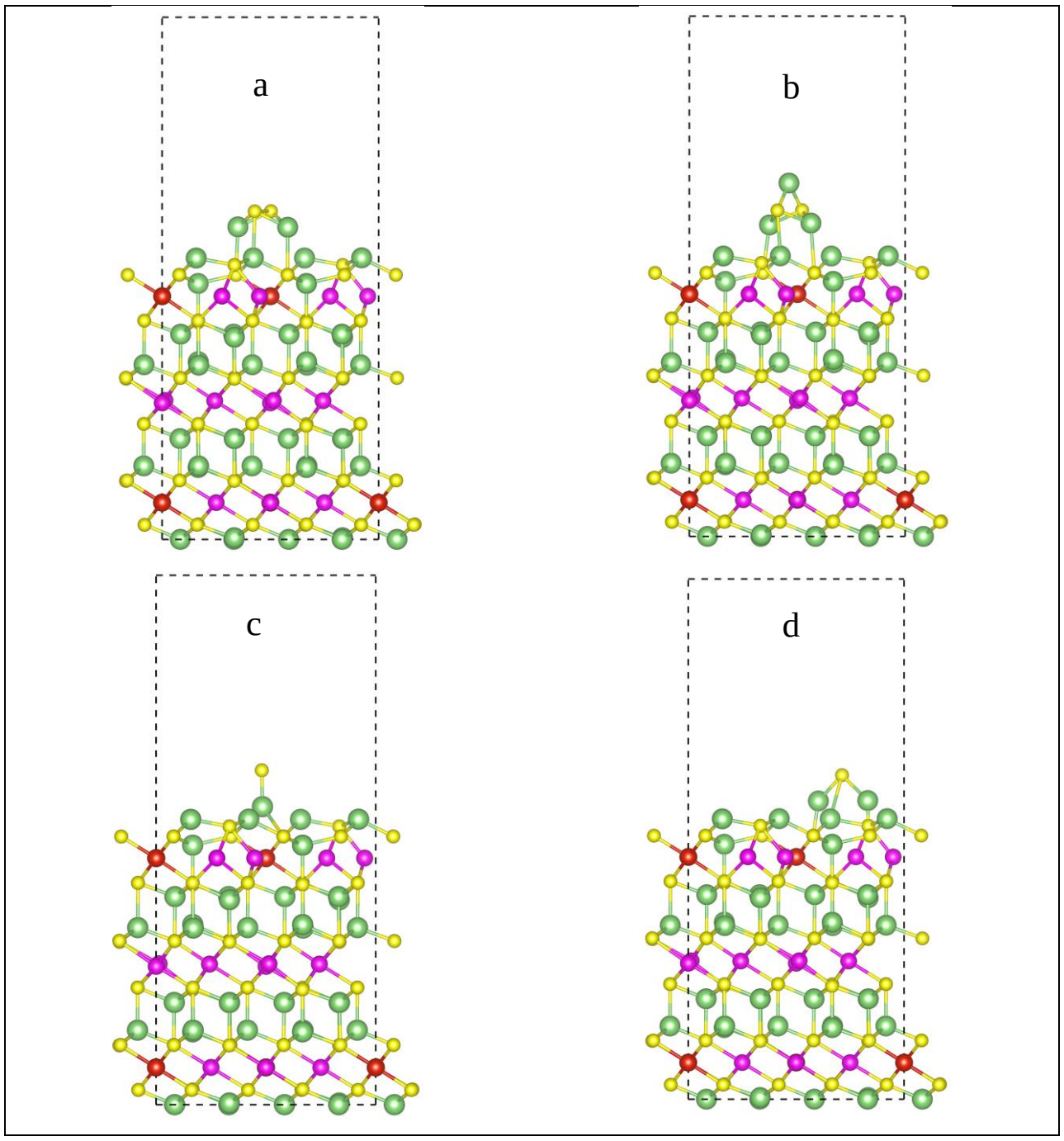


Figure S11. Li_2S decomposition paths on Li_2FeS_2(002) (a), $Li_2Fe_{0.875}Ti_{0.125}S_2$(002) (b) and $Li_2Fe_{0.875}V_{0.125}S_2$(002).