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Insight into the role of Li_2S_2 in Li-S battery: first-principles study

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Computational details

Our structural prediction approach is based on a global minimization of free energy surfaces merging *ab initio* total-energy calculations through CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology as implemented in its same-name CALYPSO code.[1,2] The structures of stoichiometry Li_mS_n (m = 1-4, n = 1−4) were searched with simulation cell sizes of 1−4 formula units (f.u.) at 1 GPa. In the first step, random structures with certain symmetry are constructed in which the atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using VASP code, [3] were done with the conjugate gradients method and were stopped when the enthalpy changes became smaller than 1×10^{-5} eV per cell. After processing the first generation structures, 60% of them with lower enthalpies are selected to produce the next generation structures by PSO. 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for the efficiency of the global search of structures. For most of the cases, the structure searching simulation for each calculation was stopped after we generated 1000 ~ 1200 structures (e.g., about 20 ~ 30 generations).

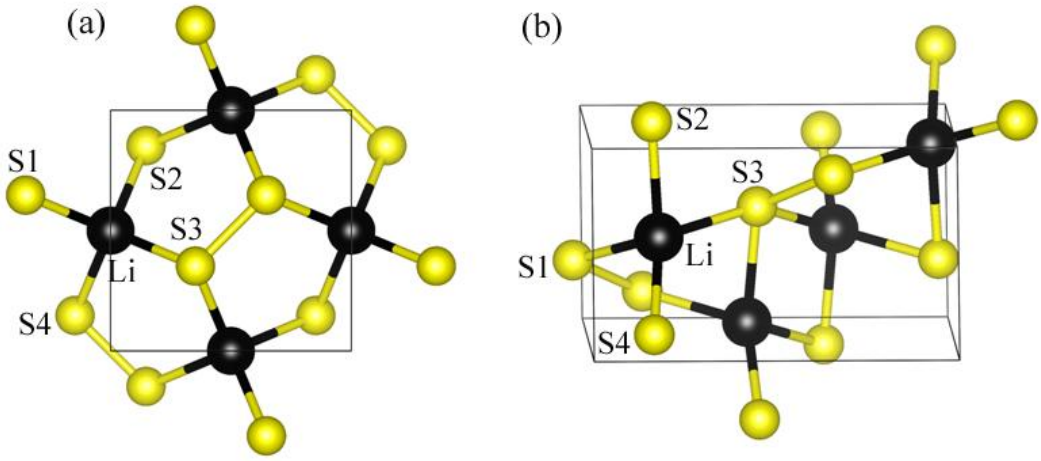
To further analyze the structures with higher accuracy, we select a number of structures with lower enthalpies and perform structural optimization using density functional theory within the generalized gradient approximation[4] as implemented in the VASP code. The cut-off energy for the expansion of wavefunctions into plane waves is set to 700 eV in all calculations, and the Monkhorst–Pack k-mesh with a maximum spacing of 0.02 $Å^{-1}$ was individually adjusted in reciprocal space with respect to the size of each computational cell. This usually gives total energy well converged within ~ 1 meV/atom. The electron-ion interaction was described by means of projector augmented wave with s^1p^0 and s^2p^4 electrons as valence for Li and S atoms, respectively.

The density functional theory with the Perdew-Burke-Ernzerh (PBE) generalized

gradient approximation was employed in the phonon calculation as implemented in the QUANTUM-ESPRESSO package.[5] The Troullier–Martins normcon pseudopotentials were generated with valence atomic configurations of $1s^2 2p^1$ and $3s^2 3p^4$ for Li and S, respectively. The electronic wave functions and the electron density were expanded by the plane-wave basis sets with a cut-off energy of 70 Ry. 14 × 14 × 12 Monkhorst–Pack grids in the Brillouin zone were adopted. The choices of the above computational parameters ensured that the convergence of the phonon frequencies were within 0.08 THz.

Table S1. (a) Bader atomic charge and (b) Mulliken atomic charges (e) of Li_2S_2.

Li_3O_4	Bader[a]	Mulliken[b]
Li	0.87	0.84
Li	0.87	0.84
Li	0.87	0.84
Li	0.87	0.84
S	-0.87	-0.84
S	-0.87	-0.84
S	-0.87	-0.84
S	-0.87	-0.84



Our structure (**a**)				
Lattice parameters	Bond lengh (Å)		Bond angle (°)	
$a = b = 5.07$	S1-Li	2.47	∠(S1-Li-S2)	112.5
$c = 6.11$	S2-Li	2.47	∠(S2-Li-S3)	112.5
$\alpha = \beta = \gamma = 90.0$	S3-Li	2.47	∠(S3-Li-S4)	112.5
	S4-Li	2.47	∠(S4-Li-S1)	112.5
	Zaghib's structure (b)			
Lattice parameters	Bond lengh (Å)		Bond angle (°)	
$a = 4.38$; $b = 4.68$	S1-Li	2.50	∠(S1-Li-S2)	109.9
$c = 7.47$	S2-Li	2.46	∠(S2-Li-S3)	88.15
$\alpha = \beta = 90.0$	S3-Li	2.49	∠(S3-Li-S4)	123.07
$\gamma = 109.7$	S4-Li	2.43	∠(S4-Li-S1)	102.61

Figure S1. Comparison of main structural parameters between our structure (a) and Zaghib's structure (b)

Table S2. The zone-center phonon modes, frequencies (cm^{-1}), Infrared and Raman activities of Li_2S_2, and the experimental value of discharge product (Ref. 6).

Mode	Calculation	Experiment	Raman	Infrared
E_u	42.5			I
A_{2u}	53.8			I
E_u	135.9			I
E_g	138.6		R	
B_{1g}	**168.5**	**174**	**R**	
B_{1u}	172.7			
A_{2g}	220.7			
E_g	302.6		R	
E_u	330.2			I
A_{1u}	338.2			
E_g	355.7		R	
E_u	355.7			I
A_{2u}	356.1			I
B_{1g}	414.8		R	
B_{2g}	450.8		R	
A_{1g}	484.8		R	
B_{2g}	**499.9**	**514**	**R**	

Table S3. The zone-center phonon modes, frequencies (cm^{-1}), Infrared and Raman activities, and experimental Raman frequencies (cm^{-1}) (Ref. 7) of Li_2S.

Mode	Calculation	Experiment	Raman	Infrared
T_{1u}	-62.9			I
T_{2u}	191.8			
T_{1u}	192.8			I
A_{2u}	227.8			
E_u	227.8			
T_{1g}	237.8			
T_{2g}	237.8		R	
T_{1u}	240			I
T_{1u}	300.2			I
T_{2g}	**360.1**	**372**	**R**	
T_{2u}	367.4			
T_{1u}	368.6			I
A_{1g}	485.5		R	
E_g	487.6		R	

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