Density Functional Theory Calculations for the Evaluation of FePS₃ as a Promising Anode for Mg Ion Batteries

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Abstract

FePS₃, a classical 2D layered material with transition metal phosphorous trichalcogenides, was investigated as an anode material for Mg ion batteries. We used density functional theory to calculate the Mg storage properties of FePS₃, such as Mg adsorption energy, theoretical specific capacity, average voltage, diffusion energy barriers, volume change, and electronic conductivity. The theoretical specific capacity of the FePS₃ monolayer is 585.6 mA h/g with a relatively low average voltage of 0.483 V (vs. Mg/Mg²⁺), which is favorable to a high energy density. The slight change in volume and good electronic conductivity of bulk FePS₃ are beneficial to electrode stability during cycling.

Keywords Mg ion battery · FePS₃ · Density functional theory · Anode material

Introduction

The growing demand for energy sources results in the excessive consumption of limited and nonrenewable fossil fuels, and consequential environmental problems have become increasingly prominent. To address this urgent issue, researchers focused on renewable energies and efficient energy storage systems [1, 2]. As one of the most successful technology for energy storage, rechargeable lithium-ion batteries (LIBs) have been widely applied to scalable energy storage systems, electric vehicles, and portable electronic

devices [3–5]. Although LIBs have become advanced and widely available rechargeable batteries, they have not been regarded as ideal sustainable sources of energy storage equipment because of the scarcity, high cost, and safety problems of lithium [6, 7]. Magnesium-ion batteries (MIBs) have attracted increasing attention because of their low cost, safety, and natural abundance. The price of Mg (35 \$/kg) is lower than that of Li (1500 \$/kg), and Mg reserves in the crust (2.33%) are around 350 times larger than Li (0.0065%) [8]. In addition, MIBs exhibit more advantages in the electrochemical process [9, 10]. First, the theoretical volumetric capacity of magnesium (3832 mA h/cm³) is higher than that of lithium (2062 mA h/cm³) [11] because of the divalent nature of Mg ion. Second, dendrite is a serious problem for lithium metal anodes, whereas magnesium metal used as an anode can achieve a dendrite-free deposition during cycling, resulting in a relatively safe cycling process [12]. As such, MIBs have been suggested as possible alternatives to battery technology. However, the reaction of Mg metal with electrolyte species causes an unstable solid electrolyte interface (SEI) and constant electrolyte consumption. Sluggish Mg ion diffusion in host materials due to the divalent nature of the Mg ion results in slow insertion/extraction reaction kinetics [13, 14].

Many efforts have been devoted to developing cathode materials, such as Mo₆S₈ [15], TiS₂ [16], and V₂O₅ [17], but a few works have designed anode materials, such as Ga [18], Sn [19], and Bi [20, 21], to replace Mg metal.

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Mo₆S₈ is one of the best cathode materials because of its good electrochemical performance and compatibility with electrolytes, but the cycling performance of MIBs remains poor because of the anode side of Mg metal, such as the large volume change during the discharge/charge process and sluggish Mg ion diffusion in a dense SEI layer [22]. To our knowledge, the use of layered materials in LIBs can significantly buffer the change in volume and promote Li-ion transfer in an interlayer space [23, 24], and this strategy can be used in MIBs. For example, layered Na₂Ti₃O₇ nanoribbons exhibit an actual reversible capacity of 78 mA h/g at 20 mA/g after 100 cycles [25]. Luo et al. [26] reported that layered Na₂Ti₆O₁₃ nanowires display a stable capacity of 51.2 mA h/g at 100 mA/g after 300 cycles. Many theoretical calculations have verified that layered materials, such as arsenene [27], MnSb₂S₄ [28], MXene [29], phosphorene [8], WS₂ [30], and C₃N₄ [31], can be promising anode materials for MIBs. Furthermore, 2D layered transition metal phosphorous trichalcogenides (MPX₃, where *M* = Mn, Fe, Ni, etc., and *X* = S, Se) have been widely explored because of their interesting physicochemical features, including electronic, magnetic, and superconductive properties [32, 33]. Hitherto, materials from the MPX₃ family serve as good candidates for LIBs because of their reversible lithium storage capacity and fast lithium ion/electron conduction [34–36]. However, no study has explored the magnesium storage capacity of MPX₃ materials.

In this work, theoretical studies on FePS₃ anode for MIB application were presented. FePS₃, a classical MPX₃ material, is expected to be a promising anode for MIBs because of its large specific surface area, abundant active sites, and fast ion diffusion. FePS₃ has a moderate electronic conductivity of 10^{−5} S/cm, which is significantly higher than that of other MPX₃ materials, such as MnPS₃, NiPS₃, and ZnPS₃ (around 10^{−9} S/cm). Herein, density functional theory (DFT) calculations were conducted to analyze Mg adsorption and diffusion properties in an FePS₃ monolayer, and the volume change and electronic conductivity of the bulk FePS₃ for its potential applications as an anode candidate for MIBs.

Computational Details

All calculations were carried out using the Cambridge Sequential Total Energy (CASTEP) package within the DFT framework in the Materials Studio Version 5.5. Generalized gradient approximation with Perdew–Burke–Ernzerhof functional (GGA–PBE) was used for the exchange correlation energy. An ultrasoft pseudopotential was used and the energy tolerance in the self-consistent field (SCF) calculations was 2 × 10^{−6} eV/atom. The convergence conditions were set as 2 × 10^{−5} eV/atom for the energy change, 0.05 eV/Å for the force change, 2 × 10^{−3} Å for the atomic

displacement and 0.05 Å^{−1} for the K-point separations. The structure was relaxed using 4 × 4 × 1 (monolayer FePS₃) and 4 × 4 × 3 (bulk FePS₃) K-point meshes.

Results and Discussion

Adsorption of Mg on an FePS₃ Monolayer

The relaxed structure of the FePS₃ monolayer is displayed in Fig. 1a, b. Similar to other MPX₃ materials, FePS₃ shows a sandwich structure with Fe atoms in the middle of monolayer. Each Fe atom bonds with three S atoms on the upper side of the FePS₃ monolayer and three S atoms on the lower side. Each P atom bonds with three S atoms and another P atom. Each S atom is situated in the same chemical environment with two S–Fe bonds and one S–P bond. The lengths of S–Fe, S–P, and P–P bonds are about 2.520, 2.045, and 2.195 Å, respectively. The lattice constants of the primitive FePS₃ cell is *a* = *b* = 5.932 Å. A 2 × 2 supercell was used to explore the adsorption properties of the FePS₃ monolayer. A Mg atom was initially placed at different sites on the surface of the FePS₃ monolayer with a certain distance of 1.50 Å. Figure 1a shows the possible sites at Fe, P, and S atoms and a hollow position, which are denoted as Fe, P, S, and H sites, respectively. Figure 1c illustrates the structures of the FePS₃ monolayer loaded with a Mg atom before and after geometric optimization. Mg adsorbed at S and H sites moves to the same position after structure relaxation. Adsorption energy (*E*_{ads}) was calculated with the following expression to find the most stable structure of the FePS₃ monolayer loaded with Mg:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{FePS}_3} - E_{\text{Mg}} \quad (1)$$

where *E*_{FePS₃} and *E*_{total} represent the energy of the FePS₃ monolayer before and after loading Mg, respectively, and *E*_{Mg} is the energy of single Mg atom. In Table 1, the largest adsorption energy (−4.45 eV) occurs at the Fe site, and the second stable adsorption energy (−4.39 eV) corresponds to the H site. The spatial distribution of the difference in the charge density of the FePS₃ monolayer (Fig. 1d) was used to explain the reason for the most stable structure of Mg adsorbed at the Fe site. Blue and yellow correspond to electron-accumulated and electron-depleted regions, respectively. Obviously, the electron-accumulated regions are at S atoms around Fe sites, which are beneficial to Mg loading. Therefore, the most stable structure is Mg adsorbed at the Fe site with three Mg–S bonds. The distances between Mg and adjacent S atoms are summarized in Table 1. The smallest distances of Mg atom with surrounded S atoms are at the Fe site, further indicating that the most stable structure is Mg adsorbed at the Fe site. The charge density difference slice

Fig. 1 **a** Top and **b** side views of the optimized structures of the FePS₃ monolayer and the possible sites for Mg adsorption, **c** Structures of the FePS₃ monolayer with Mg loaded at different sites before (left) and after structure relaxation (right), **d** Spatial distribution of

charge density difference of the FePS₃ monolayer, **e** The charge density difference slice map of the FePS₃ monolayer absorbed with Mg. Blue, yellow, pink, and green balls represent Fe, S, P, and Mg atoms, respectively

Table 1 Data of adsorption energy (E_{ads}), Mulliken charge, and distances between Mg and adjacent S at four possible adsorption sites in the FePS₃ monolayer

Adsorption site	E_{ads} (eV)	Mulliken charge ($ e $)	Distance between Mg and adjacent S (Å)		
Fe site	-4.45	1.08	2.425	2.394	2.363
P site	-3.68	0.54	3.473	3.419	3.280
H site	-4.39	0.88	3.374	2.515	2.484
S site	-4.33	0.87	3.599	2.578	2.462

map (Fig. 1e) was used to explore the nature of the Mg-S bond. Electrons tend to move close to S, indicating that the Mg-S bond approaches a polar ionic bond. The Mulliken charge of Mg (Table 1) was calculated to confirm the charge transfer from S to Mg. The Mulliken charge value of Mg at

the Fe site is 1.08 $|e|$, which is apparently larger than that of other sites, proving that more charge transfers occur. In summary, Mg prefers to be adsorbed at the Fe site of the FePS₃ monolayer to form the most stable structure.

Theoretical Specific Capacity and Voltage Profile of the FePS₃ Monolayer

In Mg_xFePS_3 , x represents the concentration of Mg in the FePS₃ monolayer. The optimized structures of Mg_xFePS_3 with different x values are depicted in Fig. 2a. Mg atoms are initially placed at Fe sites on one side of the FePS₃ monolayer by using a 2×2 supercell. Obviously, all the Fe sites on one side are successfully occupied with eight Mg atoms corresponding to the formula of MgFePS_3 . Afterward, the meta-stable H sites on the same side are also

Fig. 2 **a** Configurations of the schematic of Mg_xFePS₃ with Mg adsorbed on one side of the FePS₃ monolayer (x = 1/8 ~ 1); **b** Optimized structure of the FePS₃ monolayer with Mg adsorbed on both sides of the Fe and H sites on the same side; **c** Configurations of the schematic of

Mg₂FePS₃ with Mg adsorbed on both sides of the FePS₃ monolayer; **d** Adsorption energies with respect to Mg concentration; **e** Voltage profile with respect to Mg content from 0 to 2

considered to load Mg after the Fe sites are fully occupied. However, the Mg atoms cannot be embedded at the H sites because all Mg atoms at H sites are extruded out of the FePS₃ surface after structure relaxation (Fig. 2b). Mg storage on the double sides of the FePS₃ monolayer was calculated on the basis of the basic structure (MgFePS₃) in which Fe sites were fully occupied with Mg atoms on one side to obtain the maximum capacity. On the other side, both H sites and Fe sites can absorb Mg

ion. In Fig. S1, the structure of the FePS₃ monolayer irreversibly deforms when the H sites are fully occupied with Mg, indicating thermodynamic instability. By contrast, the structure of the FePS₃ monolayer slightly changes when the Fe sites on both sides are fully occupied with Mg. This result indicates a stable structure, corresponding to the formula of Mg₂FePS₃ (Figs. 2c and S1). Figure 2d shows the adsorption energies of Mg_xFePS₃ with an increasing absolute x (from 1/8 to 2). Obviously, the

absolute value of adsorption energy gradually decreases as Mg concentration increases due to repulsive interactions between adjacent Mg cations. As a consequence, the maximum Mg concentration in the FePS₃ monolayer corresponds to the formula of Mg₂FePS₃ with a theoretical specific capacity of 585.6 mA h/g.

Open-circuit voltage (OCV) is another important parameter for evaluating the electrochemical properties of rechargeable batteries. OCV can be obtained by calculating the average voltage (V_{avg}) within the range of $x_1 < x < x_2$ in Mg_xFePS₃. V_{avg} was calculated with the following expression:

$$V_{\text{avg}} = - \frac{E(\text{Mg}_{x_2}\text{FePS}_3) - E(\text{Mg}_{x_1}\text{FePS}_3) - (x_2 - x_1)E(\text{Mg})}{2(x_2 - x_1)e} \quad (2)$$

where $E(\text{Mg}_{x_2}\text{FePS}_3)$ and $E(\text{Mg}_{x_1}\text{FePS}_3)$ represent the energies of Mg_{x₂}FePS₃ and Mg_{x₁}FePS₃, respectively; $E(\text{Mg})$ is the energy of Mg; and e is the fundamental charge. In Fig. 2e, V_{avg} decreases as Mg concentration increases, and V_{avg} of the FePS₃ monolayer is ~0.483 V (vs. Mg/Mg²⁺). This result indicates that the FePS₃ monolayer is a suitable anode material for Mg ion batteries. Besides, V_{avg} of the FePS₃ monolayer is relatively lower than that of other anode materials, such as arsenene monolayer 0.83 V (vs. Mg/Mg²⁺) [24], phosphorene 0.833 V (vs. Mg/Mg²⁺) [8], and MnSb₂S₄ monolayer 0.77 V (vs. Mg/Mg²⁺) [25], which is beneficial to achieving a high power density in full batteries.

Mg Diffusion on the FePS₃ Monolayer Surface

The transport property of Mg ion affects the electrochemical reaction kinetics of Mg ion batteries. Therefore, the diffusion

Fig. 3 Mg diffusion on the surface of the FePS₃ monolayer through paths **a** 1, **b** 2, and **c** 3. Energy profiles of Mg diffusion through paths **d** 1, **e** 2, and **f** 3

Fig. 4 Side structures of **a** bulk FePS₃ and **b** bulk MgFePS₃; ELF slice maps of the **c** bulk FePS₃ and **d** bulk MgFePS₃; **e** Lattice constants of bulk FePS₃ and bulk MgFePS₃; **f** Density of states (DOS) of bulk FePS₃ and bulk MgFePS₃

behavior of Mg ion on the surface of an FePS₃ monolayer should be understood. In this work, the linear synchronous transit/quadratic synchronous transit (LST/QST) method was used to evaluate the energy barriers of Mg ion diffusion through different paths. In Fig. 3a–c, three possible diffusion paths are found between two equilibrium Fe sites in the FePS₃ monolayer. Path 1 is between the adjacent Fe sites (Fig. 3a), path 2 corresponds to adjacent secondary Fe sites (Fig. 3b), and path 3 connects the two Fe sites at the diagonal side of a hexagon (Fig. 3c). The calculated energy profiles of three diffusion paths are shown in Fig. 3d–f. Obviously, the results show that path 3 has a minimum energy barrier of 1.183 eV. The diffusion energy barriers of Mg ion along paths 1 and 2 are 1.426 eV and 1.620 eV, respectively. Accordingly, Mg ion tends to migrate between the Fe sites at the diagonal side of the hexagon, and the relatively low energy barrier contributes to fast ionic diffusion and electrochemical reaction kinetics.

Mg Storage Properties of Bulk FePS₃

The Mg storage properties in bulk FePS₃ were also tested. In Fig. 4a, bulk FePS₃ exhibits an A–A' stacking model after

structure relaxation. Mg was placed at the middle of the Fe sites at two consecutive layers in bulk FePS₃ in consideration of the characteristics of Mg storage in the FePS₃ monolayer. The maximum Mg storage capacity corresponds to the formula of MgFePS₃ with a theoretical specific capacity of 292.8 mA h/g. The volumetric expansion of electrode materials causes the pulverization of electrodes and unstable SEI films. The change in volume was investigated on the basis of the changes in crystal cell parameters and interlayer space in bulk FePS₃. In Fig. 4a, the distance between two Fe atoms in the two adjacent layers in the original bulk FePS₃ is 7.356 Å. After Mg insertion, the distance between the two Fe atoms decreases to 5.979 Å (Fig. 4b), indicating the volume reduction in the *z* axial direction. Lattice constant is also an important parameter to express the change in the volume of the bulk FePS₃. The lattice constants (1 × 1 cell) of FePS₃ and MgFePS₃ are summarized in Fig. 4e. In particular, the constants increase by 15.6% and 8.0% for *a* and *b*, respectively, whereas the constant decreases by 18.7% for *c*. This finding is consistent with the decrease in the interlayer space. The lattice volume of bulk FePS₃ changes from 215.48 to 206.70 Å³ after Mg insertion, indicating that the volume of FePS₃ has a little shrink but not expansion for magnesiation process. The small volumetric change is

beneficial to the structural integrity of electrodes during the insertion/extraction of Mg ion.

Volume reduction mainly results from a decrease in the interlayer space in bulk FePS_3 . Electron localization function (ELF) slice maps (Fig. 4c, d) were used to explain the phenomenon of interlayer space reduction after Mg insertion. In Fig. 4c, almost no electrons are localized at the interlayer in bulk FePS_3 , illustrating that the interlayer interaction mainly belongs to van der Waals forces. When a Mg atom inserts into the interlayer of bulk FePS_3 , electrons tend to distribute between Mg atoms and FePS_3 layers. The interlayer force becomes electrostatic interaction, which is stronger than van der Waals forces, leading to a reduction in the interlayer distance. The Mg diffusion behavior in the interlayer of bulk FePS_3 was also calculated. In Fig. S2, unlike the Mg diffusion behavior on the surface of the FePS_3 monolayer, Mg cannot diffuse along paths 2 and 3 but prefers to diffuse along path 1 during the transition state search process. Diffusion behavior differs possibly because the limited space between FePS_3 layers restricts the diffusion of Mg ion at a long distance, such as paths 2 and 3. Therefore, Mg ion tends to migrate through path 1 with a short diffusion distance (Fig. S3), and the corresponding diffusion energy barrier is 1.557 eV. Another important parameter affecting the electrochemical performance of rechargeable batteries is the electronic conductivity of electrode materials. The electronic conductivities of bulk FePS_3 and MgFePS_3 were evaluated in terms of density of states (DOS). In Fig. 4f, the electronic state at a Fermi level is not zero for FePS_3 and MgFePS_3 , indicating that they exhibit a metallic behavior. In Fig. S4, the band gap of bulk MgFePS_3 (0.306 eV) is smaller than that of bulk FePS_3 (0.550 eV), demonstrating that the insertion of Mg ion in the interlayer of bulk FePS_3 can improve electronic conductivity.

Conclusions

In this work, DFT calculations were conducted to investigate various electrochemical properties of 2D layered FePS_3 for Mg storage. FePS_3 can be used as an anode material for Mg ion batteries because of the following advantages: (1) Mg can be loaded at Fe sites in FePS_3 with a stable structure and high theoretical specific capacities of 585.6 mA h/g for monolayers and 292.8 mA h/g for bulk materials. (2) It can provide a relatively low voltage of 0.483 V (vs. Mg/Mg^{2+}), contributing a high power density in full batteries. (3) The volumetric change in FePS_3 is only 4.0% for full Mg insertion, and both FePS_3 and its reduction products of MgFePS_3 exhibit good electronic conductivity, which are beneficial to cycling stability and high-rate performance, respectively.

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