Diamond & Related Materials 90 (2018) 72–78

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Metal-N_4/graphene as an efficient anchoring material for lithium-sulfur batteries: A computational study

Tianqi Zhang[a], Zhe Chen[a], Jingxiang Zhao[a,*], Yihong Ding[b,*]

[a] College of Chemistry and Chemical Engineering, and Key Laboratory of Photonic and Electronic Bandgap Materials, Ministry of Education, Harbin Normal University, Harbin, 150025, China

[b] Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China

ARTICLE INFO

Keywords:
Lithium-sulfur battery
Shuttle effect
Metal-nitrogen/graphene
Anchoring effect
Density functional theory

ABSTRACT

Despite their high theoretical capacity, the practical commercialization of lithium-sulfur batteries have continued to face obstacles of low cycle stability and low efficiency, which stem from the dissolution and diffusion of lithium polysulfides intermediates in the electrolyte. Here, by means of comprehensive density functional theory computations, we exploited the potentials of the experimentally available metal-nitrogen/graphene as the anchoring material for high-performance Li-S batteries. Our results revealed that Cr-, Mn-, Fe-, Co-, and Cu-nitrogen/graphenes exhibit optimal interaction with soluble lithium polysulfides due to the synergistic effects between the metal and N atoms, which not only effectively traps the soluble lithium polysulfides to suppress the shuttle effects, but also well keeps their cyclic structures intact. Especially, the electronic properties of metal-nitrogen/graphenes are well preserved, and the computed voltages of discharge processes are larger than those of the well-established nitrogen-doped graphenes. Thus, the metal-nitrogen/graphene could present a kind of quite promising anchoring material for lithium sulfur battery cathodes to suppress the lithium polysulfides shuttle effect.

1. Introduction

Lithium–sulfur (Li–S) batteries, consisting of sulfur as cathode and Li metal as anode, represent one of the most promising candidates for the next-generation that shows great potential applications in portable devices and electrical vehicles due to their ultrahigh theoretical capacity of 1675 mA/g and energy density of 2600 Wh/kg [1–5]. In addition, sulfur exhibits the advantages of abundant resources, low costs, and high biocompatibility, compared to the existing lithium-ion batteries [6–10]. However, the commercialization of Li-S batteries has been greatly impeded by several challenges [7,11–15]. For example, the poor electronic conductivity of sulfur (S_8) and its lithiation products (Li_2S) would lead to the limited utilization of active material and poor rate capability. Another key problem is the so-called “shuttle effect”, caused by the dissolution of the soluble intermediate products of polysulfides (Li_2S_n, n = 8, 6, and 4) that are produced during the process of charge/discharge cycling, resulting in the rapid capacity fading of Li-S batteries.

To circumvent the above challenges, considerable efforts have been recently devoted to the design of the electrode structure and composition to increase the conductivity and prevent the Li_2S_n's dissolution by effectively trapping the sulfur species within the anchoring materials [16–25]. In general, the ideal sulfur anchoring materials for Li-S batteries should have high surface area, excellent electric conductivity, and moderate affinity to Li_2S_n species. Although carbon materials have excellent electrical conductivity and can serve as the Li-S batteries electrode materials, the relatively weak interaction between the nonpolar carbons and polar S-containing species undermines their applications as Li_2S_n adherent/anchoring material. In addition, some inorganic nanomaterials, such as transition metal oxides [26,27] and sulfides [22,28] that are inherently polar materials, have been revealed to exhibit strong binding strength with Li_2S_n species. Unfortunately, such polar anchoring materials mostly have very poor electrical conductivity. Therefore, developing a sulfiphilic and conductive anchoring material for advanced Li-S batteries is very necessary.

One effective strategy to improve the interactions with Li_2S_n species is to introduce heteroatom (dopant) to carbon nanomaterials [29–39]. Amongst, the N atom was the most widely used dopant for high-performance of Li–S batteries [40–48]. In carbon materials, the N atoms are usually considered as Lewis-bases to strongly interact with Lewis acids of Li atoms in Li_2S_n species. For example, pyrrolic and pyridinic N-doped graphenes have been shown to serve as conductive Lewis bases

* Corresponding authors.
E-mail addresses: zhaojingxiang@hrbnu.edu.cn (J. Zhao), yhdd@jlu.edu.cn (Y. Ding).

https://doi.org/10.1016/j.diamond.2018.10.008
Received 6 August 2018; Received in revised form 17 September 2018; Accepted 9 October 2018
Available online 10 October 2018

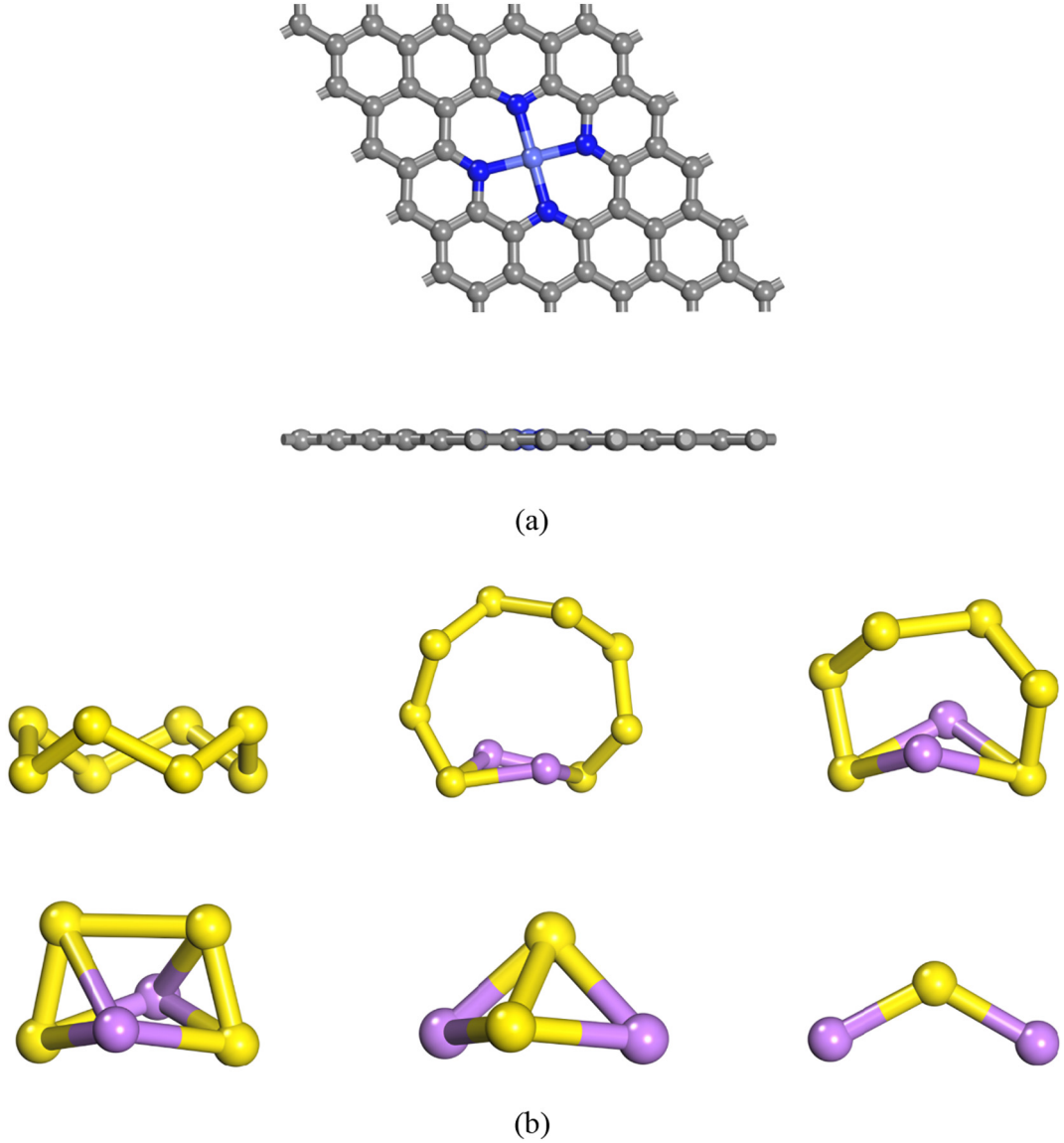

Fig. 1. The optimized structures of (a) metal-N_4/graphene and (b) S_8 and Li_2S_n (n = 8, 6, 4, 2 and 1).

and thus bind Li_2S_n more strongly than pristine graphene [40]. Interestingly, several experiments recently reported that Fe- or Co-N/graphenes exhibited superior performance for the immobilization of Li_2S_n species to suppress the so-called shuttling effects [49–51]. For example, Chen et al. reported that Co-N/carbon nanofibers could be used to trap the polysulfides and exhibit excellent cycling performance and good rate capability [49], while Song and Wang et al. independently suggested that the Li-S battery trapped by the Fe-N-C-based separators possess a greatly improved electrochemical performance [50,51].

From the aforementioned investigations, several questions then arise: (1) what is the anchoring mechanism for Fe- or Co-N/C materials to the Li_2S_n species? (2) Could other metal-N/C materials be utilized as effective anchoring materials for Li-S batteries? Recent theoretical advances have provided much evidence that the anchoring effects and mechanisms of the anchoring materials can be described computationally with adequate accuracy at atomistic level. Therefore, it is our belief that a theoretical study on the issues (1) and (2) will shed some lights on developing novel anchoring materials for Li-S batteries.

In this work, by means of density functional theory (DFT) computations, we chose the experimentally available metal-N_4/graphene (metal = Cr, Mn, Fe, Co, Ni, and Cu) as anchoring materials to explore its potential applications for Li-S batteries. Our results demonstrated that Cr-, Mn-, Fe-, Co-, Cu-N_4/graphenes can moderately interact with Li_2S_n species, and their electrical conductivities were well preserved. Therefore, introducing suitable metal-N_4 moiety into graphene can greatly enhance its anchoring effects for Li-S batteries to suppress the unwanted shuttling effects, which not only facilitates the deep understanding of the experimental results, but also opens a new door for immobilizing polysulfide with single-atom materials to exploit high-performance Li-S batteries.

2. Models and methods

The spin-polarized density functional theory (DFT) computations were performed by using the DMol^3 code [52,53]. The Perdew-Burke-Ernzerhof (PBE) functional within a generalized gradient approximation (GGA) was employed to treat the exchange-correlation interactions [54]. The empirical correction in Grimme scheme [55] was applied to treat the possible van der Waals interactions between various Li_2S_n species and anchoring materials. For evaluation of the relativistic effects of transition metals, the density functional semi-core pseudopotential (DSPP) was utilized [56], by replacing the core electrons with a single effective potential coupled with some degree of relativistic corrections. For all non-metal elements, the double numerical plus