Applied Surface Science 440 (2018) 889–896

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

SiC_2 siligraphene as a promising anchoring material for lithium-sulfur batteries: a computational study

Yuming Zhao, Jingxiang Zhao [*], Qinghai Cai

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

ARTICLE INFO

Article history:
Received 29 October 2017
Revised 9 January 2018
Accepted 21 January 2018

Keywords:
Li-S batteries
Siligraphenes
Anchoring materials
DFT

ABSTRACT

The development of stable and effective anchoring materials to immobilize the soluble lithium polysulfide (Li_2S_n) species for suppressing their shuttle effects is vital for the large-scale practical applications of lithium-sulfur (Li-S) batteries. Here, by means of density functional theory (DFT) computations, the potential applications of the experimentally available SiC_2 siligraphene (g-SiC_2) as an anchoring material of Li-S batteries are systemically investigated. Our results reveal that g-SiC_2 exhibits remarkable but not strong binding strength for the soluble Li_2S_n species due to the S-Si and Li-C interactions. Especially, the intactness of the Li_2S_n species and the good conductance of g-SiC_2 can be well preserved after anchoring the Li_2S_n species. The further comparative research demonstrate that g-SiC_2 is superior to other siligraphenes, enabling it to be a very promising material as an ideal anchoring material for the immobilization of soluble Li_2S_n species to avoid their dissolution into electrolyte.

1. Introduction

Due to the high theoretical capacity (1672 mAh g^{-1}) of sulfur cathode [1], lithium-sulfur (Li-S) batteries have been intensively explored to fulfill the urgent demand for energy storage devices. Comparing with conventional lithium-ion batteries (LIBs), Li-S batteries exhibit more than five times higher theoretical energy density (2600 Wh kg^{-1}) than LIBs [2]. In addition, the low cost, low toxicity, naturally abundant raw materials of sulfur make it prominent advantages for commercial applications [3]. Thus, Li-S batteries are regarded as one of the most promising power sources for next-generation energy storage systems [4–9].

Nevertheless, there are a few challenges that greatly hinder the practical commercial applications of Li-S batteries, including, fast capacity fading, low Coulombic efficiency, and low active material utilization [4,10–15], which stem from three main reasons: (i) dissolution of lithium polysulfides (Li_2S_n) intermediates into the electrolyte (i.e., the so-called "shuttle effect"); (ii) the inherent insulating nature of S and the discharge products Li_2S and Li_2S_2; (iii) the huge volume expansion of sulfur (~80%) upon lithiation. An effective approach to circumvent the problems listed above is utilizing nanostructures with high electrical conductivity to immobilize Li_2S_n species into hybrid materials for achieving long-term cycling stability and high-rate performance [16–21]. Hence, during the last few decades, tremendous efforts have been made to search for novel nanomaterials as an anchoring material for Li-S batteries [16–21].

Carbon-based nanomaterials [2,22–32], including nanoporous carbon [22,23], carbon nanofiber [24], carbon nanotubes [25], and so on, are expected to be promising as an anchoring material for Li-S batteries because they can enhance the conductivity of a cathode and also accommodate the electrode volume expansion of active materials during the cell operation. Due to its high electrical conductivity and large surface area, graphene, a two-dimensional sheet, has been extensively investigated for improving the electrochemical performance of Li-S battery [33–37]. However, it was reported that the nonpolar carbon-based materials cannot serve as an ideal anchoring material for Li-S batteries due to their weak interaction with polar Li_2S_n species, resulting in the easy detachment of Li_2S_n from the carbon surface and poor cycling performance [38].

The introduction of heteroatoms (such as N, B, S, P, O, or codoping) into graphene or carbon nanotube to tune their properties for the generation of polar functional group is a well-adopted strategy to enhance the interaction and immobilization of Li_2S_n species in the battery electrodes [39–60]. For example, Li et al. found that the incorporated nitrogen dopants in the graphene network exhibits a strong binding effect on the Li_2S_n species to improve electrochemical stability and promotes fast electrochemical reaction

---

[*] Corresponding author.
E-mail address: xjz_hmily@163.com (J. Zhao).

https://doi.org/10.1016/j.apsusc.2018.01.178
0169-4332/

kinetics [53], while Wu et al. showed that B-doped microporous carbon exhibits an ultrahigh cycling stability and rate capability for Li-S batteries [59]. Ai et al. reported that the co-doping of N and P can greatly enhance the anchoring effects of carbon nanotube for Li-S batteries [60]. Theoretically, by performing density functional theory (DFT) calculations, various groups have revealed the anchoring effects of doped graphenes for Li-S batteries [61–64]. For example, Yin et al. found that N-doped graphene with clustered pyridinic N-dopants can strongly attract Li_2S_n species [61], while Li et al. showed that N doping with pyrrole-like vacancy in graphene is more effective to trap Li_2S_n species due to the strong Li-N interaction [62]. In addition, our recent work revealed that the introduction of dopants and defects can also enhance the binding strength of Li_2S_n species with BN nanosheets due to the strong Li···N or S···B interaction [65].

Although the introduction of dopants can effectively immobilize soluble Li_2S_n species to suppress their shuttle effects, the anchoring site that carbon-based nanomaterials can provide is not fully achieved due to the low dopant concentration in carbon-based nanomaterials (N ~ 4–6 at.%, B ~ 0–2.24 at.%, and S ~ 1–2 at.%) to Li_2S_n species [66–68]. For practical applications, nanomaterials with a large active region are highly desired for immobilizing Li_2S_n species as far as the sensitivity is concerned [69,70]. Thus, the nanomaterial with high active sites is very desirable for immobilizing soluble Li_2S_n species to avoid their dissolution into the electrolyte.

Recently, 2D siligraphenes with graphene-like honeycomb lattice, which could be viewed as substituting carbon atoms in graphene by silicon atoms, have attracted considerable attention due to their controllable electronic properties, high reaction sites, and wide potential applications as metal-free catalysts, gas sensors, and nanoelectronics and photovoltaics [71–76]. Among these 2D siligraphenes, SiC_2 siligraphene (g-SiC_2) is particularly interesting because of its moderate band gap and superior structural and thermal stability, which has been proposed as donor material in excitonic solar cells and metal-free electrocatalysts for oxygen reduction reaction [73,76]. In particular, g-SiC_2 has been synthesized in experiments via the reaction between graphene and silicon quantum dots very recently [72].

Since the siligraphene possesses high active sites, an interesting question arises naturally: can siligraphene be utilized as the anchoring materials for Li-S batteries? To answer this question, in this work, we explored the potential of siligraphene as the anchoring material by means of comprehensive density functional theory (DFT) computations, where g-SiC_2 is mainly focused because it exhibits semiconducting nature[74] and has been experimentally synthesized [72]. Our simulations demonstrated that g-SiC_2 can strike a balance between binding strength and integrity of the soluble Li_2S_n species. Therefore, g-SiC_2 is a quietly promising anchoring material for the immobilization of soluble Li_2S_n species.

2. Computational methods and models

All computations in this work were performed within density functional theory (DFT) framework as implemented in $DMol^3$ code [77,78]. An all-electron double numerical plus polarization (DNP) was chosen as the basis set, and its accuracy is comparable to that of Pople's 6-31G(d). The Perdew-Burke-Ernzerhof (PBE) functional [79] within the generalized gradient approximation (GGA) was adopted to describe exchange and correlation effects. Especially, the vdW-DF2 functional with a Grimme approach [80] was employed to include the physical van der Waals (vdW) interaction because vdW interaction plays an important role on determining the interaction of soluble Li_2S_n species with anchoring materials [81]. Self–consistent field (SCF) computations were carried out with a convergence criterion of 10^{-6} a.u. on the energy, 0.002 Ha/Å on maximum force, and 0.005 Å on maximum displacement in the geometry optimization. To ensure high quality results, the real–space global orbital cutoff radius was chosen as high as 5.2 Å in all the computations. K point was set to $5 \times 5 \times 1$ in geometry optimization and $12 \times 12 \times 1$ for electronic properties. A 3×3 supercell was adopted for g-SiC_2 that consists of 18Si and 36C atoms, as the immobilizer of soluble Li_2S_n species. To avoid interaction of periodic images, a vacuum space of 20 Å in the z direction was adopted. All atoms in g-SiC_2 supercell were fully relaxed without symmetrical restriction.

To describe the binding strength of soluble Li_2S_n species on g-SiC_2, the binding energy (E_b) was calculated using the following formula: $E_b = E_{mol} + E_{sub} - E_{mol/sub}$, where E_{mol} and E_{sub} represent the energies of the isolated S-containing cluster and g-SiC_2, while $E_{mol/sub}$ represents the total energy of the adsorption system. Here, a positive E_b suggests attractive interaction. The larger E_{ads}, the more stable the adsorption system is. Population analysis was performed by assigning Hirshfeld charges for the optimized structures [82].

3. Results and discussion

3.1. Structures and properties of S-containing species and g-SiC_2

Recent experimental investigations have shown that some S-containing species, including S_8, Li_2S_8, Li_2S_6, Li_2S_4, Li_2S_2, and Li_2S species, are key intermediates produced during the charge and discharge process of Li-S batteries [83], in which Li_2S_8, Li_2S_6, Li_2S_4 species could be soluble in an electrolyte solvents, inducing the so-called shuttle effect and resulting in fast capacity fading of Li-S battery. According to previous theoretical computations, we built these S-containing clusters [61,63,81], and the optimized most stable configurations were presented in Fig. 1. We found that that Li_2S_n species with high S-content (i.e., Li_2S_8, Li_2S_6, and Li_2S_4) are in a three-dimensional shape instead of chains with Li atom on the terminals. The shortest Li—S bond lengths are 2.38, 2.35, and 2.36 Å, respectively, while the shortest distances of S—S bonds are 2.10, 2.11, and 2.13 Å, respectively, for Li_2S_8, Li_2S_6, and Li_2S_4 clusters. On the basis of the Hirshfeld population analysis, we found that Li atom carries positive charges of ~0.25 |*e*|, while the negative charges mainly locate on the S atoms adjacent to Li atoms (~−0.20 |e|). The amount of charge transfer from Li atoms to S atoms in Li_2S_8, Li_2S_6, Li_2S_4 clusters are about 0.52, 0.46, 0.58 |*e*|, respectively, suggesting the obvious ionic character of these soluble Li_2S_n species.

Fig. 2 presents the optimized structures of g-SiC_2, in which all atoms are in the exactly same plane with the optimized lattice parameters of $a = 5.02$ Å. Remarkably, there are two kinds of C atoms in g-SiC_2: C1 atom is the carbon atom that is trigonally coordinated with three neighboring carbon atoms, while the C2 atom denotes the carbon atom that covalently bonds with two silicon atoms and one carbon atom. The length of the Si—C2 bond is 1.79 Å, while the C1—C2 bond length is 1.44 Å, suggesting a weak C—C double bond because it is slightly longer than that of ethylene (1.33 Å), but shorter than that of ethane (1.54 Å). Also, we examined the charge distributions in g-SiC_2 by using Hirshfeld methods. Our results showed that Si atom carries more positive charges (+0.33 |*e*|) and C1 atom carries less positive charge (+0.02 |*e*|), where C2 atom carries negative charge (−0.23 |*e*|), indicating that charge transfer in g-SiC_2 mainly originates from the Si to C2 atom via Si—C2 bonding interaction, while the C1 atom is almost neutral.

3.2. Adsorption of Li_2S_n species on g-SiC_2

After determining the structural and properties of soluble Li_2S_n species and g-SiC_2, we next explored the interaction strength