Adsorption Mechanisms of Lithium Polysulfides on Graphene-Based Interlayers in Lithium Sulfur Batteries

Chi-You Liu and Elise Y. Li*

Department of Chemistry, National Taiwan Normal University, No. 88, Section 4, Tingchow Road, Taipei 116, Taiwan
**Corresponding author: eliseytli@ntnu.edu.tw*

Abstract:

One of the most critical problems in lithium-sulfur (Li-S) batteries is the shuttle effect. The transfer of soluble lithium polysulfides (LiPSs) from the sulfur cathode to the lithium anode leads to a degradation in Li-S battery capacity and life cycles. Recent studies reveal that the carbon-based interlayer materials introduced between the cathode and anode can effectively improve the shuttle effect problem and increase the battery life cycles. In this work, different types of the N-doped, S-doped, and N, S co-doped graphene surfaces are investigated by theoretical calculations. We find that a strong interaction may exist between some of the heteroatom-doped graphene surfaces and lithium ions, and that the adsorption of LiPSs may proceed via one of the three mechanisms, the dissociative, the destructive, and the intact adsorptions. Detailed structural and electronic analyses indicate that the Li-trapped N, S co-doped graphene interlayers could efficiently reduce the shuttle effect through the intact adsorption mechanism. Our results provide a plausible explanation on the observed better performance of the N, S co-doped graphene interlayers in Li-S batteries.

Keywords: Li-S battery, Heteroatom-doped graphene, Lithium polysulfides.

Computational details

The density-functional theory (DFT) and the plane-wave method, as implemented in the Vienna ab initio simulation package (VASP), are employed to calculate the energies and structures of adsorbates and surfaces. The projector-augmented-wave method (PAW) is used in conjunction with the generalized gradient-approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, with a cutoff energy of 400 eV. The dispersion correction is included by DFT-D3 method. The supercell for the graphene-based surfaces include 6 x 6 repeated unit cells and a vacuum space of over 15 Å to ensure negligible interactions between surfaces. The Monkhorst-Pack k-point grids are set as 5 x 5 x 1 for all supercells. All atoms are fully relaxed during the optimization. The Bader charge analyses is used in our calculations.

Conclusions

Through a comprehensive DFT investigation, we find the adsorption of LiPSs on different graphene surfaces may involve three mechanisms, as summarized in Figure 1. In Mechanism A (the dissociative adsorption), one or two Li atoms almost fully dissociate from the LiPS upon adsorption on some of the N-doped surfaces, leading to a strong electron transfer from the adsorbate to the surface. Even when Li-trapping is considered, the adsorption of LiPSs may still be followed by an irreducible damage of polysulfide splitting on the Li-trapped N-doped surfaces, as illustrated in Mechanism B (the destructive adsorption). In Mechanism C (the intact adsorption), the LiPSs are adsorbed without any dissociation or destruction on some of the Li-trapped N, S co-doped surfaces and shows a higher adsorption energy than on the pristine graphene or other non-Li-trapped surfaces. In conclusion, our computational results confirm the observed better performance of the Li-trapped N, S co-doped graphenes for LiPS adsorption. Our study indicates that such material systems may be an ideal candidate for Li-S battery interlayers, which could reduce the shuttle effect and increase the life cycles in a efficiency way. We hope that this mechanistic study could inspire future material designs for better Li-S battery interlayers and related applications.

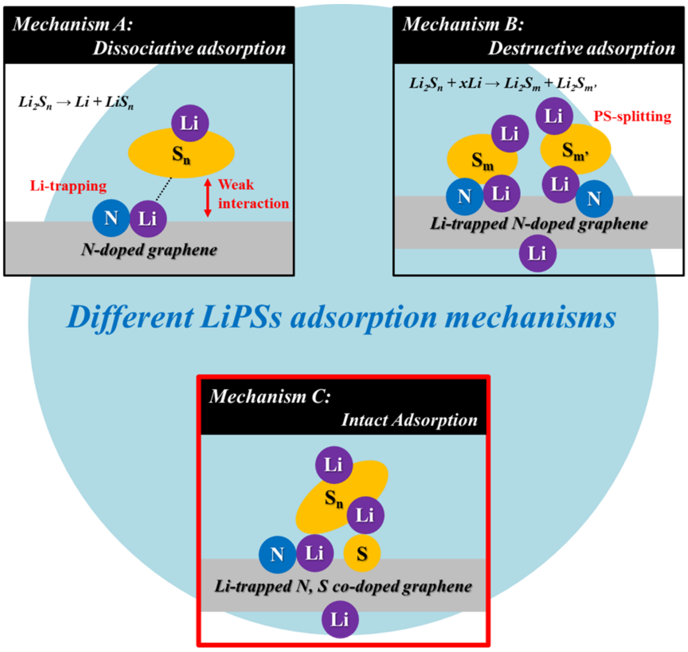

Figure 1. Proposed LiPSs adsorption mechanisms on different graphene-based interlayers.