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Monolayer Black Phosphorus as Potential Anode Materials for Mg-Ion Batteries

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ABSTRACT

Adsorption and diffusion of Mg atom on the monolayer black phosphorus (P) and its structural stability with the increasing Mg concentrations were investigated using density functional theory. The adsorption energy was -1.09 eV for the Mg adsorbed on the monolayer black P. The Mg ions showed an anisotropic diffusion behavior on the monolayer black P with diffusion barriers of 0.08 and 0.57 eV along the zigzag and armchair directions, respectively. The monolayer of black P can keep the lattice structure stable forming as the Mg_{0.5}P. These results proved that the monolayer black P can be used as a potential anode for Mg ion batteries.

Key words: Monolayer black phosphorus, Mg-Ion Batteries, density functional theory

1. Introduction

Graphite has been successfully used as the anode for commercial lithium ion batteries (LIBs) for the portable electronic devices, however, its low capacity of $371 \text{ mAh}\cdot\text{g}^{-1}$ [1-4] cannot satisfy the demand of the LIBs with large capacities required in the large-scale high-power systems such as the plug-in hybrid electric vehicle (PHEV) or plug-in electric vehicle (PEV). It was reported [5] that the capacity of graphite can be greatly increased to $740\text{-}780 \text{ mAh}\cdot\text{g}^{-1}$ by reducing the dimension of graphite to the two-dimensional graphene. Currently, the other two-dimensional materials such as MoS_2 [6], V_2O_5 [7] have also received much attention to be used as electrode materials for the LIBs. Two dimensional MoS_2 is a promising material for the LIBs with a large reversible storage capacity of $1290 \text{ mAh}\cdot\text{g}^{-1}$ and a charge-carrier $\sim 200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [8]. The electro-chemical performance of the MoS_2 can be further improved by introducing defects into the monolayer [9]. The drawback of employing the MoS_2 as anodes for the LIBs is its intermediate lithiation voltages ($1.1\text{-}2.0 \text{ V}$ vs. Li/Li^+ , depending on the degree of lithiation) [10]. Recently, the monolayer black P has been successfully synthesized [11, 12], which shows some prominent properties, such as a long cycle life, anisotropic electric conductance, and high-rate capability, etc., which are suitably used as anode materials for rechargeable ion batteries [13].

Bulk black P has been tested for the anode material for the LIBs by Park and Sohn in 2007 [11]. Their experimental results showed that the bulk black P initially had a high storage capacity of $1279 \text{ mAh}\cdot\text{g}^{-1}$ for the LIBs, but it faded to $220 \text{ mAh}\cdot\text{g}^{-1}$ after 30 cycles. In addition, the layered structure of black P tended to be fractured upon lithiation [11]. The structural changes and stress generation upon lithiation can be modified by using flexible anode

materials, such as two-dimensional (2D) thin films [14]. The monolayer black P which was successfully fabricated by Lu et al. [15] shows excellent physical properties including high free-carrier mobility (about $1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), which is much better than that of the MoS_2 . The monolayer black P can also be used as a potential anode material for rechargeable ion batteries [16]. Zhao et al. [17] reported that monolayer black P has a large storage capacity of $432.79 \text{ mAh}\cdot\text{g}^{-1}$ with small volume changes. Li et al. [18] reported that diffusion barrier of Li on the monolayer black P was lower than 0.4 eV and a charge capacity of $216 \text{ mAh}\cdot\text{g}^{-1}$ was obtained. Kulish et al. [19] reported that the theoretical specific capacities of monolayer black P were $433\text{-}865 \text{ mAh}\cdot\text{g}^{-1}$ when it was used as the anode material for sodium ion batteries. The diffusion behavior of Na on the monolayer black P shows anisotropic characters with a smallest energy barrier of 0.04 eV and a high energy barrier of 0.38 eV [19]. The hybrid structure of monolayer black P and graphene could greatly enhance the cycle life of the batteries [20]. Sun et al. [21] demonstrated that black P-carbon composite has a high initial discharge capacity of $2786 \text{ mAh}\cdot\text{g}^{-1}$ at a rate of 0.2 C and even with 80% capacity retention after 100 cycles.

Although the LIBs has been widely used in the portable electronic devices, yet the energy density and cycle life of the LIBs cannot satisfy the large demands of electric vehicles and renewable energy storage along with their potential safety issues, high cost, and resource scarcity [22, 23]. As Mg have the similar atomic radius and chemical properties of Li, Mg-ion batteries (MIBs) are considered to be an alternative choice to the LIBs with high energy storage and conversion capacities. Due to the bivalency of Mg ion, its specific volumetric capacity is $3833 \text{ mAh}\cdot\text{cm}^{-3}$, which is much higher than that for the Li ones ($2046 \text{ mAh}\cdot\text{cm}^{-3}$)

[24]. Mg is a benign and abundant metal being the 5th most abundant element in the earth's crust [25]. And it is stable enough in ambient atmosphere for handling and electrode preparation processes, thus it is safer than Li. It is urgent to find suitable anode materials for the MIBs using the similar intercalation chemistry of LIBs. In this work, we investigated the possibility of monolayer black P being used as the anode material for the MIBs, in terms of the adsorption and diffusion of Mg atoms on monolayer black P using the first-principle calculations.

2. Simulation and Calculations

The density functional theory (DFT) as implemented within the SIESTA code [26] was used for all the simulations. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functions was used to describe the electron exchange correlation term [27, 28]. The interactions between the core electrons and valence electrons were described using norm-conserving pseudo-potentials [29]. The valence electrons were expanded using a double- ζ basis set plus polarization functionals (DZP) [30]. Ionic coordinates were fully relaxed until the residual forces were below 0.01 eV/Å. For calculating the self-consistent Hamiltonian matrix elements, the charge density was projected on a real space grid with a cutoff of 200 Ry. To model the monolayer black P, a separation of 20 Å was used to avoid the interactions between periodical image layers. All the calculations were performed with $11 \times 11 \times 1$ k-point sampling for the Brillouin zone integration of the Monkhorst-Pack scheme [31].

For simulating Mg adsorption on the monolayer black P with different Mg concentrations,

models including $2 \times 2 \times 1$ and $3 \times 3 \times 1$ supercells were used. The formation energy $E_{\text{form}}(\text{Mg}_x\text{P})$ was calculated using the following equation:

$$E_{\text{form}}(\text{Mg}_x\text{P}) = (E(\text{Mg}_x\text{P}) - E(\text{P}) - x\mu_{\text{Mg}})/x \quad (1)$$

where $E(\text{Mg}_x\text{P})$ and $E(\text{P})$ are the total energies of monolayer black P with and without Mg atoms adsorption, respectively; x is the concentration of Mg atoms; μ_{Mg} is the chemical potential of magnesium.

3. Results and discussion

The obtained lattice constants for the monolayer black P are $a=3.32$ and $b=4.40$ Å, which agree with other simulation results of $a=3.32$ and $b=4.57$ [18]. There are two possible adsorption positions for Mg on the monolayer black P for the symmetry of the geometric structure, i.e. the H site which is above the center of triangle structure composed of three P atoms on the surface, and T site which is above the top of one P atom, as shown in Fig. 1. The adsorption energy (E_{ad}) for Mg adsorbed on the monolayer black P was calculated using $E_{\text{ad}} = (E_{\text{Mg+P}} - nE_{\text{Mg}} - E_{\text{P}})/n$, where $E_{\text{Mg+P}}$ and E_{P} are the total energy of monolayer black P with and without Mg adsorption, E_{Mg} is the energy of an isolated Mg atom, n is the number of adsorbed Mg atoms adsorbed. It was found that the T site is not a stable position for Mg adsorption, and the Mg atom will move from the T site to the H site after relaxation. The Mg atom prefers to be adsorbed at the H site with adsorption energy of -1.09 eV with $3 \times 3 \times 1$ supercell. The same phenomenon was observed for other atoms adsorbed on the monolayer black P, such as Li [32] and Na [19]. Larger supercell with $5 \times 5 \times 1$ supercell does affect the adsorption energy of Mg on the monolayer black P, indicating that the $3 \times 3 \times 1$

supercell is enough to be used to model the adsorption of Mg on monolayer black P. The average open circuit voltage [33] calculated for Mg intercalation on monolayer black P was about 0.89 V. The optimized structures of Mg adsorbed at the H site are shown in Fig. 1(c) and (d). The bond lengths of nearest-neighbor Mg-P for the Mg adsorbed at H sites are 2.66, 2.78 and 2.78 Å, respectively. The optimized atomic structures of Mg adsorbed at the T site are shown in Fig. 1(e) and (f), with Mg-P bond length of 2.78 Å.

The charging rate performance of the MIBs is strongly dependent on the diffusion rate of Mg ions within the anode materials, so the diffusion behavior of Mg atoms on monolayer black P surface was simulated using the constraint model [9]. The Mg was pushed along the diffusion path, but was not allowed to relax along the diffusion path, and it was allowed to relax perpendicular to the direction of the path. Two diffusion paths were investigated for the Mg on the monolayer black P as shown in Fig. 2. One of the diffusion paths for Mg mobility on monolayer black P is along armchair direction as shown in Fig. 2(a), and the other one is along zigzag direction as shown in Fig. 2(b). The two diffusion paths have been used for clarification of the Li and Na diffusion mechanisms [19, 34]. The energy barriers are 0.57 and 0.08 eV for the Mg diffusion along the armchair and zigzag directions (shown in Fig. 2(c)), respectively. The calculated ratio between energy barriers in the orthogonal directions is equal to $E_{\text{Zigzag}} / E_{\text{Armchair}} \approx 1/7$. The Mg mobility along the zigzag direction on the monolayer black P was estimated to be much faster than that along the armchair direction. The anisotropy diffusion behavior has been found for the diffusion of Li and Na [18, 35] on the monolayer black P. The diffusion anisotropy is mainly due to the non-flat and puckered structure of the monolayer black P. The high anisotropy diffusion behavior with a low diffusion barrier result

in black P to be a unique fast Mg-diffusion channel which has not been reported in other two-dimensional anode materials, such as MoS₂ and graphene [16]. With such a low energy barrier existed along the zigzag direction, the monolayer black P is a potential two-dimensional anode material for the fast charging/discharging of MIBs.

Safety is major important issue for the development of MIBs. The safety of MIBs is mainly related to the structure stability of electrode materials. So the structural stability of monolayer black P with the increasing concentrations of Mg insertion was investigated. The formation energies of Mg_xP were calculated using equation (1). The stability of the studied Mg_xP phases can be evaluated from their formation energies. The formation energies are negative, suggesting that Mg-P nanostructures are stable, as a higher absolute value of formation energies means a better structural stability. As shown in Fig. 3, the formation energies for Mg-P increases with the increase of the Mg concentrations, indicating that the structure gradually becomes instable. The atomistic configurations for the Mg_xP compounds ($x=0.0625, 0.125, 0.25, 0.5$) are shown as inset of Fig. 3. The Mg atoms prefer to stay at H sites as $x<0.5$, and Mg atoms occupy the center sites above the hexagons as $x=0.5$ with Mg-Mg bond length of 2.75 Å. With the highest concentration ($x=0.5$) for single-side Mg adsorption, the calculated formation energy is -1.31 eV, indicating that the Mg-P nanostructure is remarkably stable. As monolayer black P is a two-dimensional material, we used the evolution of area to character the volume expansion upon intercalating. The volume evolution as a function of Mg content is shown as inset in Fig. 3. There is little decrease of the volume for low Mg concentration; the volume expansion is ~11.0% for Mg_{0.5}P. The crystal deformation and expansion caused by Mg atoms insertion are relatively small. Based on the above results, it

can be concluded that the unique features of monolayer black P could be used as a potential anode material for the Mg-ion batteries.

4. Conclusion

In this paper, the adsorption and diffusion of Mg on the monolayer black P and its structural stability with the increasing concentrations of Mg adsorption were studied by using the density function theory. Result showed that the Mg atom prefers to occupy the H site with adsorption energy of -1.09 eV. The Mg shows anisotropy diffusion behavior on the monolayer black P with diffusion barriers of 0.08 and 0.57 eV along the zigzag and armchair directions, respectively. The monolayer of black P can keep the structural stability with Mg coverage to $\text{Mg}_{0.5}\text{P}$. The monolayer black P was proven to be a promising two-dimensional anode material for the MIBs.

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Compliance with Ethical Standards:

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Conflict of Interest: The authors declare that they have no conflict of interest.

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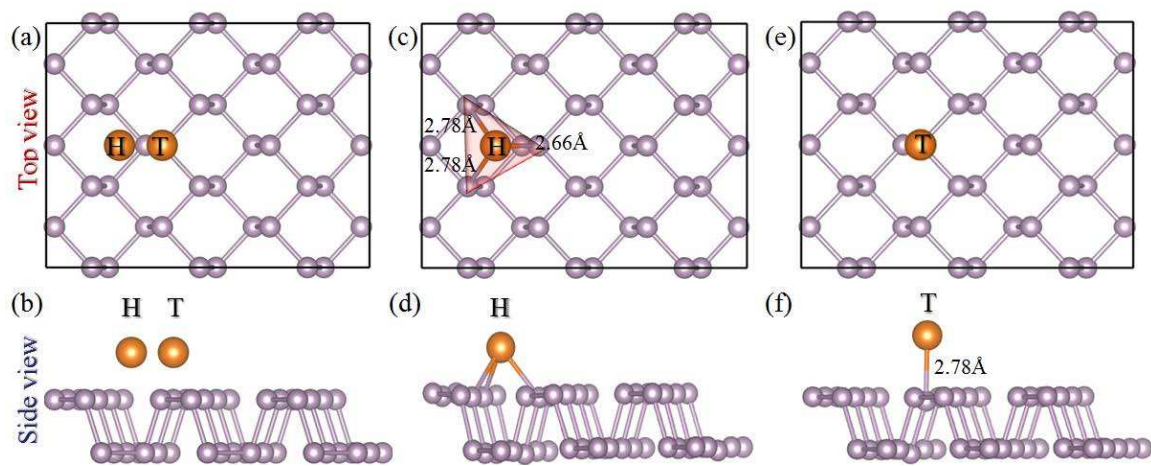
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Figure captions:

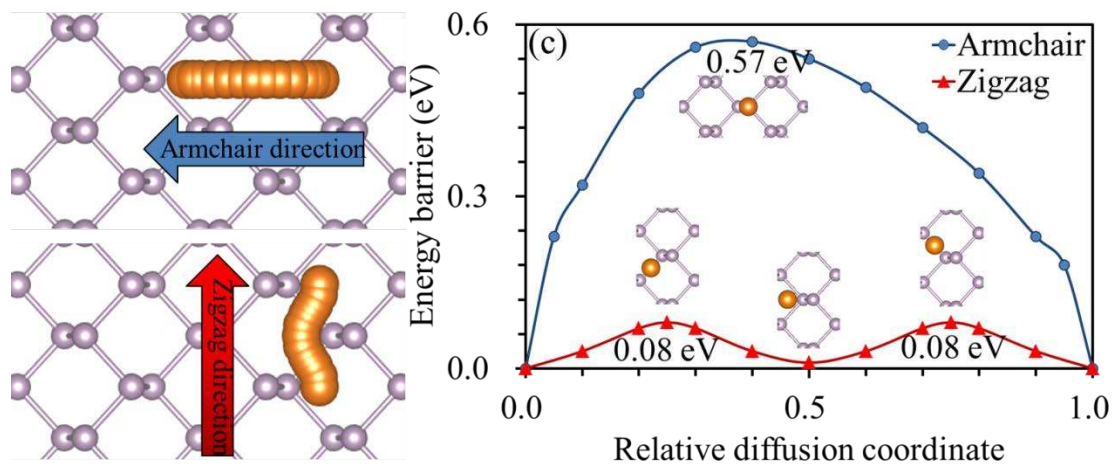
Figure 1: (a) Side view and (b) top view of possible adsorption sites of Mg in monolayer black P (H and T sites). (c) Top and (b) side view of that relaxed structure of Mg atom adsorbed on the H-site of monolayer black P.

Figure 2: Diffusion paths along (a) armchair direction and (b) zigzag direction. (c) The energy barrier profile of Mg diffusion on monolayer black P.

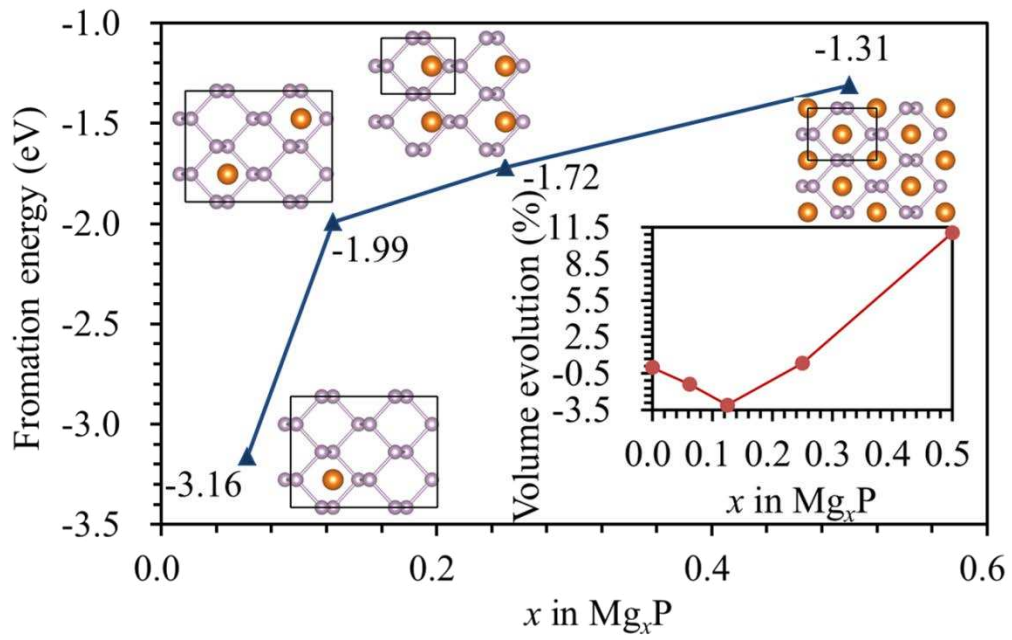
Figure 3: The formation energies as a function of Mg concentrations.



W.Jin et al. Figure 1



W.Jin et al. Figure 2



W.Jin et al. Figure 3