Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

XANES Study on Lithium Polysulfide Solids: A First-Principles Study

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1. PDOS of Li2Sx (x=2~8) solids

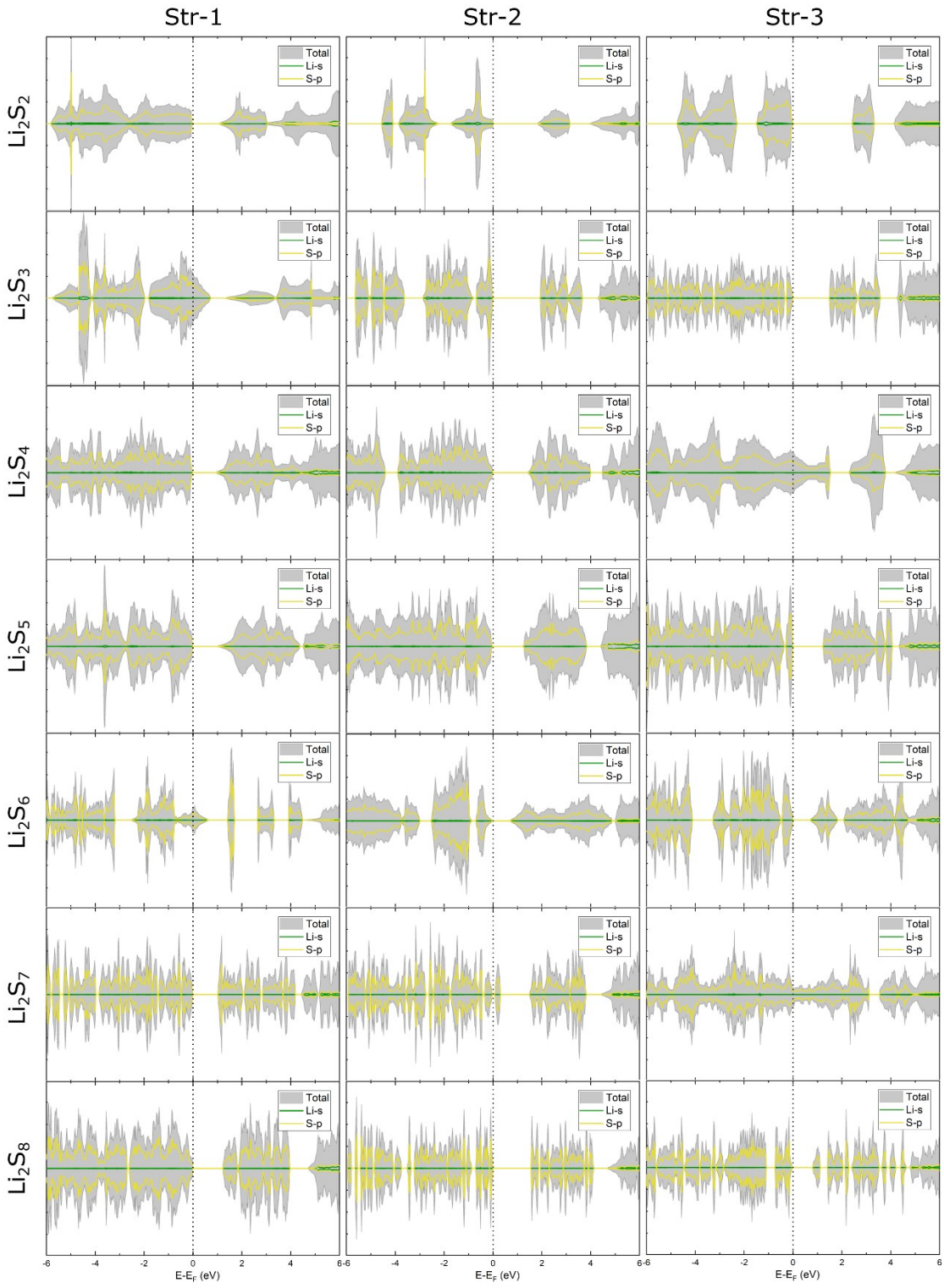

Figure S1. The projected density of states of the low energy configurations of the Li_2S_x (x= 2~8) solids.

2. PDOS of Li_2S_4-1 for S 3p orbitals and the partial charge distribution around the Fermi level.

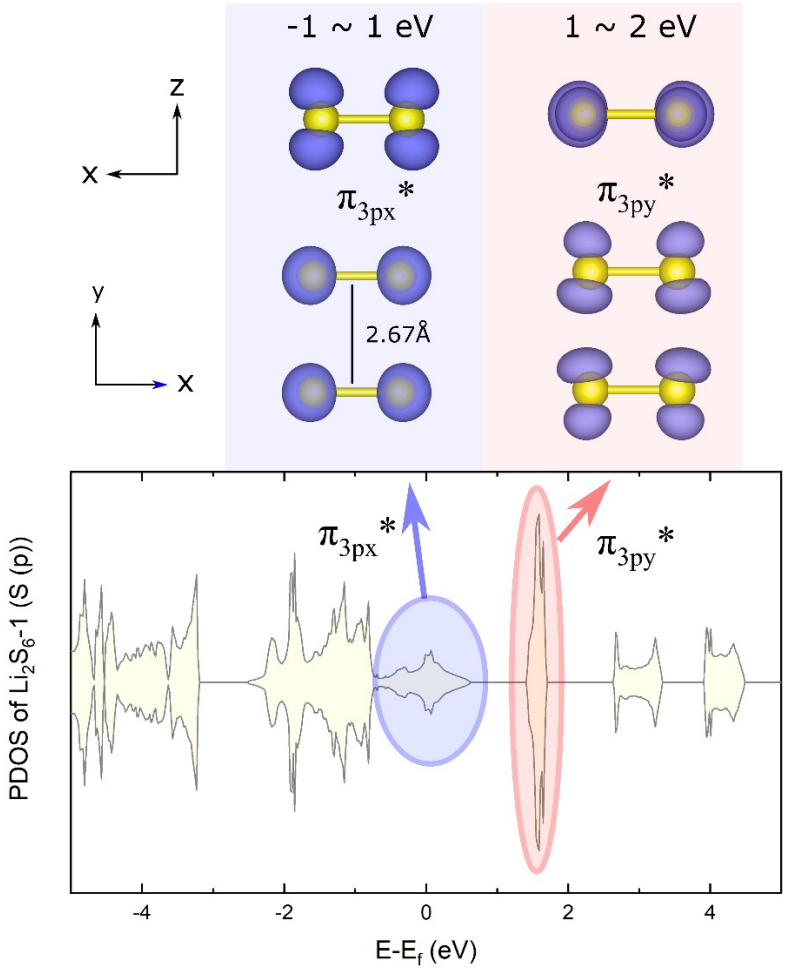

Figure S2. PDOS of S (3p) in Li_2S_6-1 structure and the partial charge distribution in energy range of -1 ~1 eV and 1 ~ 2 eV related to the Fermi level.

3. XANES of Li_2S_4-1 and Li_2S_5-3 structures

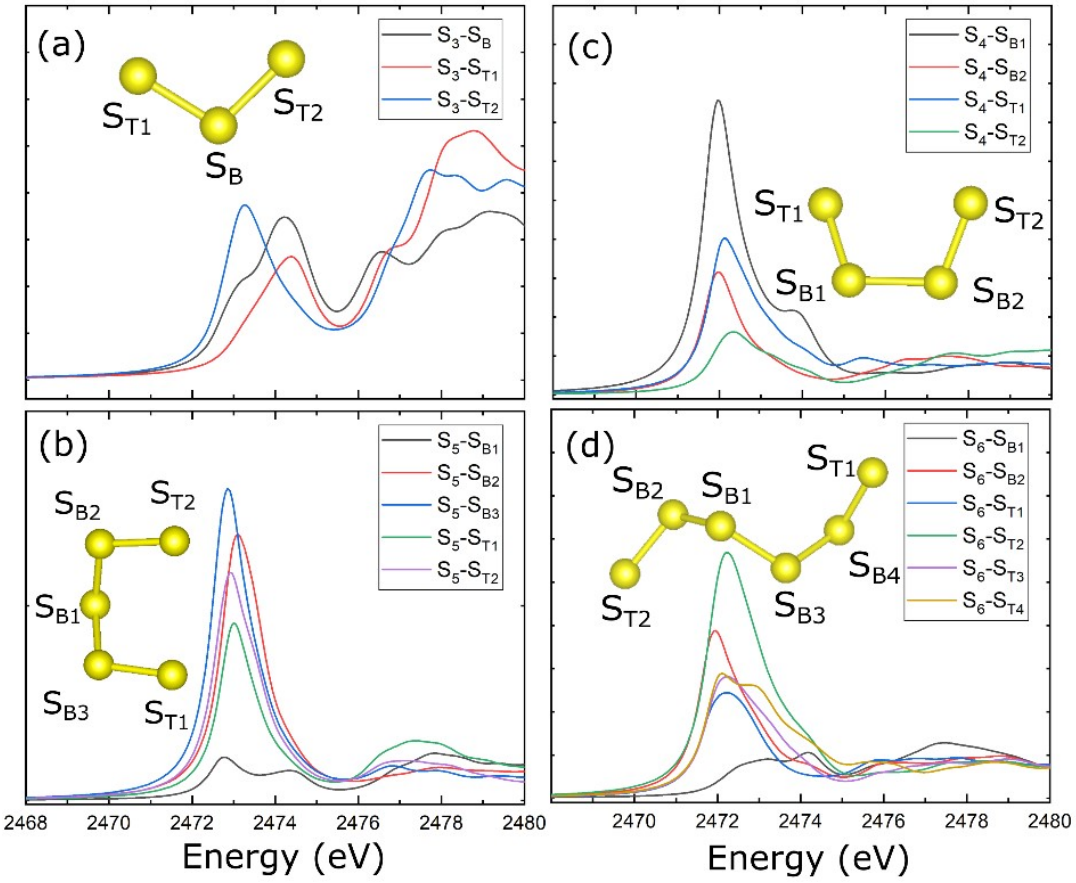

Figure S3. The calculated XANES Spectra of individual S atoms constituting the S chain: (a) S_3 and (b) S_5 of Li_2S_4-1, (c) S_4 and (d) S_6 of Li_2S_5-3

4. XANES of individual S atoms in S_3 and S_5 chains of Li_2S_4-1 with/without Li vacancy.

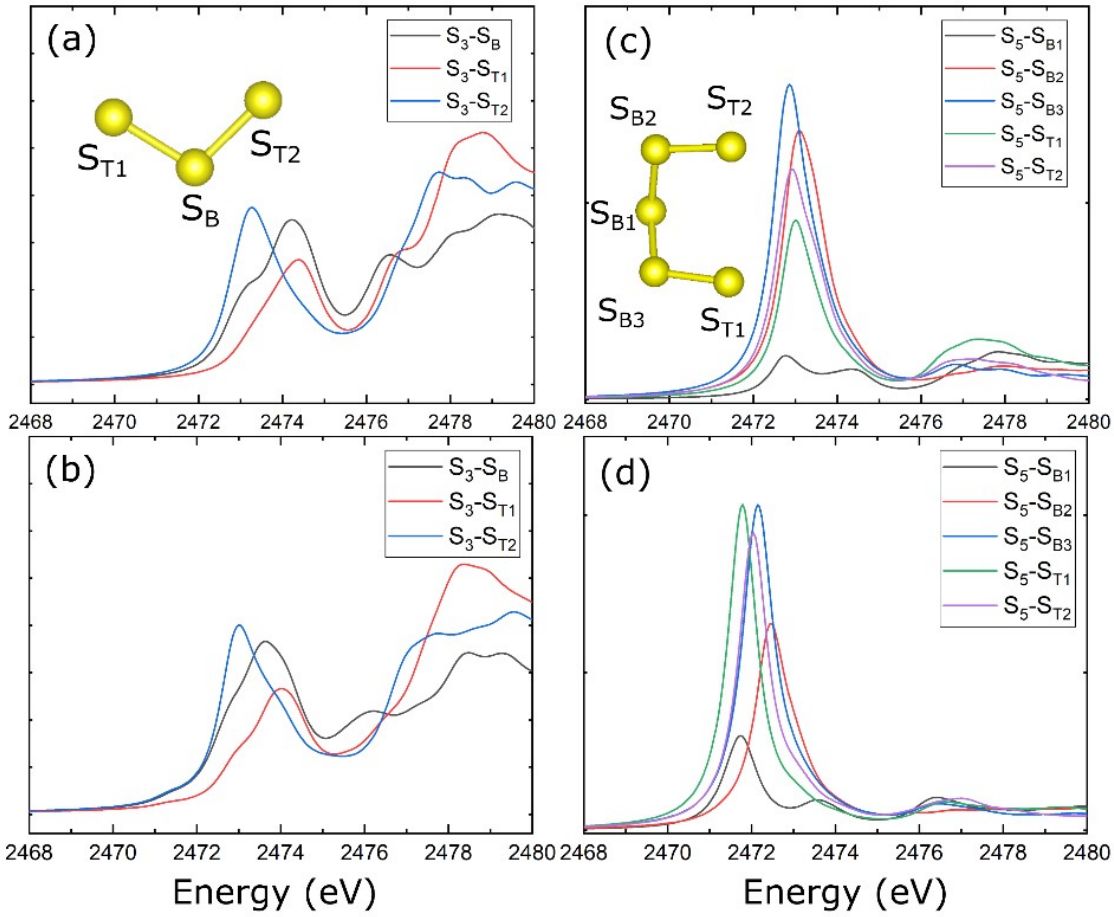

Figure S4. The calculated XANES Spectra of individual S atoms constituting (a) S_3 chain of the stoichiometric Li_2S_4-1, (b) S_3 chain of the non-stoichiometric $Li_{1.5}S_4$ containing a Li vacancy, (c) S_5 chain of the stoichiometric Li_2S_4-1, (d) S_5 chain of the non-stoichiometric $Li_{1.5}S_4$ containing a Li vacancy.

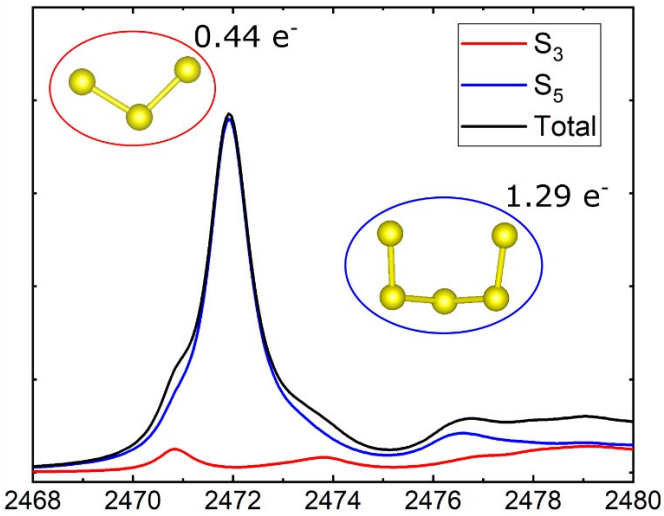

Figure S5. The XANES of Li_2S_4-1 with 2 Li vacancies projected to individual sulfur chains. The inset is the total charge carried by each S_x chain.

5. Electronic DOS projected to each S_x chain in Li_2S_4-1 and Li_2S_5-3 structures.

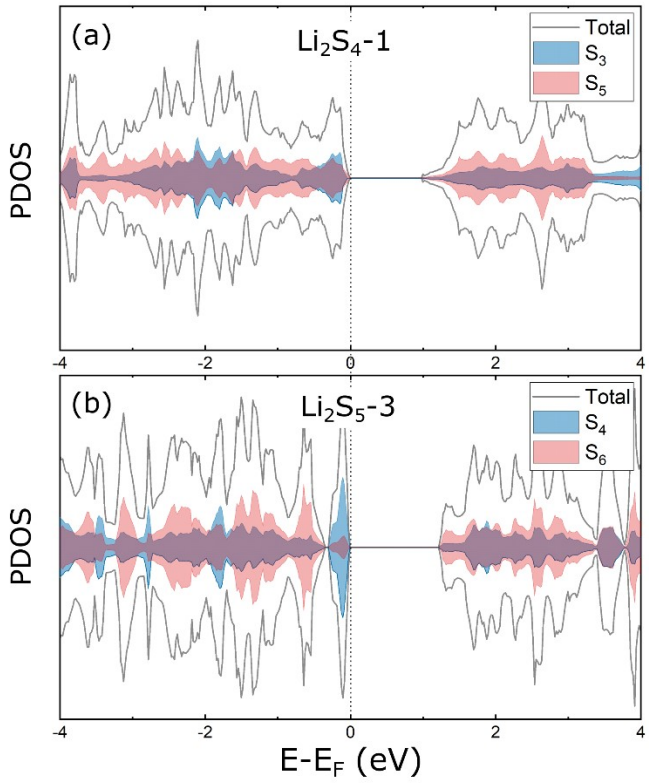

Figure S6. Electron DOS projected to each S_x chain in structure (a) Li_2S_4-1 and (b) Li_2S_5-3.

6. Bader charge and bond length of the polysulfide chains in the crystalline structures.

Table S1. Bader charge distribution of various sulfur chains. The dada of this work is from structure Li_2S_4-1 and Li_2S_5-3 which are in solid-phase. The reference data are from sulfur chains in TEGDME solvent simulation (*J. Phys. Chem. Lett. 2014, 5, 1547−1551*).

	Terminal S atoms		Internal S atoms	
Sulfur chains	This work	Ref *	This work	Ref *
S_3	-0.68	-0.74	-0.15	-0.27
S_4	-0.65	-0.69	-0.23	-0.19
S_5	-0.70	-0.67	-0.18	-0.14
S_6	-0.67	-0.66	-0.10	-0.12
S_8	-0.64	-0.63	-0.08	-0.08

* *J. Phys. Chem. Lett. 2014, 5, 1547−1551*

Table S2. Bond length of various sulfur chains. The dada of this work is from structure Li_2S_4-1 and Li_2S_5-3 which are in solid-phase. The reference data are from sulfur chains in TEGDME solvent simulation (*J. Phys. Chem. Lett. 2014, 5, 1547−1551*).

	Terminal S-S bonds		Internal S-S bonds	
Sulfur chains	This work	Ref *	This work	Ref *
S_3	2.09	2.05		
S_4	2.05	2.06	2.19	2.06
S_5	2.1	2.06	2.09	2.06
S_6	2.07	2.06	2.08	2.07

* *J. Phys. Chem. Lett. 2014, 5, 1547−1551*