



Article

Rational Design of Non-Noble Metal Single-Atom Catalysts in Lithium–Sulfur Batteries through First Principles Calculations

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Abstract: Lithium–sulfur (Li–S) batteries with a high theoretical energy density of 2600 Wh·kg^{−1} are hindered by challenges such as low S conductivity, the polysulfide shuttle effect, low S reduction conversion rate, and sluggish Li₂S oxidation kinetics. Herein, single-atom non-noble metal catalysts (SACs) loaded on two-dimensional (2D) vanadium disulfide (VS₂) as the potential host materials for the cathode in Li–S batteries were investigated systematically by using first-principles calculations. Based on the comparisons of structural stability, the ability to immobilize sulfur, electrochemical reactivity, and the kinetics of Li₂S oxidation decomposition between these non-noble metal catalysts and noble metal candidates, Nb@VS₂ and Ta@VS₂ were identified as the potential candidates of SACs with the decomposition energy barriers for Li₂S of 0.395 eV (Nb@VS₂) and of 0.162 eV (Ta@VS₂), respectively. This study also identified an exothermic reaction for Nb@VS₂ and the Gibbs free energy of 0.218 eV for Ta@VS₂. Furthermore, the adsorption and catalytic mechanisms of the VS₂-based SACs in the reactions were elucidated, presenting a universal case demonstrating the use of unconventional graphene-based SACs in Li–S batteries. This study presents a universal surface regulation strategy for transition metal dichalcogenides to enhance their performance as host materials in Li–S batteries.

Keywords: single-atom catalysts; VS₂; first-principles calculations; Li–S batteries



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1. Introduction

With the growing energy density demand in fields such as electronic devices and electric vehicles, conventional commercial lithium-ion batteries cannot meet the requirements of development. Consequently, scientists are now dedicated to developing new energy storage candidates. Among various battery systems, Li–S batteries are regarded as a promising energy storage candidate based on the abundant reserves, low cost, and non-toxic nature of sulfur, especially their impressively high theoretical specific energy density (2600 W·h·kg^{−1}) and volumetric energy density (2800 W·h·L^{−1}) [1–4]. However, the large-scale commercial application of Li–S batteries is still impeded because of the following reasons: (i) low sulfur utilization resulting from the poor conductivity of the sulfur (S₈) cathode material and the insoluble discharging products of lower-order lithium polysulfides (LiPSs) such as Li₂S₂ and Li₂S; (ii) the continuous loss of active substances due to the notorious “shuttle effect” of soluble higher-order LiPSs Li₂S_n (4 ≤ n ≤ 8) in the charging/discharging process, wherein soluble intermediate higher-order LiPSs species in the electrolyte reach the lithium anode and react with Li metal to form insoluble Li₂S_n (1 ≤ n < 4) and deposit on it, which results in the sluggish kinetics of LiPSs, quick reductions in capacity, and cycle stability issues; (iii) the pulverization of the sulfur cathode caused by large volumetric expansion during the lithiation process [5]. In 2D materials, the 100 cycle capacity retention rate using catalytic materials could be increased by about 20%

compared to not using catalytic materials; for example, the capacity retention rate of MnO increased from 76.1% to 94.4% after the addition of catalytic materials [6].

In recent years, some strategies have been proposed to address the above problems of Li-S batteries. Particularly, the composite material formed by adding additives to the cathodes of Li-S batteries is expected to solve the problem of low conductivity [7–9]. Some framework materials with physical confinement functions are expected to solve the problem of excessive volume changes to the sulfur cathode during charging and discharging processes. Meanwhile, a lot of effort has been invested in developing suitable materials to mitigate the “shuttle effect”. The so-called suitable materials should bind LiPSs to inhibit their migration and accelerate their redox kinetic process, that is, the suitable materials should be materials with anchoring functions [10]. Anchoring materials have been regarded as electrocatalysts which play a crucial role in LiPSs conversion and reduce the reaction barriers, which has attracted great attention. For example, some 2D materials [11,12], including graphene [13,14], MXenes [15], transition metal carbides [16,17], and metal sulfides [18,19], have been elucidated as promising anchoring materials for Li-S batteries due to large specific surface areas and unique physical and chemical properties. Many studies have focused on enhancing the binding of the anchoring material and LiPSs by predicting the adsorption energy based on density functional theory (DFT) simulations. However, most of these 2D materials exhibit incomplete LiPSs conversion to Li_2S_2 or Li_2S due to the sluggish redox reaction kinetics.

Recently, SAC materials consisting of monodispersed transition metal (TM) atoms supported on the surfaces of 2D materials have received much attention. Apart from the maximum metal atom utilization efficiency, SACs can offer outstanding catalytic activity with low metal loading, tunable structure, flexible selectivity, and low cost. In 2021, Cheng’s group proposed that single-atom Ti as the sulfur cathode catalyst could promote battery performance for Li-S batteries, which had the lowest electrochemical barrier to LiPSs reduction/ Li_2S oxidation and the highest catalytic activity. Because of the highly active catalytic center of single-atom Ti on the conductive transport network, high sulfur utilization was achieved with low catalyst loading (1 wt.%) and a high area of sulfur loading ($8 \text{ mg} \cdot \text{cm}^{-2}$) [20,21]. Compared with 2D materials, SACs for Li-S batteries can provide suitable adsorption strength with LiPSs and the exceptional ability to improve reaction kinetics [22–25]. It can be seen that the adsorption energy between Co and N/G (-7.99 eV) is more negative than those of CoS (-6.39 eV) and CoS_2 (-7.01 eV) [26]. Among the reported 2D materials in Li-S batteries, 2D transition metal chalcogenides have been widely researched and applied because of their abundant reserves, environmentally friendly nature, and fast reaction kinetics. In particular, T-phase 2D VS_2 has good intrinsic conductivity compared with FeS_2 , MoS_2 , NiS_2 , NbS_2 , TiS_2 , and ZrS_2 , as well as moderate adsorption strength for Li_2S_n [25,27,28]. For example, to further validate that the adsorption capacities of LiPSs on the surfaces of FeS_2 were moderate for Li_2S_n , the adsorption energies of Li_2S_4 on FeS_2 , Ti_3C_2 , CoP, and graphene surfaces were compared and measured as -4.25 , -4.16 , -4.91 , and -1.21 eV , respectively, indicating a moderate adsorption ability of FeS_2 [29].

2D VS_2 as a host material loaded the monodispersed TM atom (hereafter denoted as TM@VS_2) to constitute SAC materials, which is expected to have the dual effect of suppressing the shuttle effect and accelerating reaction kinetics [22,26,30–32]. In this work, 17 unique SACs TM@VS_2 (TM = 4d and 5d TMs) for sulfur cathodes were constructed and investigated systematically via DFT simulations. By comparing the thermal stability values of 17 TM@VS_2 , the adsorption behavior of S_8 and five LiPSs intermediates (Li_2S_n , $n = 1, 2, 4, 6$, and 8), and the conversion mechanism of Li_2S_2 to Li_2S on the TM@VS_2 , the promising SAC candidates Nb@VS_2 and Ta@VS_2 were screened out. This study provided an atomic-level understanding about the reaction mechanism of this composite material TM@VS_2 in Li-S batteries and clarified how to inhibit the shuttle effect and accelerate the reaction kinetics, which is of significance for the rational design of SACs.

2. Methods

All the DFT simulations were performed using the Vienna ab initio simulation package (VASP) [33]. Projector augmented wave (PAW) pseudopotentials and Perdew–Burr–Ernzerhof (PBE) functions with the generalized gradient approximation (GGA) were employed to investigate the electron–ion interactions and the electron–electron exchange correlations [20,34]. The kinetic energy cutoff was selected as 400 eV for the plane wave basis calculations, the energy convergence was set to 10^{-5} eV/Å, and the force convergence criterion for optimization was set to 0.05 eV/Å. A vacuum space of 20 Å was set to avoid the interactions between the periodic boundaries. The van der Waals interactions were calculated using the DFT-D3 method to provide better accuracy for the adsorption strength of polysulfides with TM@VS₂. A $4 \times 4 \times 1$ supercell of VS₂ monolayer was built and a $2 \times 2 \times 1$ K-point was set in the first Brillouin zone for the geometric optimizations and the density of states (DOS) calculation [35]. DOS and electrostatics potential were calculated by DS-PAW software (2023A) integrated in the Device Studio program [36]. In addition, ab initio molecular dynamics (AIMD) simulations of Pd@VS₂, Rh@VS₂, and Ta@VS₂ were carried out to confirm material stabilities on the $8 \times 4 \times 1$ supercell at 298.15 K within 10 ps. The decomposition properties of Li₂S were determined using the climbing-image nudged elastic band (CI-NEB) method. The SACs among 17 single TM atoms loaded on the VS₂ monolayer were first screened by calculating the adsorption energy following Equation (1):

$$E_{\text{ad}_1} = E_{\text{TM@VS}_2} - E_{\text{TM}} - E_{\text{VS}_2} \quad (1)$$

where $E_{\text{TM@VS}_2}$ and E_{VS_2} are the energies of loaded single atoms and the bare VS₂ monolayer, respectively. E_{TM} is the energy per single atom in the metallic phase. A more negative value of E_{ad_1} represents a stronger adsorption.

The adsorption energies E_{ad_2} of Li₂S_n and S₈ molecules adsorbed on the VS₂ and TM@VS₂ monolayer are calculated based on the following Equation (2):

$$E_{\text{ad}_2} = E_{\text{total}} - E_{\text{sub}} - E_{\text{mol}} \quad (2)$$

where E_{total} represents the total energy of adsorbed system Li₂S_n (or S₈) on TM@VS₂ or VS₂ monolayer, E_{sub} represents the energy of TM@VS₂ or VS₂ monolayer, and E_{mol} represents the energy of Li₂S_n ($n = 1, 2, 4, 6, 8$) and the S₈ molecule.

To visualize the charge transfer of Li₂S_n molecules on TM@VS₂ monolayers, the charge density differences (CDDs) of the adsorbed configurations were displayed by calculating from the following Equation (3):

$$\Delta\rho = \rho_{\text{total}} - \rho_{\text{sub}} - \rho_{\text{mol}} \quad (3)$$

where ρ_{total} , ρ_{TM} , and ρ_{mol} represent the charge density of the whole adsorbed system, TM@VS₂ or VS₂ monolayer, and Li₂S_n and S₈ molecule, respectively.

The Gibbs free energies can be defined as follows (4):

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S \quad (4)$$

where ΔE represents the electronic energy of the product minus that of the reactant, and ΔZPE and ΔS represent the zero-point vibrational energy and entropy change at the standard temperature and pressure, respectively.

3. Results and Discussion

3.1. Structure and Stability of the TM@VS₂ SACs

The configuration of T-phase VS₂ is shown in Figure 1a. There are three possible sites where a single TM atom can deposit on the surface of the VS₂ monolayer, including Hollow-V (H-V), Top-S (T-S), and Hollow-S (H-S). In order to screen the most suitable loaded single TM atoms on the VS₂ monolayer to constitute SACs, the adsorption energies

of 17 4d and 5d TM atoms loaded on the VS_2 surface at three possible sites were calculated based on Equation (1). Remarkably, the adsorption of single atoms at the T-S site after the optimization became higher than the H-S or H-V sites, such that the adsorption energies were higher than those of the H-S or H-V sites, even to positive values (about 0.5–7.1 eV), which indicated that the adsorption of the T-S site was unstable thermodynamically. Therefore, all the TM@VS_2 at the T-S site will not be considered in the following. The adsorption energies at H-V and H-S sites are depicted in Figure 1b. The results revealed that the single TM atoms of four species (Y, Zr, Nb, and Hf) were strong in affinity and stably adsorbed on the VS_2 surface due to the negative adsorption energies. In addition, Pd@VS_2 , Rh@VS_2 , and Ta@VS_2 displayed slightly positive adsorption energies, suggesting their comparatively weaker interactions. Further, the thermal stability of Pd@VS_2 , Rh@VS_2 , and Ta@VS_2 was considered by AIMD simulation. The final configurations of Pd@VS_2 , Rh@VS_2 , and Ta@VS_2 after AIMD simulations are depicted in Figure S1a–c. The simulation profiles revealed a consistent trend of converging energy, with the structures maintaining their original coordination environment even after 10 ps. No structural deformations or atomic clustering were observed, demonstrating the thermal stability of Pd@VS_2 , Rh@VS_2 , and Ta@VS_2 . Furthermore, Figure 1 shows that Hf, Rh, Y, and Zr atoms were preferentially adsorbed at the H-S site, while Pd, Ta, and Nb atoms preferred the H-V site. For a single TM atom, adsorption at the H-V and H-S sites on the VS_2 surface site are comparable, and the more favorable sites can be screened by calculating the COHP of TM–S bonds at the H-S and H-V sites based on a comparison of adsorption energies, with sites showing more negative adsorption energies being considered optimal. Compared to the other site, Nb–V, Ta–V, Zr–S, and Rh–S demonstrate higher ICOHP values, indicating stronger bonding strength with single atoms (Figure S2). This disparity in site behavior arises from differences in the types of single atoms and the adsorption strengths of various adsorption sites on the VS_2 substrate. The lowest adsorption energy corresponds to the most stable configuration, as shown in Figure S3a. Furthermore, different coordination numbers have different geometric structures and chemical properties. The optimized configurations of the SACs substantiate a TM–S with three coordinates on the VS_2 substrate. Typically, compared to four coordinates in TM– N_4 –graphene [37,38], TM–S with three coordinates on a VS_2 surface has fewer coordination numbers, resulting in a single atom with more unbonded electrons, and these sites can adsorb and activate reactants, facilitating the reaction.

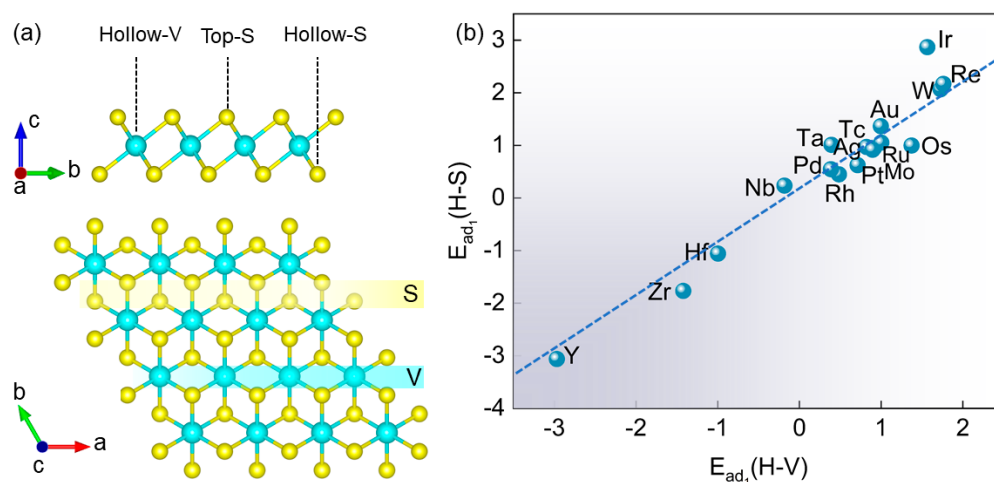


Figure 1. (a) Top and side views of VS_2 monolayer with three different adsorption sites for single atoms. (b) The adsorption energies of single atoms at H-V and H-S sites. The dashed line indicates the equal adsorption energies of H-V and H-S sites.

In addition, in order to better understand the bonding properties between the TM atom and VS_2 monolayer, the projected density of states (PDOS) of TM@VS_2 was calculated based on fully relaxed configurations, as shown in Figure 2. The results provided compelling

evidence of significant d-p orbital hybridization between the TM and S atoms, indicating that there were stable covalent bonds between TM and S atoms. Furthermore, a continuous state density across the Fermi level indicated that these TM@VS₂ were metallic. This observation carried crucial implications for enhancing the conductivity of the cathode. Specifically, the adsorption energy of the TM and VS₂ monolayer is often linked to the electron state's density, as the d orbitals of Y, Zr, and Hf exhibit more electron states above the Fermi level than other metal atoms, therefore exhibiting stronger adsorption energy.

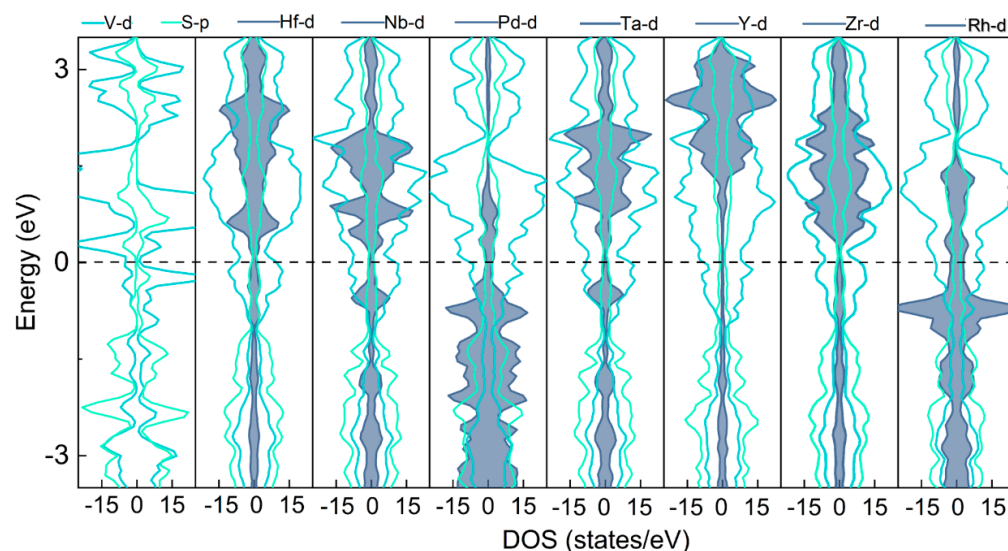


Figure 2. PDOS of VS₂ and TM@VS₂ (TM = Hf, Nb, Pd, Ta, Y, Zr, or Rh, where the d orbitals of each TM atom are multiplied by 10).

3.2. Anchoring Effect of TM@VS₂ SACs

The primary objective of catalysts of the sulfur cathode for Li-S batteries is to enhance the immobilization of sulfur and polysulfides. To investigate the anchoring effect of TM@VS₂, the adsorption energies of VS₂ and the TM@VS₂ monolayer for the intermediate polysulfides Li₂S_n ($n = 1, 2, 4, 6, 8$) and S₈ during charge–discharge processes were calculated based on Equation (2). The values of all adsorption energies were shown in Figure 3a and Table S1. The adsorption energies of Li₂S_n and S₈ on the surface of VS₂ were as follows: Li₂S (−4.613 eV), Li₂S₂ (−3.158 eV), Li₂S₄ (−2.525 eV), Li₂S₆ (−1.915 eV), Li₂S₈ (−1.918 eV), and S₈ (−0.957 eV). The corresponding optimal configurations of VS₂ are given in Figure 3b. Nb shows obvious higher electrostatic potential than that of Pd (Figure S4), which is an electrophilic center to adsorb polysulfides favorably in the reaction process, and the adsorption strength was enhanced to inhibit the shuttle effect effectively compared to the VS₂ substrate. The corresponding optimal configurations of Ta@VS₂, Pd@VS₂, Hf@VS₂, Rh@VS₂, Y@VS₂, Nb@VS₂, and Zr@VS₂ are given in Figure 3c and Figure S3b–g. There is no significant structural deformation observed after the introduction of single atoms. The results indicated that most of the adsorption energies were enhanced after the introduction of TM single atoms on the VS₂ monolayer, where the adsorption energies of Ta@VS₂, Hf@VS₂, Y@VS₂, Nb@VS₂, and Zr@VS₂ could all be enhanced for Li₂S₂, Li₂S₆, Li₂S₈, and S₈ compared with VS₂, which exhibited the sulfur immobilization ability of these non-noble metal SACs. However, noble metal atoms Pd and Rh enhanced adsorption ability partially for S₈ and LiPs compared with VS₂. In addition, the adsorption strengths of these five non-noble metal SACs for soluble higher-order LiPs Li₂S_n ($4 \leq n \leq 8$) were significantly higher than the interactions between common electrolyte components and soluble intermediates [39]; for example, the adsorption energy of 1,3-dioxolane (DOL) for Li₂S₆ was −0.75 eV, and that of 1,2-dimethoxyethane (DME) was −0.77 eV. Differently, the adsorption energies for Li₂S₆ were −3.802 eV (Nb@VS₂) and −3.860 eV (Hf@VS₂), which effectively prevented the shuttle effect of LiPs. Therefore, non-noble metal atoms Hf, Nb,

Ta, Y, and Zr loaded on VS₂ monolayer have the potential to enhance sulfur immobilization capability compared to noble metal atoms Pd and Rh.

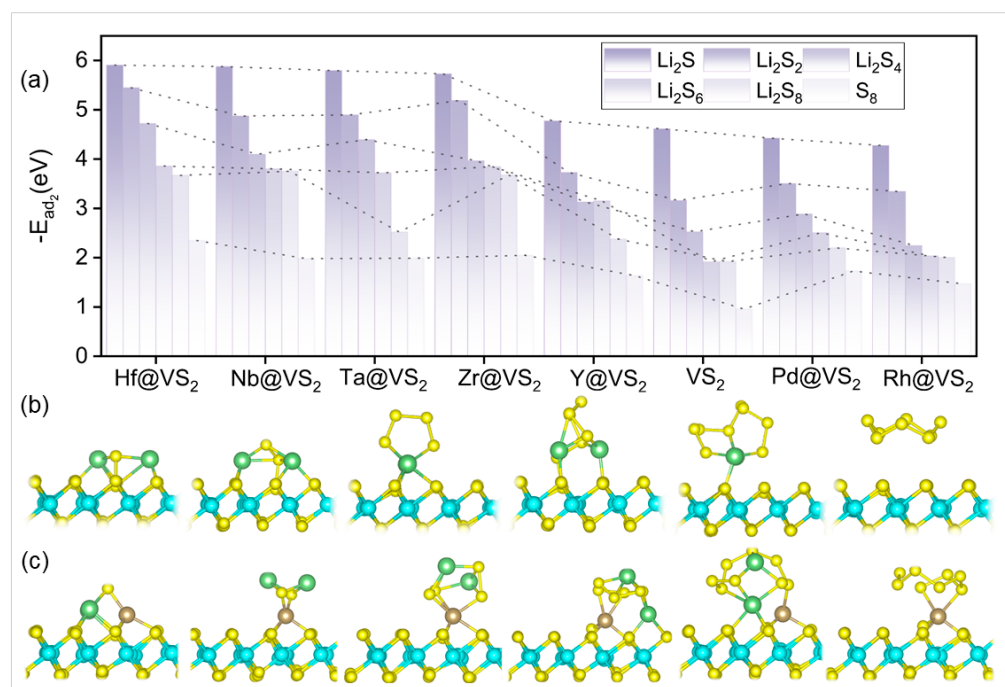


Figure 3. (a) The difference in adsorption energies between Li₂S_n/S₈ on VS₂ and TM@VS₂. The adsorption configurations of Li₂S_n/S₈ on (b) VS₂ and (c) Ta@VS₂.

Taking Ta@VS₂ as an example, the optimized adsorption configurations are shown in Figure 3b, which reveals that Ta@VS₂ forms both Li–S and Ta–S bonds during the adsorption process. Compared to the Li–S bond on the surface of VS₂, the presence of more bonding sites and species offers the potential to enhance the adsorption effect for TM@VS₂. To gain a further insight into the mechanisms between the adsorption strength and bonding, the CDD between TM@VS₂ and the adsorbed intermediates were investigated, and the results are shown in Figure S5 for VS₂, Pd@VS₂, Hf@VS₂, Rh@VS₂, Y@VS₂, Ta@VS₂, Nb@VS₂, and Zr@VS₂, respectively. The results revealed that the electron transfer primarily occurred between Li atoms and S atoms on the surface of VS₂ monolayer. However, for non-noble SACs such as Hf@VS₂, Nb@VS₂, Ta@VS₂, Zr@VS₂, and Y@VS₂, the electron transfer occurred not only between Li atoms and S atoms but also between the single TM atoms and the S atoms in Li₂S_n, forming TM–S bonds. This implies there was a more significant electron transfer between TM@VS₂ and the S atoms in Li₂S_n clusters. For all the non-noble SACs, the electron transfer from S₈ to Li₂S gradually increases, and the largest charge transfer occurred between the SACs and Li₂S, corresponding to the strongest adsorption energy. The enhanced adsorption of S₈ can also be attributed to the redistribution of charge between individual TM atoms. Furthermore, there exists a competitive bonding interaction between Li–TM@VS₂ and Li–S/S–S, wherein TM atoms interact with S atoms to form charge density accumulations during chemical bonding. Meanwhile, varying degrees of charge loss are observed in the S–S/Li–S bonds within the Li₂S_n molecules. As lithiation progresses, the strength of Li–S bonds within the Li₂S_n clusters weakened, while the adsorption capability of Li₂S_n on TM@VS₂ increased. In addition, the weakened Li–S bonds are expected to promote the reaction kinetics of Li₂S_n conversion.

3.3. The Catalytic Mechanism of TM@VS₂

To ascertain the catalytic performance of TM@VS₂ (TM = Y, Zr, Hf, Nb, Ta, Rh, Pd) in the sulfur reduction reaction, the Gibbs free energy for the conversion of S₈ to Li₂S was calculated. The energy landscape was depicted in Figures 4 and S6. The research results

revealed that the Gibbs free energies of the reaction-determining step were 0.344 (VS₂), 0.176 (Y@VS₂), 0.320 (Zr@VS₂), 0.408 (Hf@VS₂), 0.218 (Ta@VS₂), and 0.154 eV (Pd@VS₂), respectively. The Gibbs free energy of Rh@VS₂ and Pd@VS₂ are shown in Figure S6. The reactions of Rh@VS₂ and Nb@VS₂ were exothermic, indicating that the reactions proceeded readily. According to the above, Hf@VS₂ has a higher Gibbs free energy, which is unfavorable for the reaction thermodynamics. Therefore, Y@VS₂, Pd@VS₂, Zr@VS₂, and Ta@VS₂ accelerated the sulfur lithiation reaction compared to VS₂, and Nb@VS₂ and Rh@VS₂ experienced exothermic reactions, which highlighted their relatively strong catalytic activity in the sulfur reduction reaction.

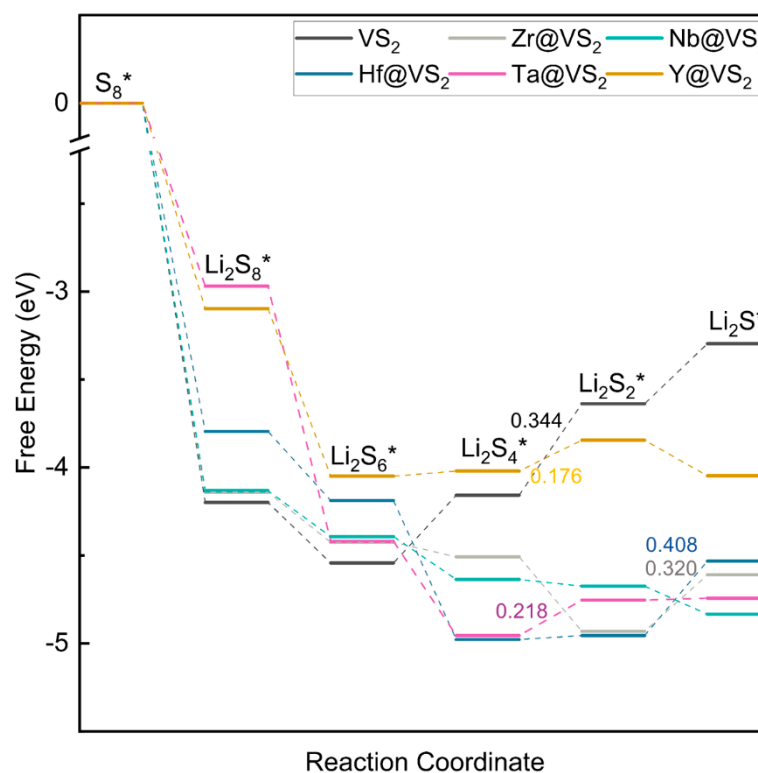


Figure 4. Gibbs free energy of S₈-to-Li₂S reaction on VS₂ and TM@VS₂ (TM = Y, Zr, Hf, Nb, Ta. The * was stand for absorbed).

In Li–S batteries, the generation of Li₂S as the final discharge product causes the challenge of sluggish reaction kinetics due to its low electronic conductivity and Li⁺ diffusion rates [40]. A crucial approach to address the slow oxidation rate during Li–S battery charging is to decrease the decomposition energy barrier of Li₂S. Therefore, it is necessary to evaluate the catalytic oxidation performance of TM@VS₂ for the charging process by examining the decomposition energy barriers of Li₂S. The calculated results are shown in Figure 5 and Figure S7, and significant differences were observed in Li₂S decomposition energy barriers on various surfaces. The decomposition energy barrier of Li₂S on the VS₂ surface was 0.366 eV. The corresponding decomposition energy barriers of Li₂S on TM@VS₂ were 0.162 (Ta@VS₂), 0.322 (Hf@VS₂), 0.396 (Nb@VS₂), 0.496 (Zr@VS₂), 0.682 (Rh@VS₂), 0.736 (Pd@VS₂), and 0.744 eV (Y@VS₂). The results indicated that TM@VS₂ (TM = Nb, Ta, Hf) could significantly reduce the decomposition energy barrier of Li₂S compared to the VS₂ surface. Among all the investigated seven TM@VS₂, Ta@VS₂ displayed the lowest decomposition energy barrier. This could be attributed to the formation of chemical bonds between the Ta and the S of Li₂S, weakening the Li–S bonds and, therefore, lowering the decomposition energy barrier of Li₂S. Taking this into account, crystal orbital Hamilton population (COHP) analysis was introduced to explore the bonding strength of Li–S and TM–S bonds in Li₂S on TM@VS₂, as shown in Figure 6. The COHPs of Ta@VS₂ and Pd@VS₂

were selected for comparative analysis as an example. Compared to Pd@VS₂, the bonding state of the Ta–S bond below the Fermi level is significantly lower in Ta@VS₂–Li₂S than that of Y–S, with ICOHP values of 5.379 and 4.706 eV, respectively. This is accompanied by an increase in bond length from 2.425 Å for Ta–S to 2.497 Å for Y–S. Meanwhile, the Li–S bonds in the adsorbed state of Li₂S exhibit an opposite ICOHP trend, with the Li–S bond in Ta@VS₂–LiS at 0.887 and in Y@VS₂–Li₂S at 1.145. The corresponding Li–S bond lengths are 2.595 and 2.500 Å for Ta@VS₂–Li₂S and 2.343 and 2.368 Å for Y@VS₂–Li₂S. This indicates a significant weakening of the Li–S bonds in Li₂S on Ta@VS₂, promoting the catalytic oxidation of Li₂S and aligning with the trend in decomposition energy barriers. Benefiting from high electronic conductivity and excellent bifunctional catalytic ability, Nb@VS₂ and Ta@VS₂ can effectively accelerate the Li₂S_n conversion reaction and improve the electrode kinetics of Li–S batteries.

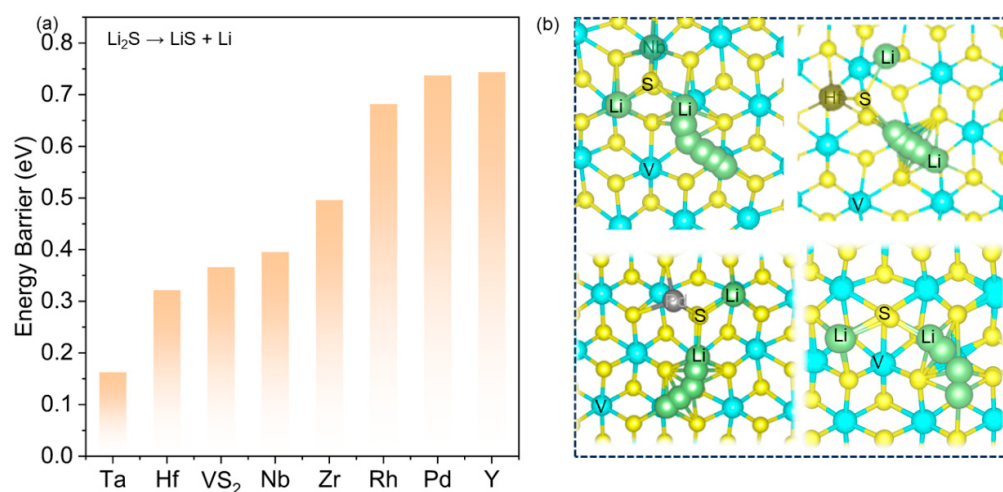


Figure 5. (a) Decomposition energy barriers of Li₂S on VS₂ and TM@VS₂. Li₂S decomposition pathway on (b) Nb@VS₂, Hf@VS₂, Pd@VS₂, and VS₂.

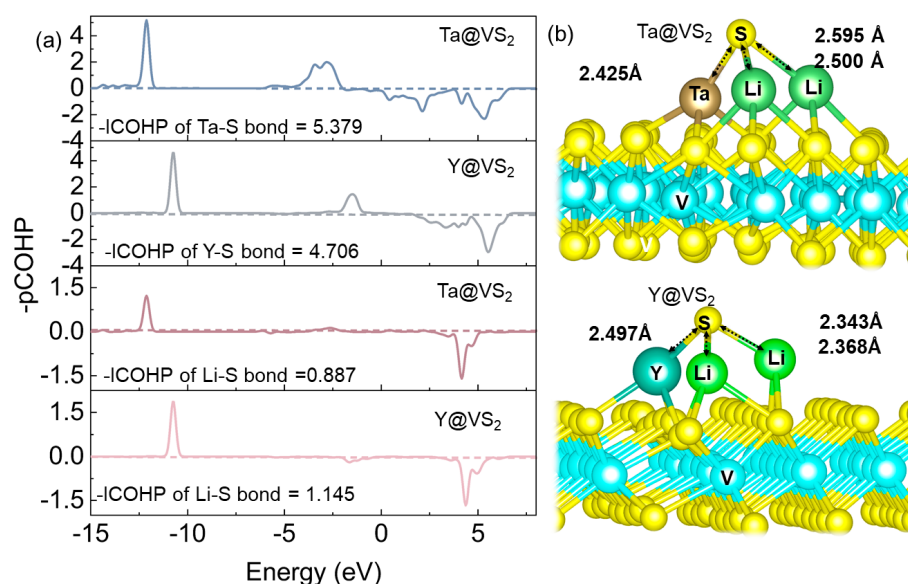


Figure 6. (a) COHP diagram of the TM–S and Li–S bonds in Li₂S on Ta@VS₂ and Y@VS₂. (b) The Li₂S adsorption configurations on Ta@VS₂ and Y@VS₂.

4. Conclusions

In summary, this study presents a systematic first-principles calculation of seven VS₂-based SACs as host materials of the cathode for Li–S batteries. The calculation results show that among the seven selected monatomic catalysts, two noble metals Pd and Rh are removed, and five non-noble metals catalysts are obtained. By comparing the adsorption properties, metal properties, and reaction kinetics, it is found that the addition of Nb and Ta into VS₂ has the potential to improve the performance of Li–S batteries. This enhancement is mainly attributed to the metallic characteristics of TM@VS₂, which improve the electronic conductivity of the sulfur cathode. The enhanced adsorption of intermediate discharge products helps suppress the dissolution and shuttle effect of lithium polysulfides. Additionally, the lower reaction-determining step and reduced energy barrier for Li₂S decomposition contribute to accelerated reaction kinetics. This work provides a universal approach for the atom-scale modification of transition metal sulfides, offering valuable insights and guidance for the development of sustainable and efficient Li–S battery technologies.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/nano14080692/s1>. Figure S1. The final configurations of (a) Pd@VS₂, (b) Rh@VS₂ and (c) Ta@VS₂. Figure S2. The ICOHP of TM–S bonds (TM@VS₂, TM = Nb, Ta, Zr, Rh) for two kind of different site (H–V, H–S). Figure S3. (a) The optimal configurations of TM@VS₂ (TM = Pd, Hf, Rh, Y, Nb, Zr). (b–g) Optimal configurations of Li₂S_n and S₈ on TM@VS₂ (TM = Pd, Hf, Rh, Y, Nb, Zr). Figure S4. The electrostatics potential of (a) VS₂, (b) Nb@VS₂, (c) Pd@VS₂ by DS-PAW method, respectively. Figure S5. Differential charge density of Li₂S, Li₂S₆ and S₈ on (a) VS₂, (b) Pd@VS₂, (c) Hf@VS₂, (d) Rh@VS₂, (e) Y@VS₂, (f) Ta@VS₂, (g) Nb@VS₂ and (h) Zr@VS₂, the iso-surface is set to 0.0025 e/A³ (Orange region indicates electron concentration and green region indicates electron deficiency). Figure S6. Gibbs Free Energy of S₈–to–Li₂S reaction on TM@VS₂ (TM = Rh, Pd). Figure S7. Decomposition energy Barriers of Li₂S on TM@VS₂. Table S1. The adsorption energies of polysulfides on TM@VS₂ (The units is electron volts (eV)). Table S2. The optimized coordinates of polysulfides on TM@VS₂.

Author Contributions: Conceptualization, Y.L. (Yao Liu) and J.Z.; Investigation, Y.L. (Yang Li); Data curation, Y.L. (Yao Liu), J.Z. and J.X.; Writing—original draft, Y.L. (Yang Li), D.W. and J.X.; Supervision, J.X.; Project administration, D.W. and J.X.; Funding acquisition, D.W. All authors have read and agreed to the published version of the manuscript.

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