Electronic Supplementary Information

Effect of lithium-trapping on nitrogen-doped graphene as an anchoring material for lithium-sulfur batteries: A theoretical study

Gyu Seong Yi, Eun Seob Sim and Yong-Chae Chung*

Department of Materials Science and Engineering, Hanyang University,

222 Wangsimni-ro, Seongdong-gu, Seoul, 04763, Republic of Korea

*Email address: yongchae@hanyang.ac.kr

In the supporting Information, some additional results for better understanding of our study are included:

1) Charge value of active site

2) Li atom adsorption on Li-trapped N-doped graphene and N-doped graphene

3) Ionic attraction between the lithium polysulfide and Li-trapped N-doped graphene

4) Adsorption configuration of lithium polysulfide with DME (1,2-dimetylethane) and DOL (1,3-dioxolane)

5) Li-trapping occurrence on N-doped graphene with lower doping rate

6) Electronic property of Li-trapped N-doped graphene

Keyword: Lithium-sulfur battery; Shuttle effect; Anchoring material; Nitrogen-doped graphene; Density functional theory

Change of active site after Li-trapping

1) Charge value of active site

Table S1 Charge value of active sites on N-doped graphene (NG) and Li-trapped NG (LiNG). Charge values of N and Li atoms for each substrate were obtained by using Bader charge analysis. For the charge value of each N site is a mean value of charge values of N atoms.

Substrate	N	Li
NG	- 0.15	-
LiNG	- 0.26	+ 0.87

2) Li atom adsorption on Li-trapped N-doped graphene and N-doped graphene

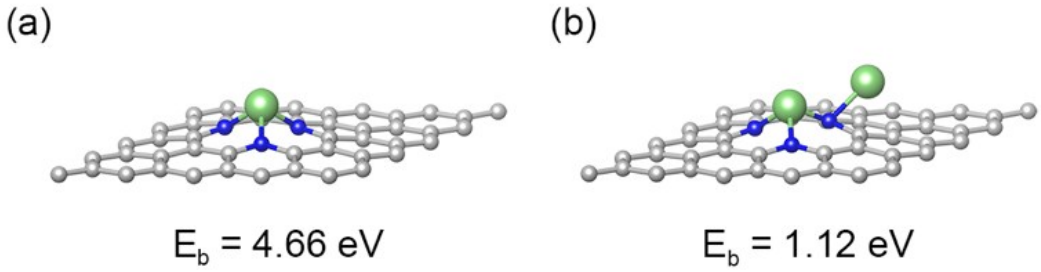

Fig. S1 Adsorption configurations and binding energies of a Li atom on (a) N-doped graphene and (b) Li-trapped N-doped graphene. The gray, blue, and green spheres represent the C, N, and Li atoms, respectively.

3) Ionic attraction between the lithium polysulfide and Li-trapped N-doped graphene

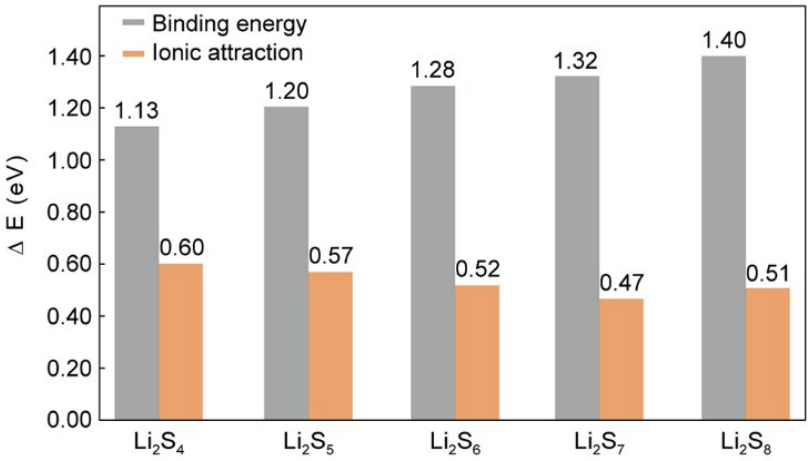

Fig. S2 Binding energies and ionic attractions of high-order lithium polysulfide (Li_2S_n, $4 \leq n \leq 8$) species. Binding energies of lithium polysulfide species on Li-trapped N-doped graphene are depicted as gray and ionic attractions are depicted as orange.

Ionic attraction means the binding energy between the lithium polysulfide and Li-trapped N-doped graphene calculated without van der Waals (vdW) force. To get this, we conducted additional calculation on fully relaxed adsorption structures without vdW scheme.

If the ionic attraction is subtracted from the binding energy, remainders would be the amount of the physical interaction which is mainly induced by van der Waals interaction between molecules. Van der Waals interaction is related to the size of interacting molecules. In this manuscript, the size of substrate is consistent and the size of LiPS changes, therefore, the size of LiPS attributes dominantly to the physical interaction. In other words, the binding energies of LiPS on LiNG substrate increase with the size of LiPS molecule.

4) Adsorption configuration of lithium polysulfide with DME (1,2-dimetylethane) and DOL (1,3-dioxolane)

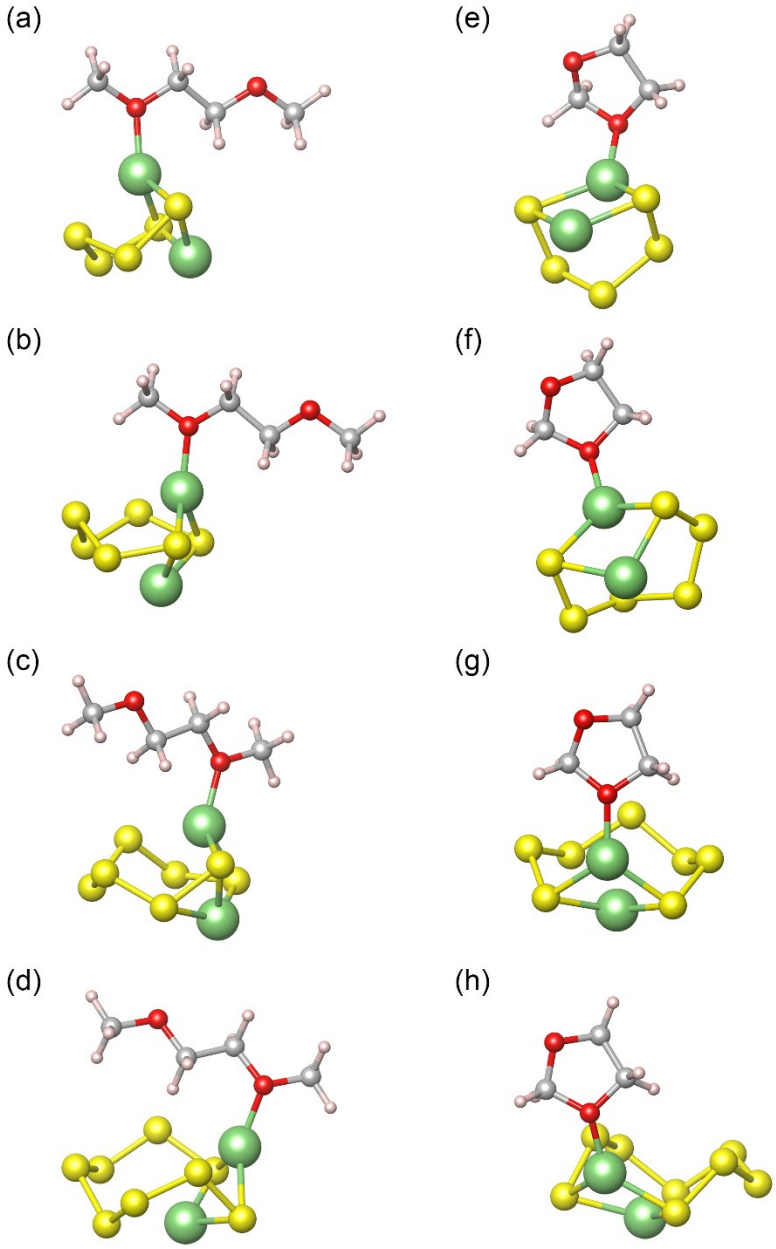

Fig. S3 Adsorption configuration of (a) Li_2S_5, (b) Li_2S_6, (c) Li_2S_7, and (d) Li_2S_8 with DME (1,2-dimetylethane) and (e) Li_2S_5, (f) Li_2S_6, (g) Li_2S_7, and (h) Li_2S_8 with DOL (1,3-dioxolane). The gray, red, pink, yellow, and green spheres represent the C, O, H, S, and Li atoms, respectively.

5) Li-trapping occurrence on N-doped graphene with lower doping rate

Since Li atom interacts with N-dopant in the N-doped graphene (NG) substrate, trapping energy would decrease as doping rate decreases. The occurrence of Li-trapping on N-doped graphene with lower doping rate was investigated by using *ab initio* thermodynamics.

The change of the Gibbs free energy of Li-trapping ($^{\Delta G_{trap}}$) on the NG with lower doping rate was calculated. The optimized configuration of substrates with lower doping rate are derived from pyridinic NG used in the manuscript (Fig. S4). 1N and 2N substrates indicate the NG substrate which include one and two N atoms, respectively.

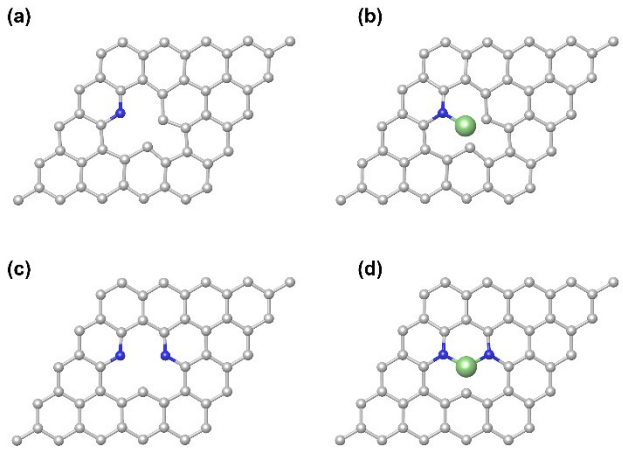

Fig. S4 Optimized structures of (a) 1N substrate, (b) Li atom adsorption on 1N substrate, (c) 2N substrate, and (d) Li atom adsorption on 2N substrate. The gray, blue, and green spheres represent the C, N, and Li atoms, respectively.

The calculated value of $^{\Delta G_{trap}}$ on 1N substrate was -1.44 eV and that on 2N substrate was -1.77 eV. Also, $^{eU_{charge}}$ is larger than 2 eV because charge potential of Li-S battery is commonly set over 2.0 V vs. Li/Li$^+$. Consequently, $^{\Delta G_{charge}}$ had a positive value according to the eqn (2) in the manuscript, therefore Li-trapping would not occur on NG with lower doping

rate.

6) Electronic property of Li-trapped N-doped graphene

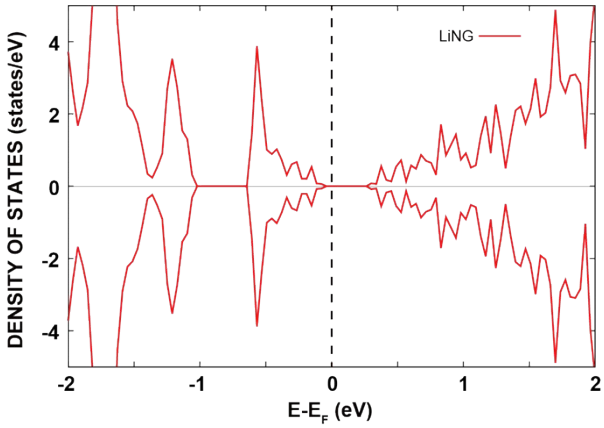

Fig. S5 Density of states (DOS) of the Li-trapped N-doped graphene (LiNG). The vertical dotted line indicates the Fermi level.