Adsorption and Diffusion of Magnesium on Nitrogen Doped Mo_2C Monolayer

Jiangfeng Ni
Jiangsu Ocean University
Kaimin Fan (fankm128@163.com)
Jiangsu Ocean University https://orcid.org/0000-0002-5794-5975
Jing Tang
Jiangsu Ocean University

Research Article

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Abstract

The Mg adsorption and diffusion behaviors on nitrogen doped (N-doped) Mo_2C monolayer have been systematically investigated by the first principles based on density functional theory (DFT). The adsorption energies of Mg on pristine Mo_2C and $Mo_2C_{1-x}N_x$ (x = 0.0625, 0.125, 0.1875 and 0.25) have been studied. The adsorption energies of Mg on N-doped Mo_2C are lower than that of pristine Mo_2C. Especially, the adsorption energies of Mg are − 1.639 eV and − 1.625 eV on T_{C1} and H_2 sites for $Mo_2C_{0.875}N_{0.125}$, which have decreased by 16.49% and 18.43%. Furthermore, the Mg diffuses along H_3-B-H_4 and H-B-H with the barriers of 0.021 eV and 0.028 eV, which indicate that $Mo_2C_{0.875}N_{0.125}$ exhibits fast diffusion properties. Additionally, the partial density of states (PDOS) reveals the interaction between Mg and $Mo_2C_{0.875}N_{0.125}$. The PDOS results indicate that nitrogen doping causes the PDOS peaks transfer to a lower energy level, which is benefit for the bonding between Mg and $MoC_{0.875}N_{0.125}$. These results suggest that the adsorption and diffusion behaviors of Mg are enhanced by nitrogen doping.

1 Introduction

Lithium ions batteries (LIBs) are widely used to in phones, laptops, digital cameras, and other portable devices [1–3]. However, safety, high costs and resource shortages have restricted the development of lithium batteries [4, 5]. With the development of the intelligent electronic applications such as new energy vehicles, energy storage plant and artificial satellite, which require high battery storage and stable cycle capacity. MIBs have been considered as the potential alternatives to LIBs, due to the natural abundance, low cost, safety and high volumetric energy density (3832 mAh cm^{-3}) [6, 7]. However, it is well-known that the performance of rechargeable batteries depends on their anode or cathode materials. Hence, a great deal of efforts has been carried out to search for novel anode materials for MIBs.

As lager surface area and excellent elctrochemistry, extensive investigations have been focused on exploring 2-dimensional materials as anodes for MIBs [8]. For example, Sibari et. Al have demonstrated that phosphorene is a good anode material for MIBs with a high capacity of 315.52 mAh.g^{-1} and diffusion barriers value of 0.05 eV along the zigzag direction [9]. The monolayer black P as anode for MIBs has also been researched by Jin et. Al based on first-principles, which exhibits excellent properties, such as large adsorption energies of Mg (-1.09 eV on H adsorption sites) and low diffusion barriers of 0.08 eV along the zigzag directions [5]. Li et al. have found that the g-Mg_3N_2 is a promising anode material for MIBs with high capacities storage (531 mAh g^{-1}) [10].

Recently, a new family of two-dimensional materials, Mxenes, such as WS_2, Sr_2C, TiS_2, has attracted extensive attention in the application of anode materials due to good conductivity, high reversible capacity and high power density [8, 11–14]. Mo_2C, a representative of two-dimensional Mxenes materials, has superconductivity and low diffusion barriers as anode materials [15–18]. In addition, Xu et. Al have succeeded in synthesizing the large-area high-quality 2D α-Mo_2C [16]. Fan et. Al have reported that Mo_2C monolayer is a potential anode material for MIBs [19].

However, the development of two-dimensional materials is restricted by the high diffusion barriers and the low cycling stability [9, 20]. Doping metal elemental, such as Cr [21], Ru [22], Zn [23], Sr [24], and nonmetal elemental, such as C [25], N [26], B [27] are typical strategies to enhance the properties of electrode materials [28]. Moreover, nitrogen doping is an effective way to enhance metal-semiconductor transition and electronic conductivity due to strong electronegativity and similar atomic radius to carbon [29–31]. Daula et. Al indicate that Si_2BN as anode materials exhibits excellent theoretical capacity of 647.896 mAh g^{-1} and low migration energy barriers between 0.08 eV and 0.35 eV for MIBs by calculations [30]. Zhang et. Al have reported that the incorporation of nitrogen into graphene like C_2N exhibits high theoretical capacities of 588.4 mAh g^{-1} as anode for MIBs [4]. In present work, the first principle calculations are implemented to investigate the adsorption and diffusion behaviors of Mg on the N-doped Mo_2C with different nitrogen doping concentrations.

2 Computational Methods

All the calculations have been carried out by using SIESTA code by the first-principles [32, 33]. Within SIESTA code, the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional (PBE) is widely applied to describe the electron exchange correlation term [34, 35]. Meanwhile, the accuracy of the computed adsorption energies has been improved by the double-basis set [36]. The energy cutoff 150 Ry has been chosen for all calculations. The present calculations are performed with 3×3×1 Brillouin zone k-point sampling. To avoid interactions between periodic permutations, we separate a large vacuum of the monolayer Mo_2C by 30 Å. In the present calculations, the 4×4×1 supercell of the sandwich structure including 32 Mo atoms and 16 C atoms has been used to simulate the adsorption and diffusion behaviors of Mg.

3 Results And Discussion

The absorption energies characterize metal ions absorption strength. The negative values of absorption energies indicate the metal ions absorption behaviors are exothermic and spontaneous. The following equation has been used to calculate the adsorption energies *Ead*:

$$E_{ad} = E_{Mo_2C_{1-x}N_xMg} - E_{Mo_2C_{1-x}N_x} - E_{Mg} \qquad (1)$$

Where x is the ratio of the number of N atoms to the number C atoms, $E_{Mo_2C_{1-x}N_xMg}$ and $E_{Mo_2C_{1-x}N_x}$ represent the total energy of $Mo_2C_{1-x}N_x$ with and without Mg absorption. E_{Mg} is the energy of the isolated Mg atom, which has been determined to be -86.461 eV. To investigate the absorption energies of Mg on N-doped Mo_2C, four supercells of $Mo_2C_{1-x}N_x$ (x = 0.0625, 0.125, 0.1875 and 0.25) have been constructed to accomplish different doping concentrations 6.67%, 14.29%, 23.08% and 33.33%, respectively. Hence, we consider one nitrogen atom, two nitrogen atoms, three nitrogen atoms and four nitrogen atoms to replace the carbon atoms in 4×4×1 supercell.

The four typical adsorption sites on pristine Mo_2C have been considered: hollow (H), top (T_C and T_{Mo}) and bridge (B) sites as shown in Fig. 1(a). Meanwhile, the adsorption energies of Mg adsorption on H_1, H_2, H_3, H_4, T_{C1}, T_{C2}, T_{Mo1}, T_{Mo2} and B_1 sites for four N-doped Mo_2C structures have been calculated. The adsorption energies of Mg calculated on the same sites for N-doped Mo_2C, the Mg adsorption on $MoC_{0.875}N_{0.125}$ represents the conformations of N-doped Mo_2C as shown in Fig. 1(b), and the results are summarized in Table 1.

Table 1
Adsorption energies (eV) of Mg on N-doped Mo_2C and Mo_2C.

	$Mo_2C_{0.9375}N_{0.0625}$	$Mo_2C_{0.875}N_{0.125}$	$Mo_2C_{0.8125}N_{0.1875}$	$Mo_2C_{0.75}N_{0.25}$	Mo_2C
H_1	-1.420	-1.567	-1.426	-1.437	-1.395
H_2	-1.423	-1.625	-1.424	-1.546	
H_3	-1.438	-1.550	-1.422	-1.430	
H_4	-1.413	-1.567	-1.409	-1.436	
T_{C1}	-1.446	-1.580	-1.483	-1.514	-1.384
T_{C2}	——	-1.639	-1.492	-1.505	
T_{Mo1}	-1.431	-1.517	-1.374	-1.376	-1.363
T_{Mo2}	-1.437	-1.595	-1.459	-1.514	
B_1	-1.430	-1.552	-1.423	-1.427	-1.361

As shown in Table 1, the negative values of absorption energies indicate the Mg adsorption behaviors are spontaneous. The absorption energies of Mg on H, T_C, T_{Mo}, B sites for pristine Mo_2C are − 1.395 eV, -1.384 eV, -1.363 eV and − 1.361 eV, respectively. The absorption energies of Mg on the four considered N-doped Mo_2C all have decreased, which suggest that N-doped Mo_2C is benefit for Mg adsorption. Especially, the adsorption energies of Mg for $Mo_2C_{0.125}N_{0.875}$ are about in the region between − 1.64 and − 1.55 eV, much lower than that of pristine Mo_2C. For example, the adsorption energies of Mg on T_{C1} and H_2 sites for $Mo_2C_{0.875}N_{0.125}$ is -1.639 eV and − 1.625 eV, which has decreased by 16.49% and 18.43%. The adsorption energies of Mg for N-doped Mo_2C show that the enhancement of Mg adsorption behaviors is attributed to nitrogen doping.

It is well-known that the diffusion barrier is an important feature to evaluate diffusion mobility of mental ions. In order to obtain the effect of nitrogen doping on Mg diffusion behaviors, the diffusion barriers of Mg on pristine Mo_2C and $Mo_2C_{0.125}N_{0.875}$ have been calculated. For pristine Mo_2C, the energy barrier of Mg diffusion along H-B-H pathway is about 0.039 eV. For comparison, three diffusion pathways (H_4-B-H_3,

H-B-H_3, H-B-H) for $Mo_2C_{0.125}N_{0.875}$ have been considered. The diffusion pathways are named path1, path2 and path3, respectively, with the corresponding diffusion energy barriers as shown in Fig. 2. It can be seen that the diffusion barriers are only 0.042 eV, 0.021 eV and 0.028 eV along three pathways, respectively, which indicate that the Mg diffusion behaviors can easily occur on $Mo_2C_{0.125}N_{0.875}$. The diffusion barrier of Mg along path1 is slightly higher than that of pristine Mo_2C, however, the diffusion barriers of Mg along the path2 and path3 is much lower than that on pristine Mo_2C. The results show that nitrogen doping is a positive approach to decrease the diffusion barriers, which is beneficial to the diffusion of Mg on $Mo_2C_{0.125}N_{0.875}$. The $MoC_{0.875}N_{0.125}$ shows lower adsorption energies and diffusion barriers of Mg, which indicate $MoC_{0.875}N_{0.125}$ is a potential anode material for MIBs.

To comprehensively understand the interaction between Mg and $MoC_{0.875}N_{0.125}$, the partial density of states (PDOS) has been calculated. The PDOS reveal the hybridization interaction of Mg and the neighboring C and Mo atoms. The present calculations indicate that the major electron contribution is mainly attributed to the s state of Mg, the p state of C and the d state of Mo, so, the PDOS of Mg-3s, C-2p and Mo-4d states are plotted in Fig. 3. As shown in Fig. 3, the Mg-3s(no), C-2p(no) and Mo-4d(no) states represent the PDOS for Mg adsorption on the pristine Mo_2C. The Fermi level has been depicted by vertical dashed line in Fig. 3. Obviously, it can be seen that the Fermi level locates at the peak of Mg-3s orbits, which suggest that the Mg adsorption on pristine Mo_2C and $MoC_{0.875}N_{0.125}$ is stable [37]. Additionally, the major electron contribution of Mo_2C and $MoC_{0.875}N_{0.125}$ is Mo-4d orbits, which is similar to Li, Na and K adsorption on Mo_2C [15, 17]. Furthermore, it is noticed that the C-2p, Mg-3s and Mo-4d states are across the Fermi level, which suggest that the metallic nature has been maintained for $MoC_{0.875}N_{0.125}$ [38, 39]. The metallicity of $MoC_{0.875}N_{0.125}$ indicate its good electronic conductivity, which is benefit for Mg diffusion [40]. Interestingly, it is found that nitrogen doping causes the peak of electron orbits transfer to lower energies. This indicate that the bonding between Mg and $MoC_{0.875}N_{0.125}$ is more stable [41]. It can be concluded that when pristine Mo_2C is doped by nitrogen, the strong interaction between Mg and $MoC_{0.875}N_{0.125}$ is beneficial to the adsorption and diffusion of Mg.

4 Conclusion

In this paper, the adsorption and diffusion properties of Mg on N-doped Mo_2C have been investigated by first-principles principles. For the adsorption of Mg on the considered N-doped Mo_2C, the adsorption energies of Mg have decreased. Especially, $MoC_{0.875}N_{0.125}$ exhibits the lowest adsorption energies. For example, the adsorption energies of H_2 and T_{C2} on $MoC_{0.875}N_{0.125}$ has decreased by 16.49% and 18.43% compared to that of pristine Mo_2C. Furthermore, the present calculations show that $MoC_{0.875}N_{0.125}$ can obtain the diffusion barriers of 0.021 eV and 0.028 eV, which are lower than that of Mg on pristine Mo2C. Moreover, the PDOS calculations reveal the strong interaction between Mg and $MoC_{0.875}N_{0.125}$ due to the presence of N. In summary, N-doped Mo_2C shows lower adsorption energies and diffusion barriers of Mg, which indicate that $MoC_{0.875}N_{0.125}$ can be regard as a potential candidate anode material for MIBs.

Declarations

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Conflicts of interest/Competing interests The authors declare no competing interests.

Availability of data and material All data generated or analysed during this study are included in this published article.

Code availability N/A

Authors' contributions Jiangfeng Ni: Calculations, writing, and data analysis. Kaimin Fan: Conceiving problem, result analysis, manuscript editing, and supervision. Jing Tang: Result analysis and manuscript editing.

Ethics approval and consent to participate N/A

Consent for publication N/A

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Figures

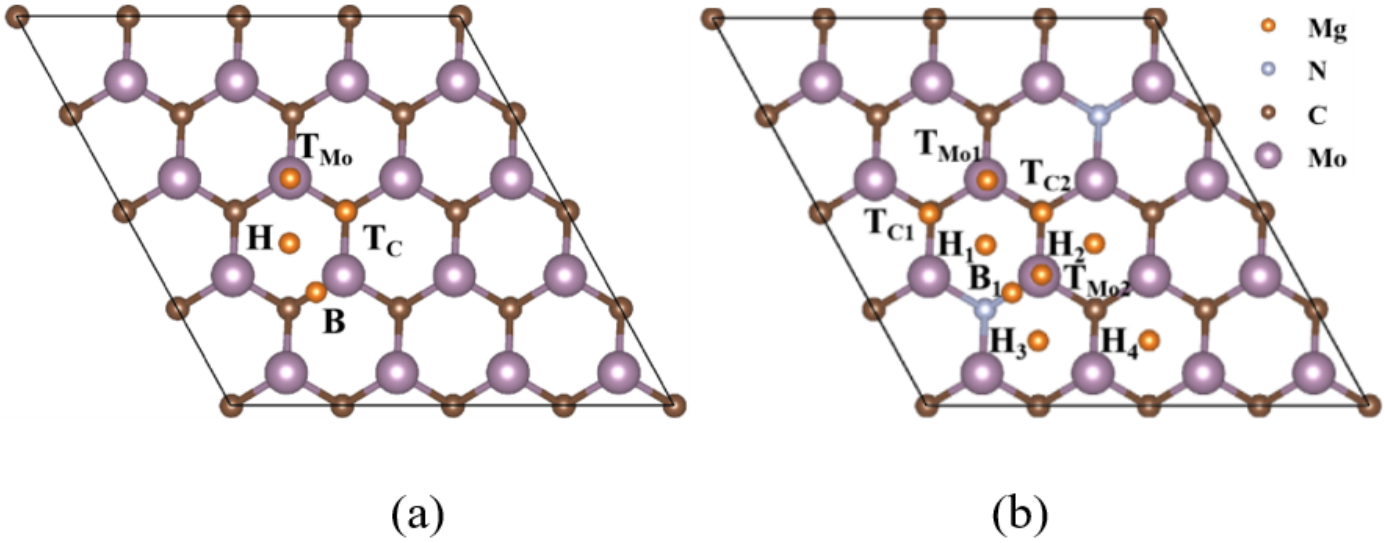

Figure 1

The configurations of Mg absorption on the (a) pristine Mo2C and (b) Mo2C1-xNx.

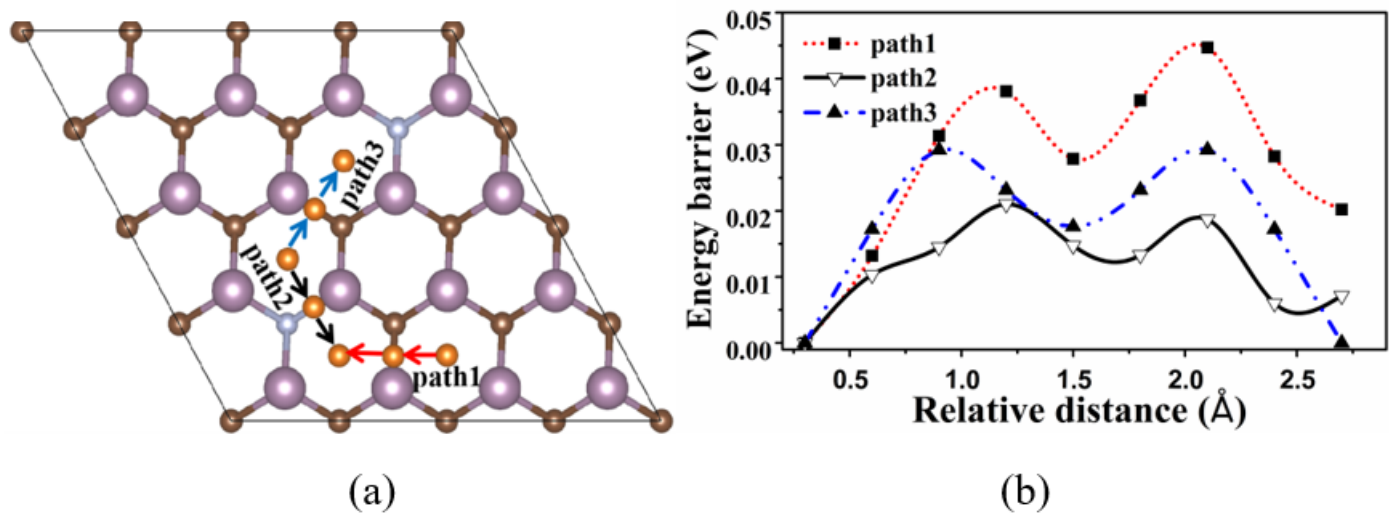

Figure 2

(a) The three diffusion paths, path1, path2 and path3 and (b) the diffusion barriers of Mg on monolayer MoC0.875N0.125.

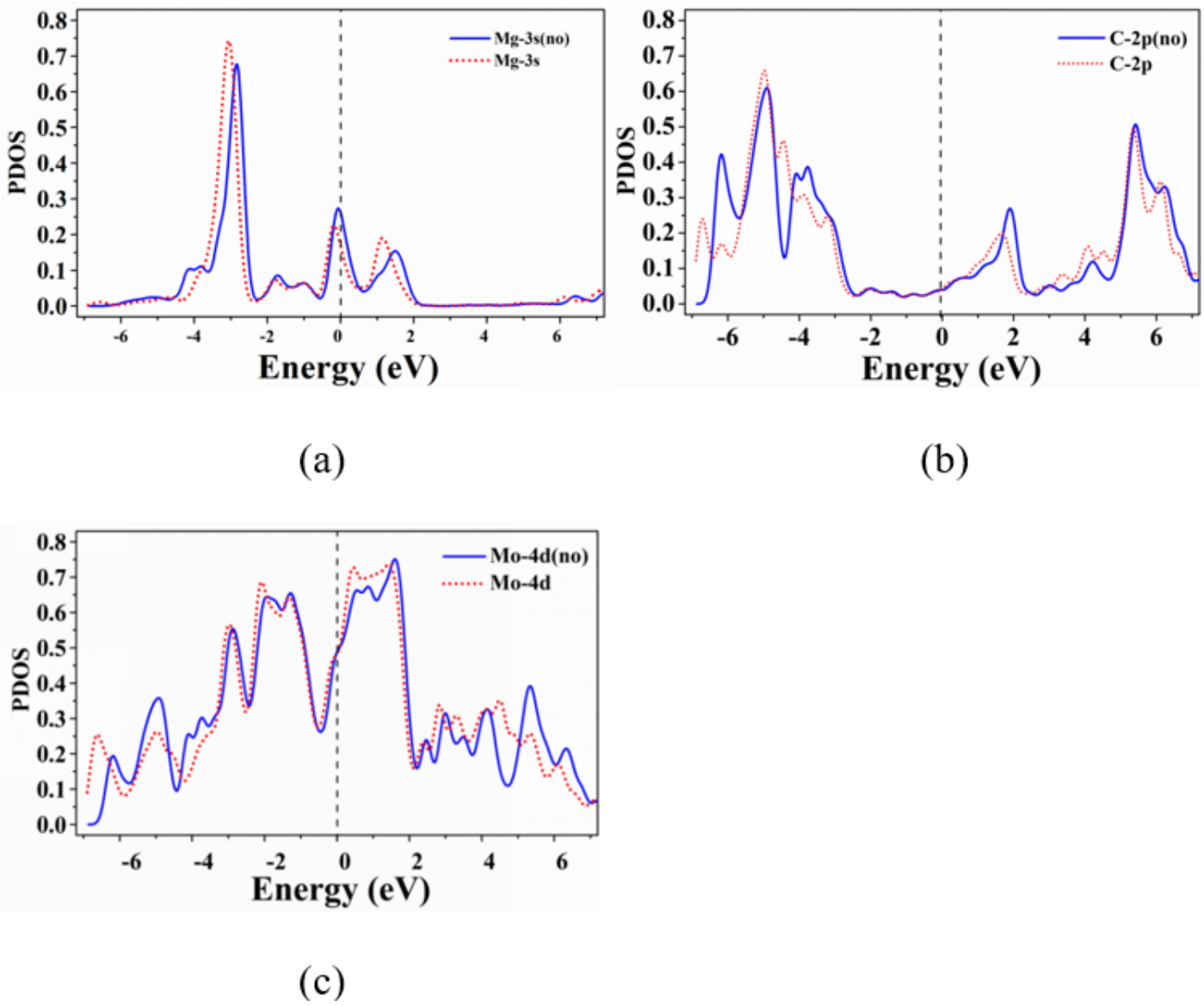

Figure 3

The partial density of states (PDOS) of Mg and its nearest neighbor C and Mo atoms, (a) C-2p , (b) Mg-3s (c) Mo-4d for Mo2C and MoC0.875N0.125 monolayer.