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

"Supporting Information"

Insights into Electrochemical Properties of Li_2FeS_2 after FeS_2 Discharging

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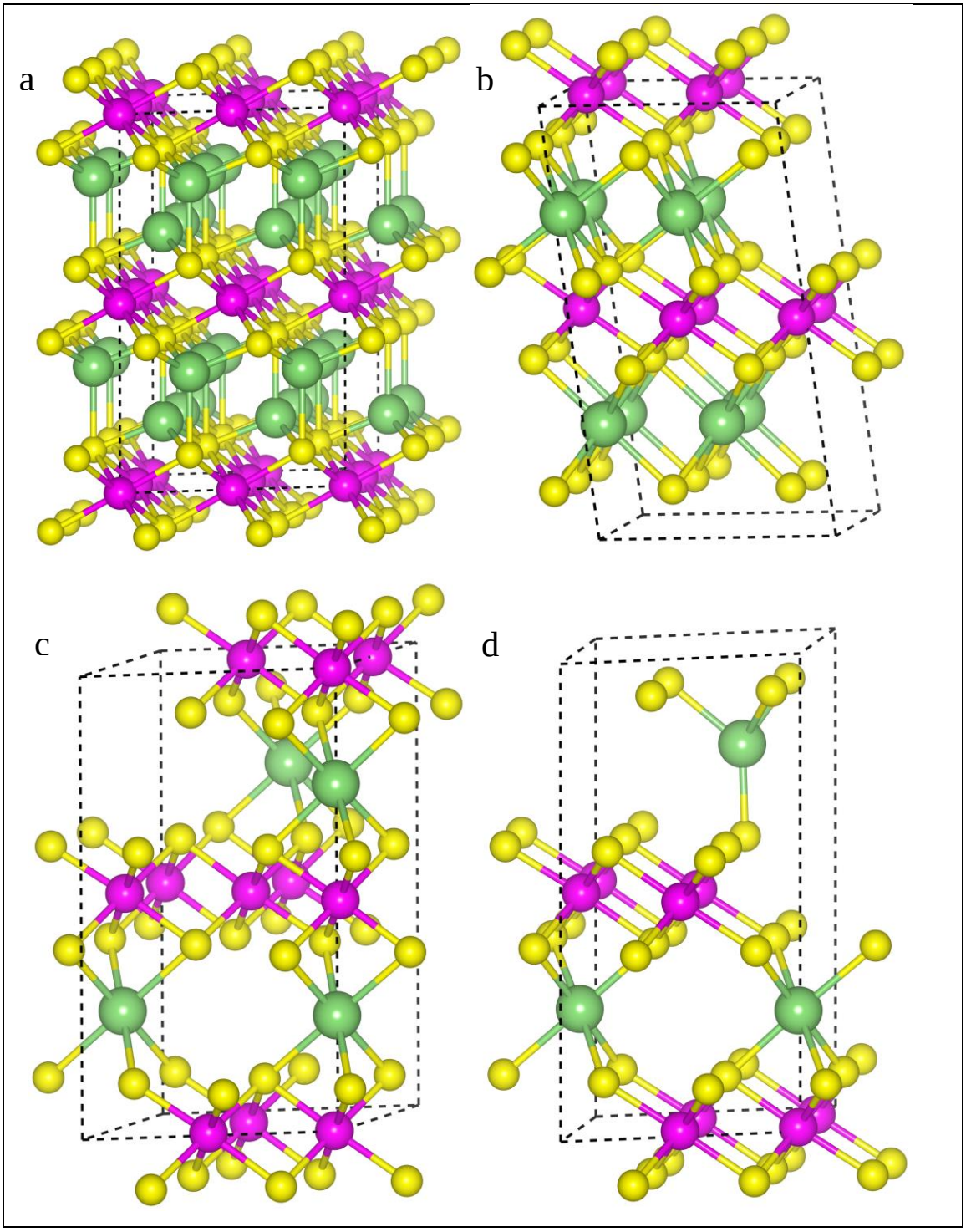
Figure S1 Relaxed crystal structure for Li_2FeS_2 (a), $LiFeS_2$ (b), $Li_{0.5}FeS_2$ (c), $Li_{0.375}FeS_2$ (d), $Li_{0.25}FeS_2$ (e), and FeS_2 (f) (yellow represents S atom, pink represents Fe atom, and green is for Li atom).



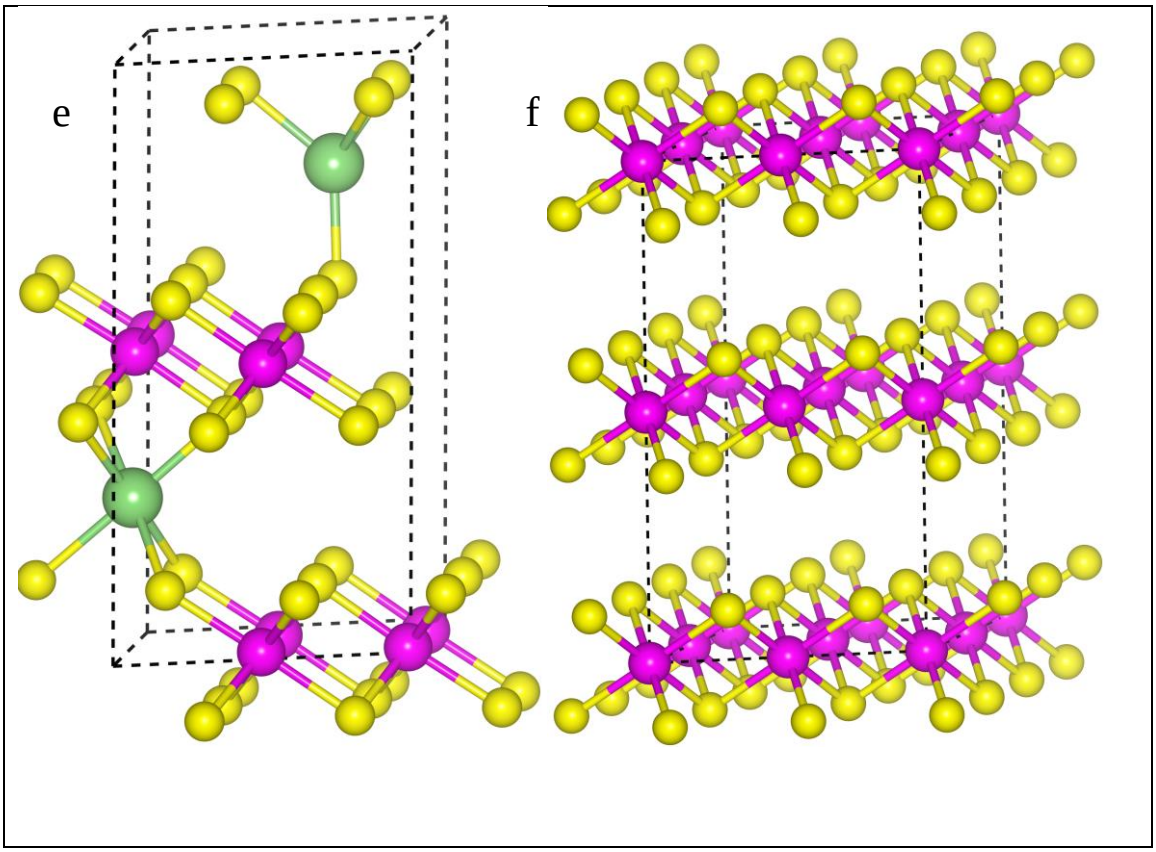

e
f

Table S1 Crystal structure parameters and atomic position information for $Li_{1-x}Fe_{0.5}S$

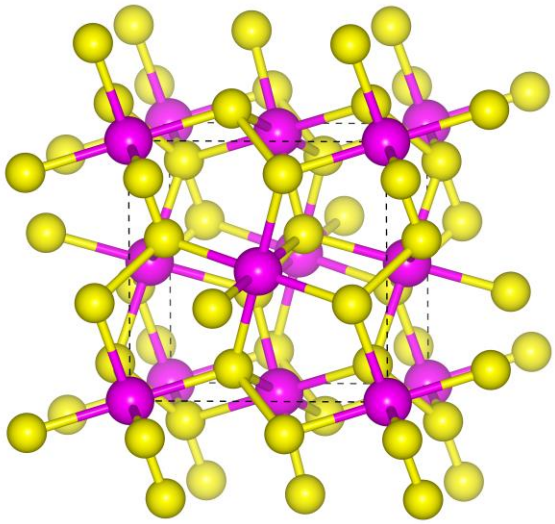
Space group	*a*	*b*	*c*	*α*	*β*	*γ*
P-1 (*C*1-1)	6.70973	6.71186	11.72047	97.36578	90.59246	118.61884
			Atom position			
$LiFeS_2$		Li1	0.484309	0.030549	0.749280	
		Li2	0.237871	0.027700	0.248394	
		Li3	0.984581	0.529524	0.749228	
		Li4	0.982723	0.033212	0.750727	
		Li5	0.732116	0.532706	0.250707	
		Li6	0.231491	0.528659	0.250121	
		Li7	0.483264	0.534016	0.750696	
		Li8	0.739117	0.033855	0.250877	
		S1	0.376730	0.314265	0.105408	
		S2	0.674963	0.910312	0.892132	
		S3	0.876772	0.814158	0.105430	
		S4	0.175054	0.410221	0.892117	
		S5	0.876460	0.314493	0.106173	
		S6	0.175248	0.909488	0.891912	
		S7	0.293161	0.153050	0.608166	
		S8	0.591361	0.748339	0.394008	
		S9	0.793320	0.652968	0.608103	
		S10	0.092505	0.247849	0.393927	
		S11	0.793453	0.152291	0.607817	
		S12	0.091892	0.748274	0.394524	
		S13	0.675504	0.409609	0.891857	
		S14	0.377680	0.813920	0.105973	
		S15	0.591924	0.248257	0.394558	
		S16	0.293555	0.652444	0.607854	
		Fe1	0.025613	0.112133	-0.001776	
		Fe2	0.525993	0.611806	0.998012	
		Fe3	0.026142	0.611966	0.998539	
		Fe4	0.525754	0.111818	0.998463	
		Fe5	0.942659	0.950465	0.501534	
		Fe6	0.443009	0.450749	0.501626	
		Fe7	0.943087	0.450279	0.501726	
		Fe8	0.442693	0.950624	0.501888	
*C*2 (*C*2-3)	6.77678	6.77678	12.05878	89.49691	90.50309	120.01967
			Atom position			
$Li_{0.5}FeS_2$		Li1	0.997924	0.997758	0.750003	
		Li2	0.997757	0.997923	0.249997	
		Li3	0.002506	0.499865	0.749873	
		Li4	0.499866	0.002507	0.250127	
		S1	0.314421	0.147623	0.105481	
		S2	0.656855	0.819311	0.890484	
		S3	0.819310	0.656854	0.109516	
		S4	0.147624	0.314422	0.894519	
		S5	0.822442	0.146994	0.108414	
		S6	0.146995	0.822443	0.891586	
		S7	0.343012	0.180982	0.609579	
		S8	0.685124	0.852792	0.394720	
		S9	0.852792	0.685123	0.605280	

		S10	0.180983	0.343013	0.390421	
		S11	0.853209	0.177597	0.608391	
		S12	0.177598	0.853210	0.391609	
		S13	0.654862	0.323783	0.896926	
		S14	0.323782	0.654861	0.103074	
		S15	0.676705	0.345625	0.396914	
		S16	0.345624	0.676704	0.603086	
		Fe1	0.979312	0.979312	0.000000	
		Fe2	0.490200	0.490200	-0.000000	
		Fe3	0.983846	0.488250	0.004285	
		Fe4	0.488250	0.983846	0.995714	
		Fe5	0.020540	0.020540	0.500000	
		Fe6	0.509942	0.509942	0.500000	
		Fe7	0.016721	0.511799	0.495601	
		Fe8	0.511799	0.016721	0.504399	
CM (*CS*-3)	6.78089	6.74430	12.50521	89.84618	90	120.17960
			Atom position			
		Li1	0.996210	0.992419	0.253119	
		Li2	0.329878	0.659754	0.783288	
		Li3	0.503545	0.007090	0.251925	
		S1	0.325627	0.155239	0.112296	
		S2	0.667125	0.832654	0.907907	
		S3	0.832731	0.665463	0.113448	
		S4	0.163253	0.326506	0.909865	
		S5	0.829612	0.155239	0.112296	
		S6	0.165528	0.832654	0.907907	
		S7	0.336513	0.171763	0.594682	
		S8	0.668938	0.842149	0.390213	
		S9	0.833119	0.666238	0.592760	
		S10	0.169777	0.339553	0.390306	
$Li_{0.375}FeS_2$		S11	0.835249	0.171763	0.594682	
		S12	0.173211	0.842149	0.390213	
		S13	0.664815	0.329630	0.908254	
		S14	0.331813	0.663627	0.113134	
		S15	0.669951	0.339902	0.390619	
		S16	0.336193	0.672387	0.590585	
		Fe1	0.995389	0.990778	0.008655	
		Fe2	0.500409	0.497624	0.011802	
		Fe3	-0.002784	0.497624	0.011802	
		Fe4	0.496568	0.993136	0.008511	
		Fe5	0.003793	0.007584	0.494497	
		Fe6	0.501791	0.500349	0.491386	
		Fe7	-0.001442	0.500349	0.491386	
		Fe8	0.506520	0.013040	0.494875	
CM (*CS*-3)	6.78089	6.74430	12.50521	89.84618	90	120.17960
			Atom position			
		Li1	0.329878	0.659754	0.783288	
		Li2	0.503545	0.007090	0.251925	
		S1	0.325627	0.155239	0.112296	
$Li_{0.25}FeS_2$		S2	0.667125	0.832654	0.907907	
		S3	0.832731	0.665463	0.113448	
		S4	0.163253	0.326506	0.909865	
		S5	0.829612	0.155239	0.112296	

		S6	0.165528	0.832654	0.907907	
		S7	0.336513	0.171763	0.594682	
		S8	0.668938	0.842149	0.390213	
		S9	0.833119	0.666238	0.592760	
		S10	0.169777	0.339553	0.390306	
		S11	0.835249	0.171763	0.594682	
		S12	0.173211	0.842149	0.390213	
		S13	0.664815	0.329630	0.908254	
		S14	0.331813	0.663627	0.113134	
		S15	0.669951	0.339902	0.390619	
		S16	0.336193	0.672387	0.590585	
		Fe1	0.995389	0.990778	0.008655	
		Fe2	0.500409	0.497624	0.011802	
		Fe3	-0.002784	0.497624	0.011802	
		Fe4	0.496568	0.993136	0.008511	
		Fe5	0.003793	0.007584	0.494497	
		Fe6	0.501791	0.500349	0.491386	
		Fe7	-0.001442	0.500349	0.491386	
		Fe8	0.506520	0.013040	0.494875	
P-3*M*1	6.66862	6.66862	11.84888	90	90	120
			Atom position			
FeS_2		Fe1	-0.000000	-0.000000	-0.000000	
		Fe2	0.500000	-0.000000	-0.000000	
		Fe3	-0.000000	0.500000	-0.000000	
		Fe4	0.500000	0.500000	-0.000000	
		Fe5	-0.000000	-0.000000	0.500000	
		Fe6	0.500000	-0.000000	0.500000	
		Fe7	-0.000000	0.500000	0.500000	
		Fe8	0.500000	0.500000	0.500000	
		S1	0.333333	0.166667	0.891324	
		S2	0.666667	0.833333	0.108676	
		S3	0.833333	0.166667	0.891324	
		S4	0.166667	0.833333	0.108676	
		S5	0.833333	0.666667	0.891324	
		S6	0.166667	0.333333	0.108676	
		S7	0.333333	0.166667	0.391324	
		S8	0.666667	0.833333	0.608676	
		S9	0.833333	0.166667	0.391324	
		S10	0.166667	0.833333	0.608676	
		S11	0.833333	0.666667	0.391324	
		S12	0.166667	0.333333	0.608676	
		S13	0.666667	0.333333	0.108676	
		S14	0.333333	0.666667	0.891324	
		S15	0.666667	0.333333	0.608676	
		S16	0.333333	0.666667	0.391324	

Figure S2 The crystal structure (a) and density of states (b) for FeS_2 (yellow represents S atom, pink represents Fe atom).

a



b

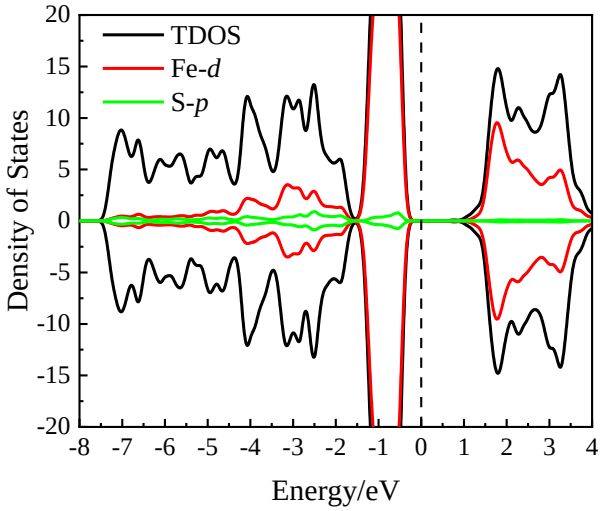


Figure S3 Li/Li-vacancy Frenkel defect pairs for Li_2FeS_2

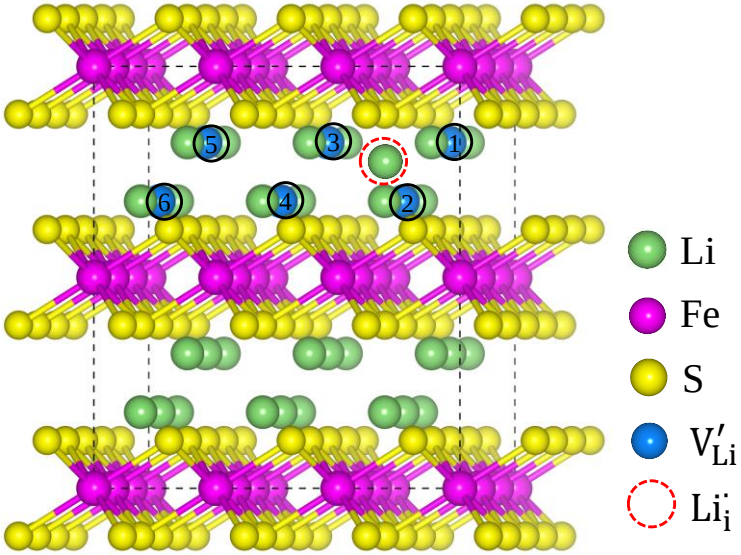


Table S2 Different energy for Li/Li-vacancy Frenkel defect pairs in Li_2FeS_2

Defect types	Defect sites	Defect pairs distance (Å)	Defect energy (eV)
Frenkel defect ($V'_{Li} - Li^{\cdot}_{i}$)	1	4.408	-419.066
	2	2.476	-419.103
	3	2.209	-419.176
	4	2.409	-419.182
	5	4.346	-419.146
	6	5.740	-418.993

Figure S4 Li_2S Schottkt defect pairs for Li_2FeS_2

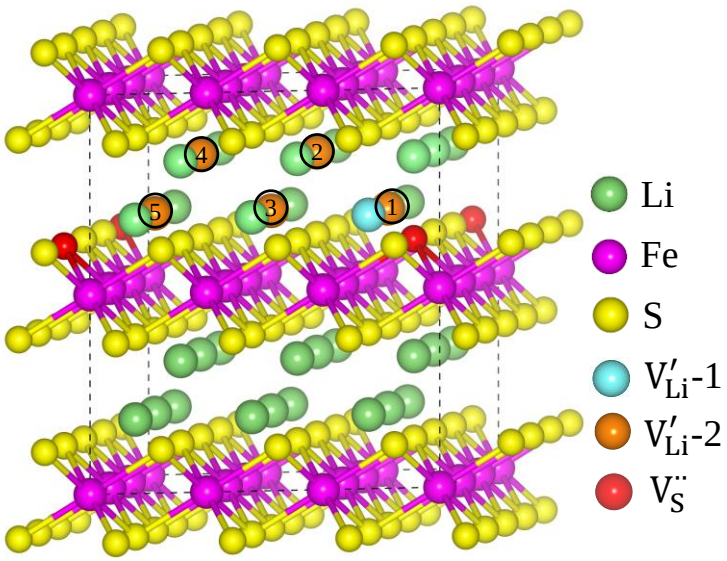


Table S3 Different energy for Li_2S Schottkt defect pairs in Li_2FeS_2

Defect types	Defect sites		Defect pairs distance (Å)	Defect energy (eV)
		Li-1	Li-2	
Schottky defect ($2V'_{Li} - V_S^{\cdot\cdot}$)	1	2.189	2.145	-406.37
	2	2.189	4.438	-405.74
	3	2.189	4.257	-405.82
	4	2.189	6.791	-405.78
	5	2.189	7.699	-405.88