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Adsorption and Diffusion of Lithium on MoS_2 Monolayer: The Role of Strain and Concentration

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Using first-principles calculations, we investigate the effects of external strain and lithium concentration on the adsorption and diffusion of lithium on the MoS_2 monolayer. The calculated results show that lithium atoms prefer to adsorb on the top sites of Mo atom from two sides of MoS_2 monolayer. Our calculations demonstrate that the binding energy decreases with increasing the external strain, whereas it is not sensitive to the lithium concentration. Additionally, the diffusion energy barrier of lithium adatom does not have evident dependence on both the lithium concentration and external strain. Our calculations suggest that MoS_2 monolayer could be a promising electrode material for lithium ion batteries in terms of lithium storage capacity and diffusion kinetics.

Keywords: lithium ion battery; Electronic structure; adsorption; diffusion

1. INTRODUCTION

Currently, lithium ion battery (LIB) [1-2] is one of the most important energy storage devices for consumer electronics, electric vehicles (EVs) and so on. Generally, the anode of LIB is made from graphitic carbon material [3] while the cathode is built out of transition metal oxide [4]. Ideally, a good cathode (anode) material should have high (low) lithium intercalation voltage, high lithium mobility, high capacity and good reversible electrochemical cycling abilities. [5-6] At present, the limited storage capacity of currently used batteries blocks the way of wide application of EVs in practical. [7] Pushed by the urgent needs in power supplies for EVs, the higher energy density electrode materials for LIB are widely studied in both academic and industrial fields in the past few years.

In recent years, many layered materials have been investigated as the candidates for the high capacity electrodes for LIB. Typically, lithium adsorption characteristics on graphene [8-9] and silicene [10] have been explored. Garay-Tapia et al. [8] found that a strong ionic interaction characters at low adsorbent densities and the formation of a chemically bond lithium layer features at larger concentration. Additionally, the presence of vacancy defects can increase the ratio of Li/C largely and boost the diffusion of lithium to some extent [9]. Likewise, the adsorption characteristics and stability of lithium on silicene had been studied by Osborn and Farajian [10]. More recently, molybdenum disulfide (MoS_2) material has attracted widespread attention as an alternative to graphitic carbon due to its high energy capacity of ~1200 mAh/g [11-14], which is much higher than that of commercial graphite (372 mAh/g) [15] and graphene nanosheets (600-900 mAh/g) [16-18]. Chen et al. [19] found that the modifications or doping of bulk MoS_2 can promote lithium ion extraction and improve the electrochemical cycling reversibility. Excitingly, Li et al. [20] demonstrated that ZMoS2NRs (zigzag MoS2 nanoribbons) have a remarkably enhanced binding interaction with lithium without sacrificing the lithium mobility. The calculations by Reshak et al. [21] showed that the location of the lithium intercalation in bulk MoS_2 significantly influenced the electronic and optical properties.

To our best knowledge, the investigation of lithium adsorption on single-layer MoS_2 substrate has been seldom reported. Moreover, the characteristics of adsorption and diffusion of lithium under external strain and different lithium concentration are especially important for battery performance. In this work, therefore, we systematically investigate the adsorption and diffusion of lithium adatom on MoS_2 monolayer material with external strain and different lithium concentration by means of density functional theory (DFT). Our calculations indicate that the strain can decrease lithium binding energy, but it has little effect on the lithium diffusion. Additionally, the lithium concentration has weak effect on both the adsorption and diffusion of lithium.

2. COMPUTATIONAL DETAILS

We perform first-principles calculations based on DFT, using the Vienna Ab-initio Simulation Package (VASP) [22]. The generalized gradient approximation (GGA) in the form of the Perdew and Wang (PW91) functional is used to approximate exchange and correlation potential. [23] Interactions between electrons and ion cores are described by the projector augmented wave (PAW) potential. [24] A cutoff energy of 550 eV is employed for the plane wave expansion of the wave functions. In order to study the effects of lithium concentration on the adsorption and diffusion of lithium, we construct the 3×3×1 supercell, which contains 18 S atoms and 9 Mo atoms. Integrations over the Brillouin zone use Monkhorst-Pack special k point mesh of 3×3×1 for the supercell. Periodic images of the monolayer along the surface normal are separated by a distance of 18 Å, so that the interactions between these images are negligible. Atomic and geometric relaxations are carried out by employing the conjugated-gradient (CG) algorithm. Full structural relaxations are performed until all the forces acting on ions are smaller than 0.005 eV/ Å.

Two crystal phases of MoS_2 monolayer have been reported: 1H and 1T phases, the former with trigonal prismatic coordination of molybdenum atom and the later with octahedral coordination of molybdenum atom. [25-26] As the 1H phase is more stable than the 1T phase, only the 1H phase MoS_2 monolayer is considered in our calculations. As shown in Figure 1, the upper panel and the lower panel are the top view and the side view of MoS_2 monolayer, respectively. Apparently, for the 1H phase, the basic unit of MoS_2 monolayer is composed of a molybdenum atom coordinated with six sulfur atoms.

It is organized in two layers of sulfur atoms forming a sandwich structure, with a layer of molybdenum atoms in the middle, and the S atoms in the upper layer are located directly above those on the lower layer.

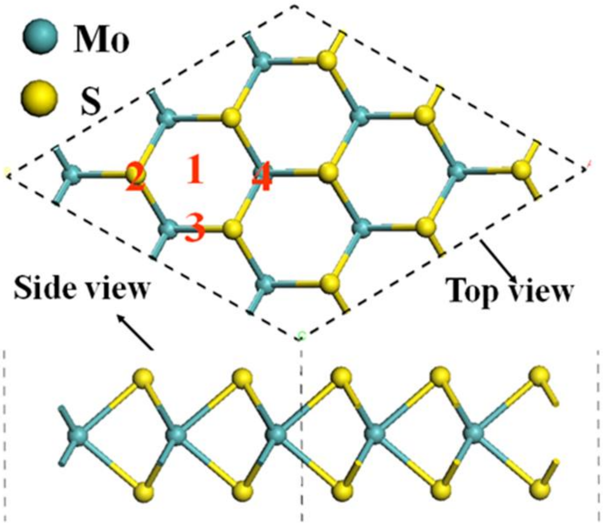

Figure 1. Optimized structures of MoS_2 monolayer with four adsorption sites (1) hollow site, (2) top site of the S atom, (3) Mo-S bridge site, and (4) top site of the Mo atom.

Each sulfur atom is coordinated with three molybdenum atoms within a single layer of MoS_2. The S-Mo bond length is 2.42 Å and the optimized lattice constant of MoS_2 monolayer is 3.18 Å, which is consistent with the previous prediction [27].

3. RESULTS AND DISCUSSION

We first study the adsorption behavior of a single lithium atom on the MoS_2 monolayer. Initially, four typical adsorption sites are considered: (1) the hollow site in hexagonal center, (2) top site of an S atom, (3) the bridge site between S-Mo bond, and (4) top site of a Mo atom, as shown in Figure 1. After full relaxation, the lithium atom at adsorption site 2 and 3 respectively moves to the top of Mo atom. However, the lithium atoms at adsorption site 1 and 4 are immovable. From our calculations, the total energy of adsorption site 4 is the lowest, indicating that one lithium atom prefers to adsorb at the top of a Mo atom.

For the practical use of the electrode material of LIB, we not only pay attention to the adsorption behavior of lithium atoms on the MoS_2 monolayer, but also look at the effects of strain on the materials. Examples have shown that stress/strain always change the electronic structures of transition metal oxides. [28] Then, we turn to study the adsorption of a single lithium atom under different external strain. For this purpose, the binding energies of a single lithium atom as the function of the lattice constant ranging from 9.26 to 9.97 Å are carefully examined, as shown in Figure 2. In our calculations, the binding energy is defined as below:

$$E_{\mathrm{ad}} = (E_{\mathrm{MoS_2}} + nE_{\mathrm{Li}} - E_{\mathrm{total}})/n, \qquad (1)$$

Where E_{total} is the total energy of the MoS_2 monolayer with n Li atoms adsorption, $E_{\mathrm{MoS_2}}$ is the total energy of MoS_2 monolayer, and E_{Li} is the energy of a single lithium atom. From Figure 2, it can be seen that the binding energy decreases quickly with elongating (or shortening) of the lattice constant. Namely, the binding energy decreases with tensile strain or compressive strain, suggesting that the binding energy is more sensitive to the external strain.

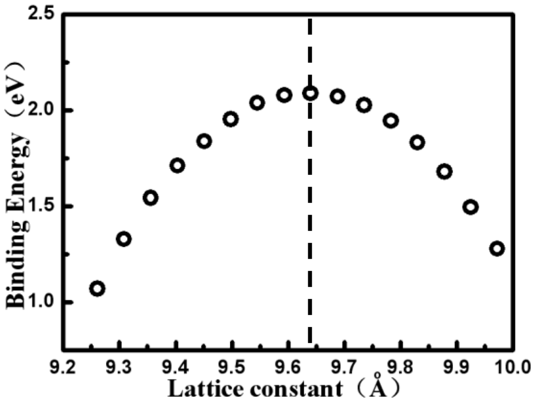

Figure 2. Binding energies of a single Li atom as the function of lattice constant, the dashed line denotes the equilibrium lattice constant.

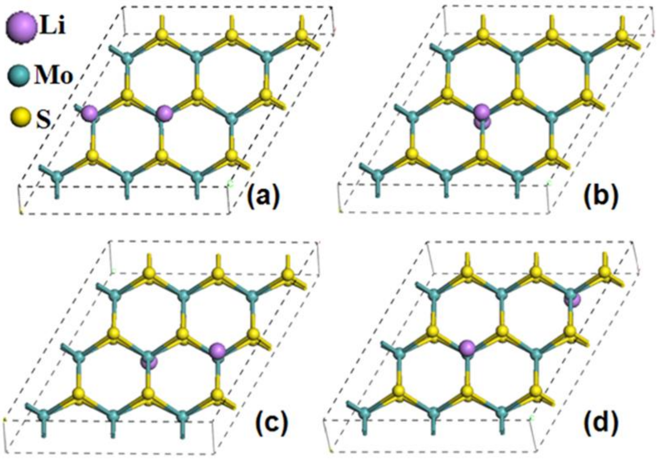

Figure 3. Optimized structures of two lithium atoms adsorbed on the MoS_2 monolayer. (a) On one side, (b), (c) and (d) on two sides. (b) On the opposite sides of a Mo atom, (c) on the nearest neighboring Mo atoms, and (d) on the next nearest neighboring Mo atoms.

Next, we focus on the adsorption behavior of more lithium atoms on the MoS_2 monolayer. In the present work, the adsorption behaviors of lithium atoms from two to eighteen are examined. First, for the case of two lithium atoms, we consider two individual lithium atoms respectively adsorbed on one side and two sides of the monolayer, as shown in Figure 3 (a) and (b). As a result, the energy of model (a) is higher by about 0.29 eV than that of model (b). This confirms that two lithium atoms are energetically favorable to adsorb on two sides of the monolayer. The strong chemical bond between the lithium atom and the molybdenum atom is formed when the lithium atom is adsorbed, causing the distortion of the MoS_2 monolayer structure. Two lithium atoms respectively adsorbed on two sides of the monolayer just counteracts the structural distortion. Therefore, two lithium atoms adsorbing on two sides of MoS_2 is more stable than the case on one side. Second, for bifacial adsorption on monolayer, we consider three cases, that is, two lithium atoms are adsorbed on top sites of a Mo atom (i.e. up-down Li pairs adsorbed on the top site), on the nearest neighboring Mo atoms and on the next nearest neighboring Mo atoms, respectively, as shown in Figure 3 (b), (c) and (d). The calculation results show that the (c) and (d) models are 0.02 eV and 0.05 eV higher in energy than that of (b) model, suggesting that two lithium atoms energetically prefer to adsorb on the top sites of one Mo atom. Likewise, for more than two lithium atoms, we construct the structures in a way similar to the case (b).

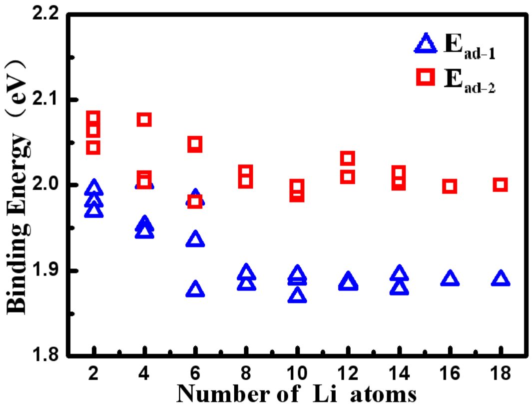

Figure 4. Binding energies as a function of the number of lithium atoms. E_{ad-1} (blue triangle) and E_{ad-2} (red square) denote the binding energies of lithium atom without and with lattice relaxation, respectively.

Then, we examine the binding energies of different lithium concentration, as shown in Figure 4. The E_{ad-1} (blue triangle) denotes the binding energy with n Li atoms adsorbed on two sides of the MoS_2 monolayer. For one lithium concentration, we considered different lithium distribution configurations and therefore different values are presented for each lithium concentration. As a whole, it can be seen that the E_{ad-1} is not very dependent on the lithium concentration. Especially, the binding energies display a flat trend and maintain about 1.9 eV from eight to eighteen lithium adatoms. In addition, we find that the strain of the lattice as lithium concentration increases. Therefore, we relax the lattice constant again to release the stress. The binding energies after relaxation with different lithium concentration are denoted by the E_{ad-2} (red square), as shown in Figure 4. Apparently, the binding energies without strain (E_{ad-2}) are always higher than those with strain (E_{ad-1}), suggesting that the strain decreases the binding energy. This is in agreement with the result of a single lithium adatom under external strain. On the other hand, we note that the $E_{\text{ad-2}}$ maintains about 2.0 eV from four to eighteen lithium adatoms, thus it is also not sensitive to lithium concentration.

Additionally, for the case of eighteen lithium adatoms on the MoS_2 monolayer, we also examine the total energies of other two models. One is that eighteen lithium atoms are respectively adsorbed on the hexagonal center, and the other is that nine lithium atoms occupy the top site of molybdenum atom and the rest adsorb on the hexagonal center. The two structures are less stable with 2.23 eV and 1.22 eV higher in total energy respectively than the structure in our present calculations. This is different from the adsorption of lithium on perfect graphene, where the lithium atoms prefer to adsorb on the hollow sites with a very low concentration, but on the top sites with high lithium concentration. [9]

It is known that the rate performance of the electrode material is determined by the electrical conductivity and lithium diffusion characters. Thus the diffusion of lithium adatom on MoS2 monolayer is examined in our calculations. The climbing image nudged elastic band (CI-NEB) method [29] is used to seek the saddle points and minimum energy path. In the case of a single lithium adatom on the MoS_2 monolayer, one path of lithium diffusion is studied as an example, that is, lithium diffusion from T1 site to T2 one (T1→T2), as shown in Figure 5 (a).

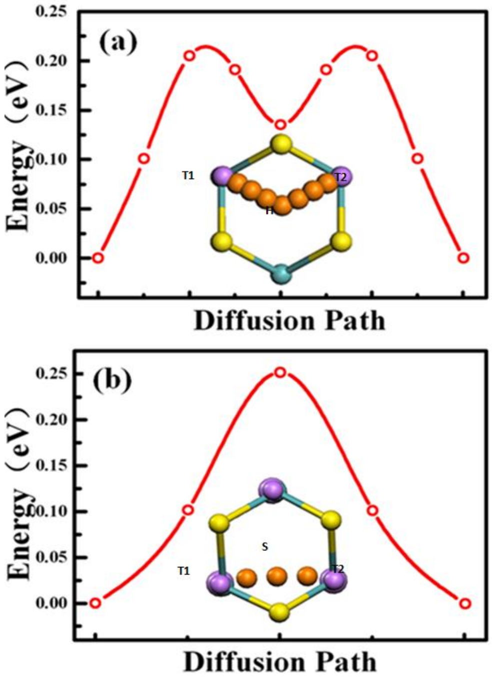

Figure 5. Lowest energy diffusion paths of a single lithium atom and calculated energy profiles along the paths for (a) one Li atom adsorbed on the MoS_2 monolayer, (b) seventeen Li atoms adsorbed on the MoS_2 monolayer.

For this model, the pathway is characterized by the two symmetrical maximums and one local minimum for the diffusion barrier. Positions atop the Mo atoms (T1 and T2) represent the absolute energy minima, and position at the hollow site (above the center of hexagonal ring, H) represents the secondary adsorption minima. An optimal path of lithium diffusion is from a T1 site to the nearest neighboring T2 site passing through an H site, which features a zigzag path way. The calculated diffusion barrier for this path of a lithium adatom is 0.21 eV. Compared with the lithium diffusion from a hollow site to a nearest neighboring one on perfect graphene (0.277 eV for diffusion barrier), [30] the diffusion barrier for lithium migration on MoS_2 decreases by about 0.07 eV. This suggests that the rate performance can be better for MoS_2 monolayer comparing to that of graphene.

To better understand the diffusion behaviors of lithium adatom at high concentration, extremely, we remove a lithium atom from the case of eighteen lithium adatoms (i.e. maximum of lithium concentration), namely, the diffusion path for seventeen lithium atoms adsorbed on the MoS_2 monolayer is studied in detail as a representative. The calculated diffusion energy barrier is presented in Figure 5 (b). As it is shown in Figure 5 (b), the diffusion path of T1→T2 is between two nearest neighboring Mo atoms. In this process, lithium atom diffusion from a T1 site to the nearest neighboring T2 site passes through a saddle site S (corresponding to the maximum of energy), which features an arc path way. The diffusion energy barrier is 0.25 eV, which is comparable with that of a single lithium atom adsorbed on the MoS_2 monolayer (0.21 eV), indicating that the lithium concentration has a weak effect on the diffusion of lithium adatom.

Generally speaking, the dynamic properties of an electrode material under strain can be different to the normal conditions for lithium storage material. For instance, the dynamic performance of λ-MnO_2 can be tuned through external strain. Namely, the lithium ion diffusion energy barriers are increased with tensile strains while decreased with compressive strains. [31] Then, we examine the diffusion barriers of a single lithium adatom on the MoS_2 monolayer under external strain. According to our calculations, we found the same trend as that in λ-MnO_2. However, the diffusion energy barrier changes only 0.03 eV when the strain ranges from the maximum compressive strain (lattice constant = 9.02 Å) to the maximum tensile strain (lattice constant = 9.97 Å). These results show that the energy barrier of lithium diffusion is also not very sensitive to the external strain.

4. CONCLUSIONS

In summary, we systematically study the effects of external strain and lithium concentration on the adsorption and diffusion of lithium on the MoS_2 monolayer material using first-principles density functional calculations. It is found that lithium atoms tend to adsorb on the top sides of Mo atom from two sides of MoS_2 monolayer. The binding energies are significantly reduced by strain, regardless of tensile or compressive. However, it is not sensitive to lithium concentration. The diffusion energy barrier of lithium adatom is slightly affected by the external strain and lithium concentration.

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