Sulfur-doped Bi$_2$Se$_3$ Monolayer as Potential electrode Materials for Mg-ion batteries

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Abstract. Magnesium-ion batteries (MIBs) are a front-runner among the alternative battery technologies suggested to substitute the state-of-the-art lithium-ion batteries (LIBs). Searching for proper electrode materials for MIBs is critical for the development of MIBs. Using density functional theory (DFT) calculations, Bi$_2$Se$_3$ monolayers with sulfur-doping as potential electrode materials for MIBs were investigated in this work. The effect of S doping on adsorption and diffusion behaviors of Mg ions was mainly studied. The results showed that Mg atoms first prefer to occupy the H sites of both perfect and S-doped Bi$_2$Se$_3$ surfaces. Doping of S atom reduces the corresponding adsorption energy and diffusion barrier of Mg on the surface. The present results give expectation of excellent battery performance by S doping and it is one way to improve electrode materials for the fast charging/discharging of MIBs.

1. Introduction
Magnesium-ion batteries (MIBs) are a front-runner among the alternative battery technologies suggested to substitute the state-of-the-art lithium-ion batteries (LIBs) [1]. MIBs have attracted much attention in recent years due to their high safety, high specific capacity, and low price [2]. To further improve the overall battery performance of MIBs, a variety of materials have been studied to be used as anodes and cathodes for MIBs [3]. A search for high-efficiency electrode materials is crucial for the development of MIBs.

Recently, bismuth selenide (Bi$_2$Se$_3$) has been applied in LIBs and exhibited excellent electrochemical storage ability for Li$^+$ [4]. Especially, doping strategies have been employed to create S-doped and In-doped Bi$_2$Se$_3$ which were successfully synthesized with great potential in energy storage as the anode of LIBs [5]. Despite the good electrochemical performance in Li$^+$ storage, Bi$_2$Se$_3$ has not been reported as an electrode material for MIBs. In this study, we investigated adsorption and diffusion behaviors of Mg ions on S-doped Bi$_2$Se$_3$ monolayer surface using DFT calculations. The effect of S doping on adsorption and diffusion behaviors of Mg ions was mainly studied to explore S-doped Bi$_2$Se$_3$ monolayer as a potential electrode material for MIBs.

2. Simulation and calculations
All calculations were performed using the spin-polarized density functional theory (DFT), as implemented in the SIESTA code [6]. Electron-ion interaction and electron exchange-correlation were described by the projector augmented wave (PAW) method [7, 8] and the generalized gradient
approximation using the Perdew-Burke-Ernzerhof (PBE) function [9], respectively. The valence electron wave functions were expanded by using a double-ζ basis set and the residual forces on each atom were smaller than 0.02 eV/Å. For calculating the self-consistent Hamiltonian matrix elements, the charge density was projected on a real space grid with a cutoff of 150 Ry.

In order to model the monolayer Bi₂Se₃, a vacuum thickness of 20 Å was used to avoid the interaction between atomic layers. A (4 × 4) supercell was used to investigate the adsorption and diffusion behaviors of Mg ion on monolayer Bi₂Se₃ with and without S-doped surfaces.

3. Results and discussion

Bulk Bi₂Se₃ has a layered structure stacked together via van der Waals interactions and can be exfoliated into thin 2D layers. Monolayer Bi₂Se₃ is formed by five covalently bonded atomic sheets Se-Bi-Se-Bi-Se, shown in Fig. 1b. Three different adsorption configurations of Mg ion are identified on monolayer Bi₂Se₃, which are shown using top and side views in Fig. 1. The corresponding adsorption energies are reported in Table I. According to the definition of adsorption energy, negative adsorption energy means a favorable exothermic reaction. The most stable site for Mg adsorbed on Bi₂Se₃ surface is a fcc hollow site with the adsorption energy of -1.47 eV, marked as H adsorption configuration in Fig. 1a. The bond lengths of nearest-neighbor Mg–Se for the Mg adsorbed at H-site are 2.60 Å. The remaining two adsorption structures identified on Bi₂Se₃ surface are denoted as Tₘe and Tₜbi sites, shown in Fig 1c and 1e, respectively. Tₘe configuration has the highest adsorption energy of -0.43 eV, where Mg atom is one-coordinated with a Mg–Se distance of 2.79 Å. When Mg is at the Tₜbi site, it has 3 nearest neighbors with a Mg–Se distance of 2.68 Å and the corresponding adsorption energy is -1.20 eV.

![Figure 1](image)

**Figure 1.** Top and Side views of three adsorption configurations for Mg on monolayer Bi₂Se₃. (a), (b) correspond to H site; (c), (d) correspond to Tₘe site; (e), (f) correspond to Tₜbi site. Orange, purple and green balls represent magnesium, bismuth and selenium atoms, respectively.

**Table 1.** Adsorption energies and diffusion barriers for Mg ion on pure and S-doped Bi₂Se₃ monolayer surfaces.

|                | Bi₂Se₃ | H   | Tₘe | Tₜbi | Tₘs | Path 1 | Path 2 | Path 3 |
|----------------|--------|-----|-----|------|-----|--------|--------|--------|
| Eₐd (eV)       |        | -1.47| -0.43| -1.20| --- | 0.88   | 1.04   | 0.42   |
| S-dop Bi₂Se₃  | -1.56  | -0.51| -1.26| -0.43| 0.66| 1.05   | 0.50   |

Monolayer Bi₂Se₃ with a low S doping level, *i.e.* BiₓSe₃₋ₓSₓ (x=0.0625), was investigated in this study. As shown in the Fig. 2a, there are four adsorption sites for Mg on S-doped Bi₂Se₃ surface. The corresponding adsorption energies are listed in Table I. Comparison reveals that H site at the hollow site of S-doped Bi₂Se₃ surface is the most stable for Mg location with the adsorption energy of -1.56 eV, as
shown in Fig. 2b. The bond length of Mg to its neighboring two Se atoms is 2.59 Å while bond length of Mg–S is 2.43 Å. For S-doped Bi$_2$Se$_3$ monolayer, T$_{Se}$, T$_{Bi}$ and T$_S$ sites are above Se, Bi and S atoms with the adsorption energy of -0.51, -1.26 and -0.43 eV, respectively. Compared with pure Bi$_2$Se$_3$ monolayer, Mg atom is more easily adsorbed on S-doped Bi$_2$Se$_3$ surface with lower adsorption energy. About the adsorption process, two points need to be illustrated: (1) Mg atoms first prefer to occupy the H sites of both pure and S-doped Bi$_2$Se$_3$ monolayers; (2) doping of S atoms reduces the corresponding adsorption energy of Mg on the surface, indicating a descending thermodynamic stability.

**Figure 2.** (a) Four adsorption sites for Mg on S-doped monolayer Bi$_2$Se$_3$ surface. (b-e) corresponding adsorption configurations. Orange, yellow, purple and green balls represent magnesium, sulfur, bismuth and selenium atoms, respectively.

Examination of the intrinsic Mg mobility on the pure and S-doped Bi$_2$Se$_3$ monolayers is significant and meaningful in terms of its actual application as an electrode material of MIBs. In this section, we studied the diffusion properties of the adsorbed Mg ion on the surface of perfect and S-doped Bi$_2$Se$_3$ monolayers. The most favorable adsorption site H was set as initial diffusion site. Three possible diffusion pathways between two neighboring adsorption sites were predesigned. As illustrate in Fig. 3a, three pathways of Mg diffusion on perfect Bi$_2$Se$_3$ monolayer surface, i.e. H→H, H→T$_{Se}$→H and H→T$_{Bi}$→H, are marked by orange, purple and green lines, respectively. Corresponding energy profiles are plotted in Fig. 3b. For pure Bi$_2$Se$_3$ monolayer, H→T$_{Bi}$→H pathway (path 3) is the most favorable diffusion path, associated with energy barrier of only 0.42 eV. Thus, Mg ion can migrate on the Bi$_2$Se$_3$ monolayer surface freely, indicating an excellent rapid charge/discharge capability. The calculated energy barriers for path 1 and path 2 are 0.88 and 1.04 eV, respectively.
Figure 3. Mg diffusion pathways on (a) perfect and (c) S-doped monolayer Bi$_2$Se$_3$ surfaces. The corresponding diffusion energy curves are shown in (b) and (d), respectively.

With surface S doping, there is no apparent change in diffusion barriers of Mg along H→T$_S$→H (path 2) and H→T$_H$→H (path 3) pathways, shown in Fig. 3d. While the energy barrier decreases by 0.22 eV as Mg diffusing along H→H (path 1) pathway on S-doped Bi$_2$Se$_3$ monolayer surface. Clearly, in the case of S doping, Mg ion diffusion along path 1 is much easier than before.

4. Conclusion
In summary, DFT calculations have been carried out to investigate the potential usage of S-doped Bi$_2$Se$_3$ monolayer as electrode materials for MIBs. Our studies show that Mg ions prefer to occupy the H sites of both pure and S-doped monolayer Bi$_2$Se$_3$ surfaces. Doping of S atoms reduces the corresponding adsorption energy and diffusion barrier of Mg on the surface. The present results give expectation of excellent battery performance by surface modification, such as S doping, and it is one way to improve electrode materials for the fast charging/discharging of MIBs.

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