Properties of S-Functionalized Nitrogen-Based MXene (Ti$_2$NS$_2$) as a Hosting Material for Lithium-Sulfur Batteries

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Abstract: Lithium-sulfur (Li-S) batteries have received extensive attention due to their high theoretical specific capacity and theoretical energy density. However, their commercialization is hindered by the shuttle effect caused by the dissolution of lithium polysulfide. To solve this problem, a method is proposed to improve the performance of Li-S batteries using Ti$_2$N(Ti$_2$NS$_2$) with S-functional groups as the sulfur cathode host material. The calculation results show that due to the mutual attraction between Li and S atoms, Ti$_2$NS$_2$ has the moderate adsorption energies for Li$_2$S$_x$ species, which is more advantageous than Ti$_2$NO$_2$ and can effectively inhibit the shuttle effect. Therefore, Ti$_2$NS$_2$ is a potential cathode host material, which is helpful to improve the performance of Li-S batteries. This work provides a reference for the design of high-performance sulfur cathode materials.

Keywords: Li-S batteries; first-principles study; S-functionalized Ti$_2$N

1. Introduction

Presently, the continuous development of electric vehicles and electronic devices puts more requirements on rechargeable batteries [1]. At present, the technology of lithium batteries is relatively mature, but the low theoretical capacity of them cannot meet the needs of future development [2]. Therefore, new rechargeable battery technologies need to be developed. In the next generation of rechargeable batteries, Li-S batteries have received widespread attention because of their high theoretical specific capacity and high energy density. The charge and discharge of Li-S batteries are based on a chemical reaction: $S_8 + 8Li_2 \rightarrow 8Li_2S$. During discharging process, the lithium anode is oxidized to form lithium ions and electrons. The lithium ions and electrons travel to the cathode via a membrane and an external circuit, respectively. Sulfur is reduced at the cathode and reacts with lithium ions and electrons to first form soluble intermediates Li$_2$S$_6$, Li$_2$S$_4$, Li$_2$S$_3$, and then form insoluble Li$_2$S$_2$ and Li$_2$S (Figure 1). The charging process is reversed [3,4]. The theoretical specific capacity of Li-S batteries can reach 1675 mAh·g$^{-1}$, and the theoretical energy density can reach 2600 Wh·kg$^{-1}$ [5–7]. In addition, as a cathode material, the sulfur has the advantages of large storage capacity, low cost, environmental friendliness, and non-toxicity [8–10]. However, in the process of charging and discharging, the long-chain soluble polysulfides (Li$_2$S$_6$, Li$_2$S$_4$, Li$_2$S$_3$, Li$_2$S$_2$, Li$_2$S) produced at the cathode of Li-S batteries are easily dissolved in the electrolyte. These soluble lithium polysulfides (LiPSs) can shuttle with the electrolyte to the anode (“shuttle effect”), causing the loss of cathode active materials. As a result, the coulombic efficiency of the Li-S batteries is reduced, and the cycle stability is
deteriorated [11–13]. In addition, sulfur and its discharge products Li₂S/Li₂S₂ have poor conductivity [14]. The application of Li-S batteries is hindered by these problems.

Figure 1. (a) Schematic of the electrochemistry, reprinted from [3]. Copyright 2016 with permission from Royal Society of Chemistry. (b) Charge-discharge profiles of Li-S batteries, reprinted from [4]. Copyright 2016 with permission from Elsevier.

To solve the above-mentioned problems, a lot of efforts have been made. Physical confinement is one of the effective methods [15]. Various structures, such as the open porous structure [16] and the lithium permeable shell [17], have been shown to inhibit the shuttle effect. In 2009, Nazar et al. [18] used CMK-3, a mesoporous carbon, as a conductive skeleton loaded with elemental sulfur, greatly improving the performance of the cathode. In 2018, Ma [19] et al. used the hollow carbon sphere structure as the main body of the sulfur cathode, which effectively improved the stability of the lithium–sulfur batteries.

Another effective method is chemical binding, which uses host materials with high conductivity and appropriate affinity to capture LiPSSs [20]. Therefore, a variety of materials have been introduced into sulfur cathodes as host materials, such as graphene [21–23], two-dimensional transition metal sulfides and oxides [24–26], phosphorene [27–29], etc., which have been proved to be possible as cathode host materials.

Recently, MXenes, a new type of two-dimensional materials, have received extensive attention due to their high specific surface area, good electrical conductivity and stable structure [30–32]. It is considered to have great potential to become excellent sulfur cathode host materials. In 2015, Xiao Liang et al. [33] introduced Ti₃C into the cathode of Li-S batteries and produced the 70 wt.% S/Ti₃C composite materials, which proved that there was a strong interaction between LiPSSs and Ti atoms on the surface of Ti₃C. This allowed the specific capacity of the sulfur cathodes to reach 1200 mAh·g⁻¹, therefore improving the cycle performance of the sulfur cathodes. The sulfur cathodes still had a capacity retention rate of 80% after 400 cycles of charging and discharging at a rate of 0.5 C. In 2018, Chang Du et al. [34] used TiO hollow nanospheres to wrap sulfur, which was then embedded in the Ti₃C interlayer to produce the S@TiO/Ti₃C composite materials as the cathodes of Li-S batteries. When the S@TiO/Ti₃C composite cathode was charged and discharged at a rate of 0.2 C, its initial capacitance reached 1408.6 mAh·g⁻¹. Under the conditions of 2 C and 5 C high-rate charging and discharging after 200 cycles, it could maintain the specific capacities of 464.0 mAh·g⁻¹ and 227.3 mAh·g⁻¹, respectively.

As MXenes are etched with HF acid, functional groups are inevitably left on the surface of MXenes [35]. Common natural functional groups are –O, –F, –OH [36]. The presence of functional groups affects the anchoring effects of MXenes on LiPSSs. In 2019, Dashuai Wang et al. [37] studied the anchoring effects of Ti₃C₂ surface functional groups on LiPSSs through first-principles calculations. The results showed that the anchoring effects of O-functionalized Ti₃C₂ (Ti₃C₂O₂) on LiPSSs were better than those of F-functionalized Ti₃C₂ (Ti₃C₂F₂). Recently, some studies have shown that it is possible to introduce non-natural functional groups, such as S-functional groups, through experimental means. Unlike natural functional groups, there are few studies on non-natural functional groups. In this work, through first-principles calculations, the adsorption capacity, electronic properties
and catalytic capacity of S-functionalized Ti$_2$N (Ti$_2$NS$_2$) for LiPSs are studied. The research results show that Ti$_2$NS$_2$ has a moderate adsorption capacity for LiPSs, which is stronger than O-functionalized Ti$_2$N (Ti$_2$NO$_2$). In addition, Ti$_2$NS$_2$ has good electrical conductivity, and it still has good electrical conductivity after adsorption of Li$_2$S$_x$ species. Therefore, Ti$_2$NS$_2$ has the potential to become host materials for the cathodes of Li-S batteries.

2. Method and Computational Details

In this work, all first-principles calculations are based on the CASTEP package. The exchange-correlation functional is described by the Perdew-Burke-Ernzerhof (PBE) functional within generalized gradient approximation (GGA) [38]. The Grimme of DFT-D2 is used to describe the van der Waals (vdW) interaction between the substrate and LiPSs [39,40]. The models of MXenes are constructed using $3 \times 3$ super cells. The size of the vacuum layer is set to 20 Å along the Z-axis to avoid layer-to-layer interaction. To ensure the accuracy of the calculation, 520 eV is selected as the cut-off energy of the plane wave base. The $6 \times 6 \times 1$ k-point grid is used for structural optimization, and the $9 \times 9 \times 1$ k-point grid is used for the calculation of the density of states. Meanwhile, the maximum values of the energy standard, force standard position and displacement standard for structural convergence are $2 \times 10^{-5}$ eV/atom$^{-1}$, 0.05 eV/Å$^{-1}$ and 0.002 Å, respectively. The electron transfer is calculated using the Hirshfeld population analysis method.

The adsorption energy ($E_{ads}$) between Li$_2$S$_x$ species and MXenes is defined by the following formula:

$$E_{ads} = E_{\text{species+MXene}} - (E_{\text{species}} + E_{\text{MXene}})$$

where $E_{\text{species+MXene}}$ represents the energy of the entire system after MXenes adsorb Li$_2$S$_x$ species, while $E_{\text{MXene}}$ and $E_{\text{species}}$ represent the energy of isolated MXenes and Li$_2$S$_x$ species, respectively. By definition, the more negative the value, the stronger ability of MXenes to adsorb Li$_2$S$_x$ species.

3. Results and Discussion

3.1. Structure and Adsorption Performance

First, the structures of Li$_2$S$_x$ species are studied (Figure 2). S$_8$ presents a folded ring structure, and the shortest S-S bond length is 1.96 Å. The shortest S-Li bond lengths of soluble Li$_2$S$_8$, Li$_2$S$_6$, and Li$_2$S$_4$ are 2.39 Å, 2.41 Å, and 2.37 Å, respectively, and the shortest S-S bond lengths are 2.05 Å, 2.04 Å, and 2.08 Å, respectively. For insoluble Li$_2$S$_2$ and Li$_2$S, the shortest S-Li bond lengths are 2.24 Å and 2.11 Å, respectively. For insoluble Li$_2$S$_2$ and Li$_2$S, the shortest S-Li bond lengths are 2.24 Å and 2.11 Å. All molecules present a 3D structure, not a chain structure, which is consistent with previous work [41].

Secondly, we establish the model of Ti$_2$N (Figure S1). The lattice constant is $a = b = 3.01$ Å, and the Ti-N bond length is 2.07 Å. Based on Ti$_2$N, the model of Ti$_2$NS$_2$ is established (Figure 3). The fully relaxed Ti$_2$NS$_2$ presents the hexagonal structure. The lattice constant is $a = b = 3.17$ Å. The triangular carbon layer in the middle is sandwiched by two triangular titanium layers, while the outermost layer of S atoms is located directly above the lower layer of titanium. Compared with the original Ti$_2$N, the Ti-N bond length of Ti$_2$NS$_2$ changes from 2.07 Å to 2.18 Å. The bond length of the Ti-S bond is 2.39 Å. This is in line with the results of previous research [42], indicating the correctness of the Ti$_2$NS$_2$ model.
Figure 2. The structures of (a) S₈, (b) Li₂S₈, (c) Li₂S₆, (d) Li₂S₄, (e) Li₂S₂ and (f) Li₂S. Purple balls represent Li atoms. Yellow balls represent S atoms.

Figure 3. (a) Side and (b) top views of Ti₂NS₂. Yellow balls represent S atoms. Gray balls represent Ti atoms. Blue balls represent N atoms.

Figure 4 shows the density of states of Ti₂NS₂. The dotted line represents the Fermi energy levels. It can be clearly seen from the figure that the Fermi level appears in the electronic state, which indicates that the Ti₂N with S-functional group presents the metallicity. The metallicity is mainly provided by the d-orbital of titanium. At the same time, the p-orbital of the sulfur atom also contributes to the metallicity of Ti₂NS₂. The electrical conductivity of the host materials facilitates the charge-discharge reaction in Li-S batteries, since it can provide the electrons needed for the reaction.

After understanding the structure of Li₂Sₓ species and Ti₂NS₂, the interaction between Li₂Sₓ species and Ti₂NS₂ is studied. To find the stable structures, different positions of the Li₂Sₓ species on Ti₂NS₂ are tried. For Li₂Sₓ, the possible adsorption orientations include S-Top, Li-Side and S-Down (Figure S2). Among the three adsorption orientations, the S-Down becomes the S-Top after optimization, and the adsorption energies of the S-Top and Li-Side are −3.42 eV and −1.56 eV, respectively. Therefore, the S-Top is the most favorable adsorption orientation. The adsorption of Li₂S₂, Li₂S₄, Li₂S₆, Li₂S₈ and S₈ on Ti₂NS₂ is considered in a similar manner. The final optimized structures are shown in Figure 5. Table 1 shows the adsorption energies (E_ads), shortest distances between Li₂Sₓ species and Ti₂NS₂ (d), and transfer charge (Q) when Ti₂NS₂ adsorbs Li₂Sₓ species. The ring structure of the S₈ molecule remains intact, parallel to the surface of Ti₂NS₂, and the adsorption energy is −0.57 eV. The shortest distance between the S atom of S₈ and the S atom on the surface of Ti₂NS₂ is 3.52 Å. For insoluble Li₂S and Li₂S₂, their Li atoms tend to combine...
with the S atoms of Ti$_2$NS$_2$. Li atoms of Li$_2$S and Li$_2$S$_2$ are surrounded by three S atoms on the surface of Ti$_2$NS$_2$, and the distances from the nearest S atoms are 2.38 Å and 2.43 Å, respectively, and the adsorption energies are $-3.42$ eV and $-2.36$ eV, respectively. As for the soluble Li$_2$S$_4$, Li$_2$S$_6$, Li$_2$S$_8$, their adsorption energies are $-1.31$ eV, $-0.90$ eV, $-0.95$ eV, respectively. Similar to the insoluble Li$_2$S and Li$_2$S$_2$, Li atoms tend to combine with the S atoms of the Ti$_2$NS$_2$, and the shortest distances between them are 2.47 Å, 2.54 Å and 2.51 Å, respectively. Generally speaking, the adsorption energies of Ti$_2$NS$_2$ for Li$_2$S$_x$ are between $-0.57$ eV~$-3.42$ eV, showing an increasing trend with the deepening of lithiation.

Figure 4. Density of states of Ti$_2$NS$_2$ (the dotted line indicates the Fermi energy level).

Figure 5. The optimized structures of Ti$_2$NS$_2$ absorbing (a) S$_8$, (b) Li$_2$S$_8$, (c) Li$_2$S$_6$, (d) Li$_2$S$_4$, (e) Li$_2$S$_2$, and (f) Li$_2$S. Purple balls represent Li atoms. Yellow balls represent S atoms. Gray balls represent Ti atoms. Blue balls represent N atoms.
Since the shuttle effect is caused by the dissolution of soluble polysulfides (Li$_2$S$_4$, Li$_2$S$_6$, and Li$_2$S$_8$) into the electrolyte, we calculate the adsorption energies of electrolyte solvent molecules (DOL and DME) for Li$_2$S$_4$, Li$_2$S$_6$, and Li$_2$S$_8$ (Figure S3). The results show that the adsorption energies of electrolyte solvent molecules are between $-0.76$ to $-0.84$ eV, which are fewer than those of Ti$_2$NS$_2$ ($-0.90$ to $-1.31$ eV). Furthermore, the adsorption energies of Ti$_2$NS$_2$ are in the range of $-0.8$ to $-2.0$ eV [43], and the adsorption energy intensity is moderate. Therefore, Ti$_2$NS$_2$ can effectively inhibit the shuttle effect. In addition, to form a comparison, the model of Ti$_2$NO$_2$ is constructed (Figure S4). The structure of Ti$_2$NO$_2$ is similar to that of Ti$_2$NS$_2$, presenting a hexagon structure. The lattice constant of Ti$_2$NO$_2$ is $a = b = 3.07$ Å, and the length of the Ti–O bond is 1.85 Å, which is shorter than that of Ti$_2$NS$_2$, mainly because the size of the oxygen atom is smaller than that of the sulfur atom. After that, the adsorption energies of Ti$_2$NO$_2$ for Li$_2$S$_x$ species are calculated (Figure S5, Figure 6). The results show that the adsorption energies of Ti$_2$NO$_2$ for Li$_2$S$_x$ species are $-2.07$ eV, $-2.21$ eV, $-1.29$ eV, $-0.66$ eV, $-0.90$ eV, $-0.43$ eV, respectively, which are fewer than those of Ti$_2$NS$_2$. Therefore, Ti$_2$NO$_2$ is less effective than Ti$_2$NS$_2$ in inhibiting the shuttle effect. The S-functional groups have an advantage over the O-functional groups.

**Figure 6.** Adsorption energies of Ti$_2$NS$_2$ and Ti$_2$NO$_2$.

To further explore the adsorption mechanism of Ti$_2$NS$_2$, the charge transfer and charge density difference between Li$_2$S$_x$ species and Ti$_2$NS$_2$ are calculated.

It can be seen from Table 1 that the transferred electrons between S$_8$ and Ti$_2$NS$_2$ are $0.13$ e, which indicates that the force between S$_8$ and the substrate is weak, and the adsorption energy depends on van der Waals force. Similar to S$_8$, the transferred electrons of Li$_2$S$_8$ and Li$_2$S$_6$ are $0.15$ e and $0.13$ e, respectively, so the adsorption energies also mainly depend on van der Waals force. Later, with the deepening of lithium, the transferred electrons become more. The transferred electrons of Li$_2$S$_4$, Li$_2$S$_2$ and Li$_2$S are $0.22$ e, $0.34$ e and $0.38$ e, respectively. Meanwhile, the adsorption energies become higher, indicating that the transferred electrons affect the adsorption energies.

**Figure 7** shows the charge density difference between Li$_2$S$_x$ species and Ti$_2$NS$_2$. The blue regions indicate the accumulation of charge, and the red regions indicate the depletion...
of charge. The blue regions are mainly concentrated near the Li atoms of Li$_2$S$_x$ and the S atoms of Ti$_2$NS$_2$ surface, which indicates that the transferred electrons between Li$_2$S$_x$ species and Ti$_2$NS$_2$ surface are mainly provided by Li atoms of Li$_2$S$_x$ species. For long-chain sulfides (Li$_2$S$_8$, Li$_2$S$_6$, Li$_2$S$_4$), the blue regions are significantly smaller than those of short-chain sulfides (Li$_2$S$_2$, Li$_2$S), indicating that the transferred electrons of long-chain sulfides are fewer than those of short-chain sulfides, so Ti$_2$NS$_2$ has a stronger adsorption capacity for short-chain sulfides.

Figure 7. Charge density difference between (a) S$_8$, (b) Li$_2$S$_8$, (c) Li$_2$S$_6$, (d) Li$_2$S$_4$, (e) Li$_2$S$_2$, (f) Li$_2$S and Ti$_2$NS$_2$. The isosurface level is set to 0.025 e/Å$^3$. The blue regions indicate charge accumulation, and the red regions indicate charge depletion.

In addition, to better explore the influence of van der Waals forces on adsorption, we take Li$_2$S$_2$, Li$_2$S$_4$ and Li$_2$S$_6$ as examples to calculate the ratio of vdW interaction ($R$), as shown in Figure 8. The $R$ is defined as follows:

$$R = \frac{E_{vdW}^{ads} - E_{vdW}^{nonvdW}}{E_{vdW}^{ads}} \times 100\%$$ (2)

where $E_{vdW}^{ads}$ and $E_{vdW}^{nonvdW}$ represent the adsorption energies with and without the vdW interaction, respectively. It is clear that the ratio of van der Waals forces decreases and the ratio of chemical interactions increases as the degree of lithium increases. For long-chain sulfides, van der Waals force is the main source of adsorption energy.

3.2. Electronic Properties

It is well known that good conductivity is very important for batteries. However, sulfur, the cathode material of Li-S batteries, is very poor in conductivity. An excellent cathode host material should not only have good conductivity itself, but also have good conductivity after absorbing Li$_2$S$_x$ species. Therefore, the density of states of the whole systems after Ti$_2$NS$_2$ adsorbed Li$_2$S$_x$ species is calculated. Figure 9a shows the density of states of the whole system after Ti$_2$NS$_2$ adsorbed S$_8$, and the dotted line in Figure 9 represents the Fermi energy level. Similar to the density of states of Ti$_2$NS$_2$, S$_8$@Ti$_2$NS$_2$ composites still possess metallic properties due to Ti atoms. The electronic properties of S$_8$ are changed by Ti$_2$NS$_2$. In addition, Figure 9b–f show the density of states of the systems which are formed after the adsorption of long-chain sulfides Li$_2$S$_8$, Li$_2$S$_6$, Li$_2$S$_4$ and short-chain sulfides Li$_2$S$_2$ and Li$_2$S by Ti$_2$NS$_2$. Affected by Ti$_2$NS$_2$, the composite materials formed by Li$_2$S$_x$ species and Ti$_2$NS$_2$ still have an electronic state at the Fermi level. All systems exhibit metallic properties, including S$_8$, Li$_2$S, and Li$_2$S$_2$, which are originally poor conductivities. This indicates that the sulfur cathodes can maintain high conductivity
during the entire lithiation and delithiation process. This is very beneficial for improving the cycle performance and rate performance of Li-S batteries.

Figure 8. Ratios of vdW interaction for Li$_2$S$_x$ (x = 2, 4, 6) species on Ti$_2$NS$_2$.

Figure 9. Density of states of (a) S$_8$, (b) Li$_2$S$_8$, (c) Li$_2$S$_6$, (d) Li$_2$S$_4$, (e) Li$_2$S$_2$ and (f) Li$_2$S anchored on Ti$_2$NS$_2$ (The dotted line indicates the Fermi energy level).
4. Conclusions

In this work, the performance of S-functionalized Ti$_2$N (Ti$_2$NS$_2$) as the host materials for the cathodes of Li-S batteries is studied through first-principles calculations. The results show that the adsorption energies of Ti$_2$NS$_2$ are moderate, stronger than those of Ti$_2$NO$_2$, especially the adsorption energies of LiPSs are stronger than those of electrolytes, which can effectively inhibit the shuttle effect. At the same time, Ti$_2$NS$_2$ has good conductivity without adsorption of Li$_2$S$_x$ species. After adsorption of Li$_2$S$_x$ species, it still has a high conductivity, which can improve the conductivity of sulfur cathodes and enhance the electrochemical activity during the charge/discharge process. Therefore, Ti$_2$NS$_2$ has the potential to be the cathode host materials for Li-S batteries. This work provides a reference for the design of high-performance cathode host materials.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/nano11102478/s1. Figure S1: (a) Side and (b) top views of Ti$_2$N. Gray balls represent Ti atoms. Blue balls represent N atoms. Figure S2: The possible orientation of Li$_2$S with respect to Ti$_2$NS$_2$. Figure S3: The optimized structures of DME and DOL absorbing (a) S$_8$, (b) Li$_2$S$_6$, (c) Li$_2$S$_8$, (d) Li$_2$S$_4$, (e) Li$_2$S$_2$, and (f) Li$_2$S. Figure S4: (a) Side and (b) top views of Ti$_2$NS$_2$. Red balls represent O atoms. Gray balls represent Ti atoms. Blue balls represent N atoms. Figure S5: The optimized structures of Ti$_2$NO$_2$ absorbing (a) S$_8$, (b) Li$_2$S$_6$, (c) Li$_2$S$_8$, (d) Li$_2$S$_4$, (e) Li$_2$S$_2$, and (f) Li$_2$S. Purple balls represent Li atoms. Red balls represent O atoms. Gray balls represent Ti atoms. Blue balls represent N atoms.

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