##### Theoretical Insights into the Conversion Mechanism of Li2S2 to Li2S in Lithium-Sulfur Batteries based on VO(1-x)S(1+x) Alloys

Yuhan Wang *a*, Jinyan Chen *a*, Chao Gao *a*, Ruiyu Hao *a* and Jianhua Hou *a*,*b* \*

*aSchool of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, PR China*

*bEngineering Research Center of Optoelectronic Functional Materials, Ministry of Education, Changchun 130022, PR China*

Corresponding authors: houjh163@163.com

**ABSTRACT:** Lithium-sulfur batteries are regarded as the most promising energy storage system due to their high theoretical capacity (1675 mAh/g) and natural abundance of elemental sulfur. Nevertheless, the sluggish reaction of the rate-limiting step Li2S2 to Li2S conversion severely hampers the practical application of lithium-sulfur batteries. The resolution of this issue is contingent upon a thorough comprehension of the conversion mechanism of the rate-limiting step. To this end, we have developed the two-dimensional VO(1-x)S(1+x) alloy catalysts by ATAT and have constructed a theoretical model that can accurately predict the thermodynamic energy barrier of the rate-limiting step in lithium-sulfur batteries. Our model relates the energy barrier of the rate-limiting step to the *p*-band center of the nonmetallic and the *d*-band center of the metallic for the VO(1-x)S(1+x) alloy. This model facilitates the identification of the VO(1-x)S(1+x) alloy as a potential cathode catalyst for lithium-sulfur batteries.

**KEYWORDS:** lithium-sulfur batteries, ATAT, Li2S2 conversion, first-principles study, non-metallic doping

1. **Introduction**

As modern society continues to develop and advance, the demand for energy is correspondingly increasing. In the context of today's energy-based civilization, the development of new energy storage devices is a crucial necessity[1-5]. Among them, lithium-ion batteries have become the preferred energy storage devices for mobile electronic products, automobiles, and other fields due to their high specific capacity, high energy density, green and environmental protection advantages[4, 6-9]. However, the widely used lithium-ion batteries are approaching their theoretical energy density limit and are no longer able to meet our growing needs, as well as becoming progressively more expensive[10]. Lithium-sulfur batteries are regarded as the most promising energy storage system, with a high theoretical capacity (1675 mAh/g) and a natural abundance of elemental sulfur[11-14]. However, despite these advantages, there are numerous challenges in achieving commercial viability due to several key issues that negatively impact cycle reversibility and rate capabilities[15, 16]. During the discharge process, elemental sulfur is reduced to form polysulfides. High-order LiPSs (Li2Sn, 4≤n≤8) dissolve into the electrolyte, thereby causing the "shuttle effect" as a result of the combined influence of electric field force and concentration gradient force[16]. This phenomenon gives rise to several issues, including rapid capacity decay, low Coulomb efficiency, and a shortened cycle life. It is noteworthy that the Li2S2 to Li2S conversion in the second discharge platform accounts for 75% of the total discharge capacity. Nevertheless, the high activation energy and insulating properties of Li2S2 result in the kinetics of this conversion reaction being markedly slow, leading to a premature end of the discharge[17-21]. Therefore, by increasing the conversion rate of Li2S2 to Li2S, the utilization rate of the active ingredient can be further improved, effectively suppressing the "shuttle effect"[22-25].

Several studies have demonstrated that rechargeable batteries utilizing two-dimensional electrode materials exhibit satisfactory electrochemical properties, including high energy density and high rate capability[26-28]. Among numerous two-dimensional materials, layered transition metal dichalcogenides (TMDs) are extensively utilized in Li-S batteries due to their unique crystal structure and favorable physicochemical properties[29-32]. For example, Ren et al. calculated the Gibbs free energy change for distinct reaction steps of LiPSs on PtS2[29]. The only step that exhibits a heat absorption capacity is the reduction of Li2S2 to Li2S, which serves as the rate-determining step for the entire reaction. The free energy change is 3.29 eV, lower than that of TiPc (4.33 eV) and Metallic C5N monolayers (4.53 eV). Yu et al. prepared 1T'-MoTe2 quantum dot-modified 3D graphene and employed it as a catalyst for Li-S batteries to improve polysulfide conversion kinetics[30]. The importance of 1T’-MoTe2 is revealed by the fact that the 1T’-MoTe2 monolayer has a stronger facilitating effect than graphene on the Li2S6 to Li2S4, Li2S4 to Li2S2, and Li2S2 to Li2S production processes. Nevertheless, the catalytical active sites of ideal TMDs materials observed in experiments are present only at the edges, with the basal surface exhibiting minimal reactivity. To enhance this situation, researchers have modified the physical and chemical characteristics of the materials by introducing dopants on the surface of the materials, intending to optimize the electrochemical performance of the cells. However, Li2S2 conversion is a two-electron process that cannot be treated as a single fundamental step to fully and accurately describe the reaction[33], for which the mechanism of the reduction of insoluble Li2S2 to Li2S conversion by these electrocatalysts is not known[34]. In addition, their integration typically requires a large amount of conductive carbon to improve conductivity, with this extra carbon reducing the total energy density and decreasing the utilization of active materials within the cell[35, 36].

Numerous reports have shown that replacing some elements from TMDs with another metallic or non-metallic element to obtain alloyed TMDs is expected to design new energy storage devices with unique properties[37-41]. For example, through DFT calculations, Barik et al. investigated the transition metal disulfide alloy Mo1-xWxS2 as an efficient lithium storage material[38]. After lithiation, the alloys undergo a semiconductor-to-metal phase transition, which ensures good electrical conductivity. Then Jha et al. tuned the composition of Nb(SxSe(1-x))2 alloy nanosheets by colloidal synthesis[37]. The introduction of S elements into the NbSe2 lattice broadened the DOS near the Fermi energy level, modifying the electronic structure of NbSe2 thereby contributing to the improvement of catalytic activity. Recently, Wang et al. investigated the properties of monolayer SnS2(1-x)Se2x alloys as anode materials for lithium-ion batteries[39]. The findings indicate that the band gap of SnS2(1-x)Se2x alloys exhibits a decline with an increase in Se concentration. The SnS2(1-x)Se2x alloy system exhibits a lower barrier energy and enhanced adsorption strength compared to the pristine SnS2 system. Consequently, this means of alloying effectively modulates the intrinsic physicochemical properties of TMDs, resulting in increased active sites, accelerated reaction kinetics, and enhanced electrical conductivity[42, 43].

In this paper, we analyze the Li2S2 to Li2S conversion mechanism in lithium-sulfur batteries by introducing different concentrations of O element into two-dimensional VS2 to form VO(1-x)S(1+x) alloys. The VO(1-x)S(1+x) structures were obtained using the Cluster Expansion (CE) method[44], and the formation energies of the alloys were calculated. The structure with the lowest formation energy for each ratio is employed as the ground state structure for subsequent calculations. Subsequently, we examined the adsorption behavior of Li2S2 and Li2S on VO(1-x)S(1+x), and the optimal adsorption configurations were ascertained. Ultimately, in order to address the transfer of the two electrons in a step-wise manner, the reaction is divided into a series of elementary steps. In this context, two potential intermediates (namely, \*Li3S2, and \*LiS) are presented[45], which represent plausible reaction pathways. Furthermore, the Gibbs free energy difference for each step are calculated on VO(1-x)S(1+x) surfaces with different O concentrations. In this study, we also considered the effects of the *p* orbitals of nonmetallic atoms and the *d* orbitals of metallic atoms on the conversion of Li2S2 to Li2S. We established theΔ(*d*-*p*) based combinational descriptor to characterize the relation with ΔG. The above work allows us to describe the reaction mechanism of Li2S2 conversion more comprehensively and to screen potential anode catalyst materials for lithium-sulfur batteries.

1. **Computational methods**

We used density functional theory (DFT) based DMol3 to perform adsorption and catalytic calculations[46]. The exchange-corrected interactions in the generalized gradient approximation (GGA) are described by PBE generalizations. The double numerical polarization (DNP) is chosen as the basis set. An all-electron relativistic approach is used to manage the core and valence electrons[46, 47]. The geometry was optimized using an energy convergence threshold of 1.0×10-5 Ha, a force convergence threshold of 0.002 Ha/Å, and a displacement convergence threshold of 0.005 Å. The monolayers VO(1-x)S(1+x) use a 4×4 supercell to simulate the adsorption of LiPSs in a vacuum space of about 30 Å. To ensure the accuracy of the results, a global orbital truncation radius of 4.8 Å was chosen and a smearing value of 0.001 Ha was used to accelerate the convergence[48]. The Grim dispersion correction (DFT-D2) accurately describes the remote van der Waals interactions[49]. Bader analysis was used to determine the charge transfer between LiPSs and VO(1-x)S(1+x) alloy.

The cluster expansion (CE) method is mainly developed from the generalized Ising model[44], where the CE procedure is carried out using the MIT ab initio phase stability (MAPS) code implemented in the Automated Toolkit for Alloy Theory (ATAT)[50, 51]. The CE method is combined with DFT calculations to calculate convex envelope diagrams for the convex envelope map of the VO(1-x)S(1+x) alloy. For this purpose, the formation energies of nearly 60 alloy structures with up to 48 atoms per cell were evaluated using DFT calculations. These data were then used to generate CE using the ATAT code and to predict formation energies for a further nearly 845 structures.

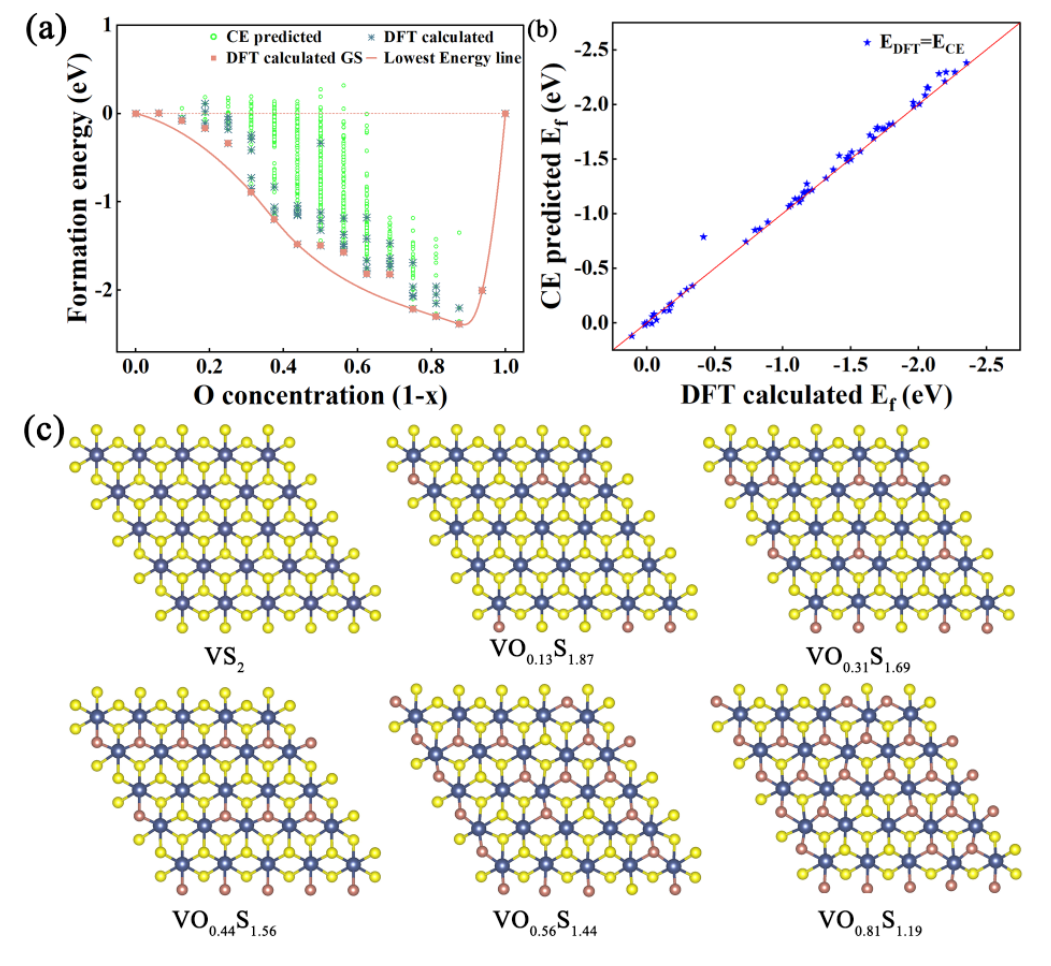
1. **Results and discussion**

**3.1 Determination of the ground state structure of VO(1-x)S(1+x) alloys**

The formation energies of the VO(1-x)S(1+x) alloy were then determined by CE. For a specific configuration σ of the VO(1-x)S(1+x) alloy, its formation energy is defined as [44]:

(1)

where denotes the total energy of the VO(1-x)S(1+x) alloy, , and denotes the total energy of the S atom. Figure 1(a) demonstrates the relationship between the formation energy of VO(1-x)S(1+x) alloys and O concentration. Each data point in green "x" shows a different supercell with a specific alloy ratio created by CE fitting. We have used CE to calculate the total energy of at least 845 different configurations with different O concentrations. As shown in Figure 1(a), for most of the configurations, the formation energy is negative. This means that these alloys are energetically stable, homogeneous, and able to form spontaneously. The formation energy of the alloys lie on the ground state line representing the ground state configuration (the orange line in the figure), suggesting that the alloys are energetically stable at 0K. Then, we calculated the energies of 60 random alloys by DFT, as shown in Figure 1(a), and the energies obtained by using DFT (the blue crosses in the figure) are coincident with those of the CE fitting, which verifies the reliability and stability of the CE fitting. Here, we choose the structure with the lowest energy among the different O concentrations as the ground state structure for the subsequent calculations (the orange points in the figure).



**Figure 1: (a) Predicted structures obtained using CE Hamiltonian (yellow forks). Blue forks indicate known structures calculated using DFT and orange squares indicate confirmed ground states. (b) CE model fit accuracy (values predicted by the blue pentagram delegation cluster expansion method). (c)** **Schematic representation of the surface of part of the ground state structure.**

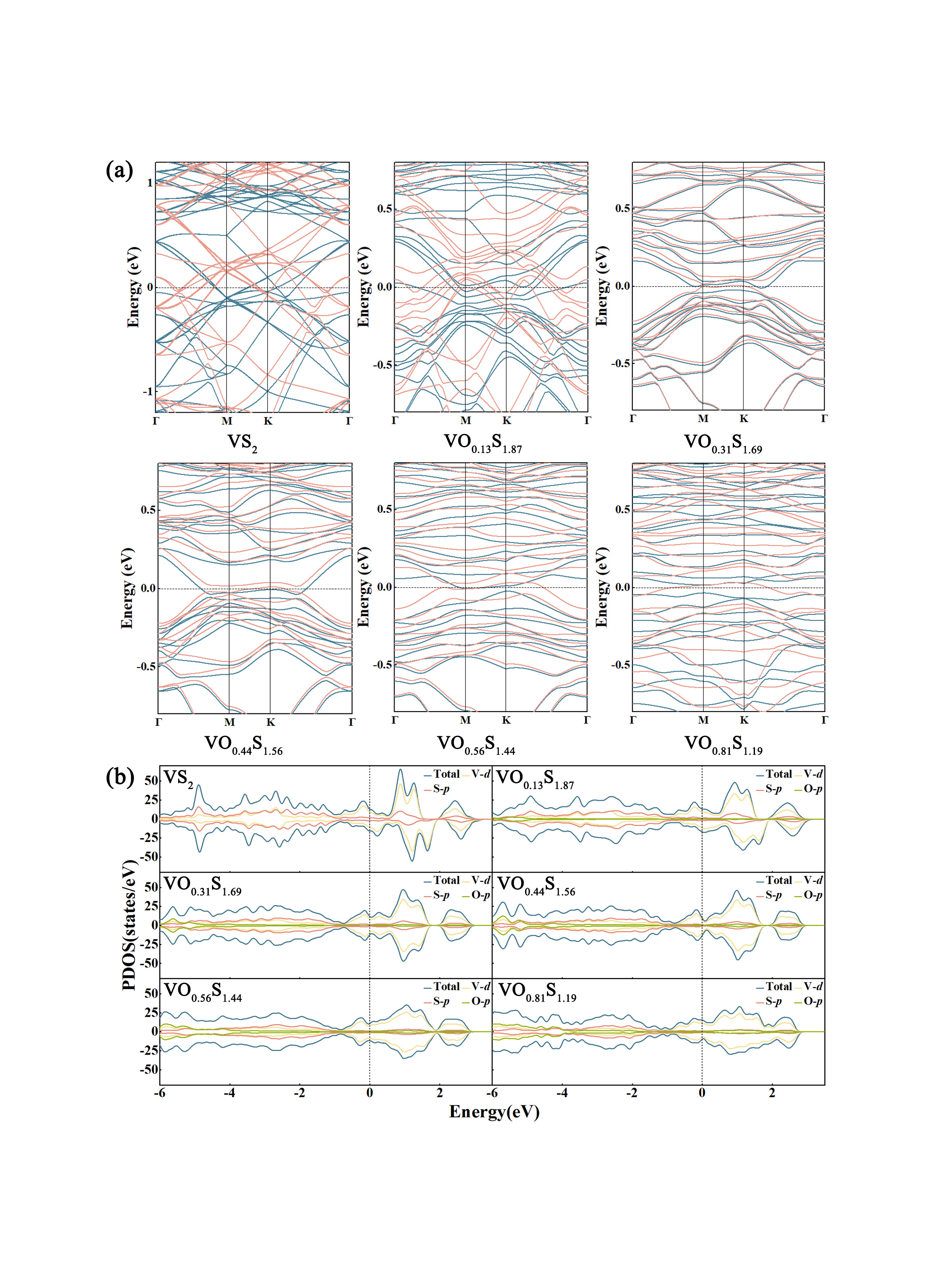
In order to assess the reliability of the cluster expansion calculations, a comparison was made between the values obtained from first principles and the energies of the CE fits, using cross-validation scores (CV)[50]:

(2)

where is the energy predicted by the CE based on M-1 configurations and is the corresponding energy calculated by first principles (here M = 60). Figure 1(b) illustrates the correlation between the cluster expansion fit and the energy values calculated from first principles, with a cross-validation score of approximately 0.063 eV. From the figure, it can be observed that all the structures are distributed along straight lines, which correspond to perfect fits or predictions. This indicates that the energy values fitted by CE accurately predict the variation of the formation energy of the VO(1-x)S(1+x) alloys as a function of O concentration. Hence, the ground state structures we predict are probably the structures that exist in nature.[52].

To observe the changes in the VO(1-x)S(1+x) ground state structure compared to the original VS2 structure, we first optimized the structure of pristine VS2 to obtain its lattice constants as: a=3.17 Å, b=3.17 Å respectively, and these results are comparable to those available in the literature[53]. Then we optimized all the VO(1-x)S(1+x) structures and obtained the lattice constants of all the structures. The optimized structures are presented in Figure 1(c) and S1, which maintain the shape of the triangular (T)-phase crystal cell of the pristine VS2. Figure S2 illustrates the impact of oxygen concentration on the internal lattice constant of VO(1-x)S(1+x) alloys, which exhibits a nearly linear decline with increasing O concentration. This phenomenon is likely attributed to the fact that the atomic radius of oxygen atoms is smaller than that of sulfur atoms. Although the alloys of different compositions exhibit completely distinct lattice constants, the V-S and V-O bond lengths remain largely consistent within these structures, aligning with the bond lengths observed in VS2 and VOS (2.37 Å and 1.96 Å).

**3.2 Electronic properties of VO(1-x)S(1+x) alloys**



**Figure 2: Partial VO(1-x)S(1+x) ground state structure of (a) energy band structure and (b) projected state density.**

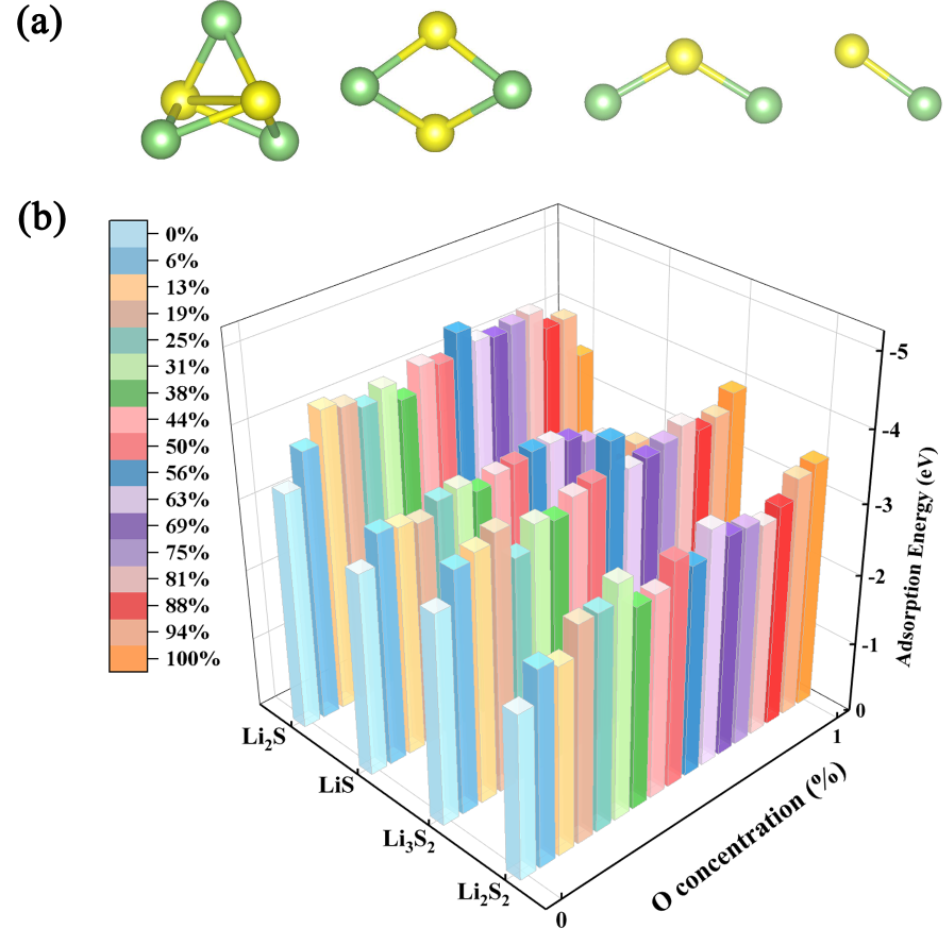
As an electrode material, its conductive properties are of significant importance. In order to investigate the effect of the variation of O concentration on the electrical conductivity of VO(1-x)S(1+x) alloys, an in-depth study of their electronic structure has been conducted. Firstly, we calculated the energy band structure of VO(1-x)S(1+x) alloys at different O concentrations. As illustrated in Figure 2(a) and S3, the energy bands of all VO(1-x)S(1+x) alloy materials cross the Fermi energy level, indicating a metallic character that preserves the high electrical conductivity of the original VS2. Subsequently, the projected density of states (PDOS) for the VO(1-x)S(1+x) alloy was calculated, as illustrated in Figure 2(b) and Figure S4-S7. Metallic V-*d*, non-metallic S-*p*, and non-metallic O-*p* orbitals were also determined as part of the analysis. It is observed that the electronic states of all VO(1-x)S(1+x) alloys located at the Fermi level were nonzero, demonstrating their metallic property. It means that the addition of O atoms maintains the metallic properties of the original VS2. The 3*d* orbital of the V atom and the 2*p* orbital of the S atom mainly contributed to the electronic density of state at the Fermi energy. With a gradual increase in O concentration, there are also significant O-*p* orbitals near the Fermi energy level. Furthermore, there is an evident orbital overlap between the S-*p* and O-*p* orbitals at the Fermi energy level, indicating the potential for covalent interactions between S and O. This could lead to the formation of new active sites that are conducive to the adsorption and catalytic conversion of reactants.

**3.3 Adsorption properties of VO(1-x)S(1+x) alloys**

The 16 VO(1-x)S(1+x) alloys with varying O concentrations, as previously screened by ATAT, are employed as an electrocatalyst model for the calculation of the adsorption energies of Li2S2 and Li2S. In addition, the adsorption energies of Li3S2 and LiS that are possible intermediates in the Li2S2 reduction reaction[45,54] are also calculated. Figure 3(a) illustrates the schematic structure of the optimized transformed molecule. By optimizing the different positions of the LiPSs molecules adsorbed on the substrate, we obtained the best adsorption configurations as shown in Figure S8-S12. It was observed that LiPSs had the lowest adsorption energies when adsorbed above non-metallic O atoms and that the Li atoms in LiPSs preferred to bond with the O atoms in the substrate. Therefore, we used to place the LiPSs molecules on the top of the O atoms to calculate their adsorption energies in this study. The adsorption energy is calculated as follows:

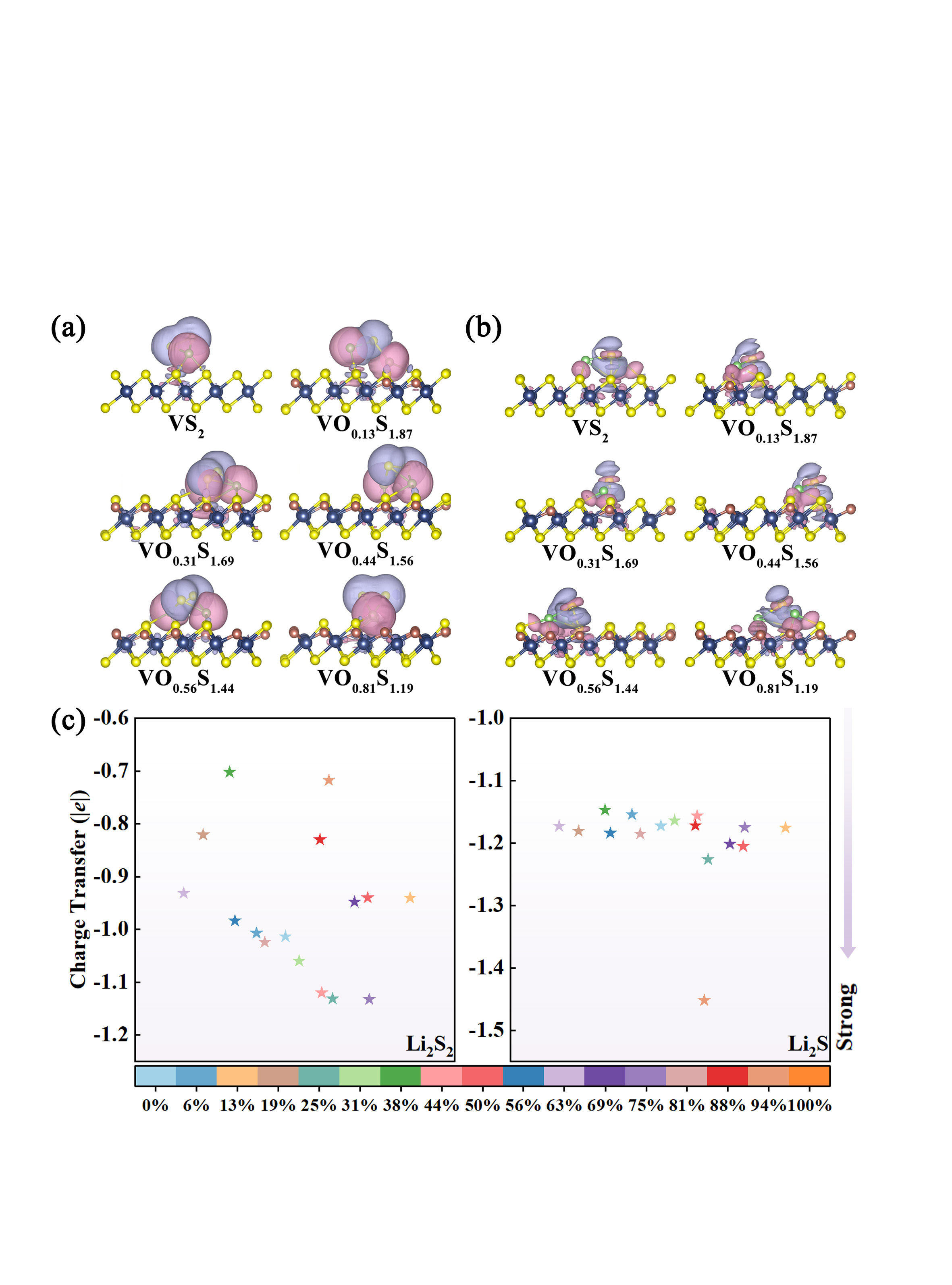
(3)

where , , and refer to the energies of the VO(1-x)S(1+x) substrates with adsorbed LiPSs, the VO(1-x)S(1+x) substrates and LiPSs respectively. The adsorption energies of these structures are illustrated in Figure 3(b) and Table S1. It can be observed that the energy differences between the various adsorption configurations are essentially minimal. As the oxygen concentration increased gradually, the adsorption energy of the VO(1-x)S(1+x) alloy for the LiPSs also increased. This finding suggests that within a specific range, the increase in oxygen concentration within VO(1-x)S(1+x) alloys enhances their capacity for the adsorption of LiPSs. However, the adsorption energy of VO(1-x)S(1+x) alloys for partial LiPSs exhibited a decreasing trend, indicating that oxygen concentrations excessively high or insufficient may weaken the ability of the VO(1-x)S(1+x) alloys to adsorb LiPSs.



**Figure 3: (a) Structures of optimized Li3S2, Li2S2, Li2S, and LiS molecules. (b) Adsorption energies for Li2S2, Li3S2, LiS, and Li2S on VO(1-x)S(1+x) surfaces with different O concentrations.**

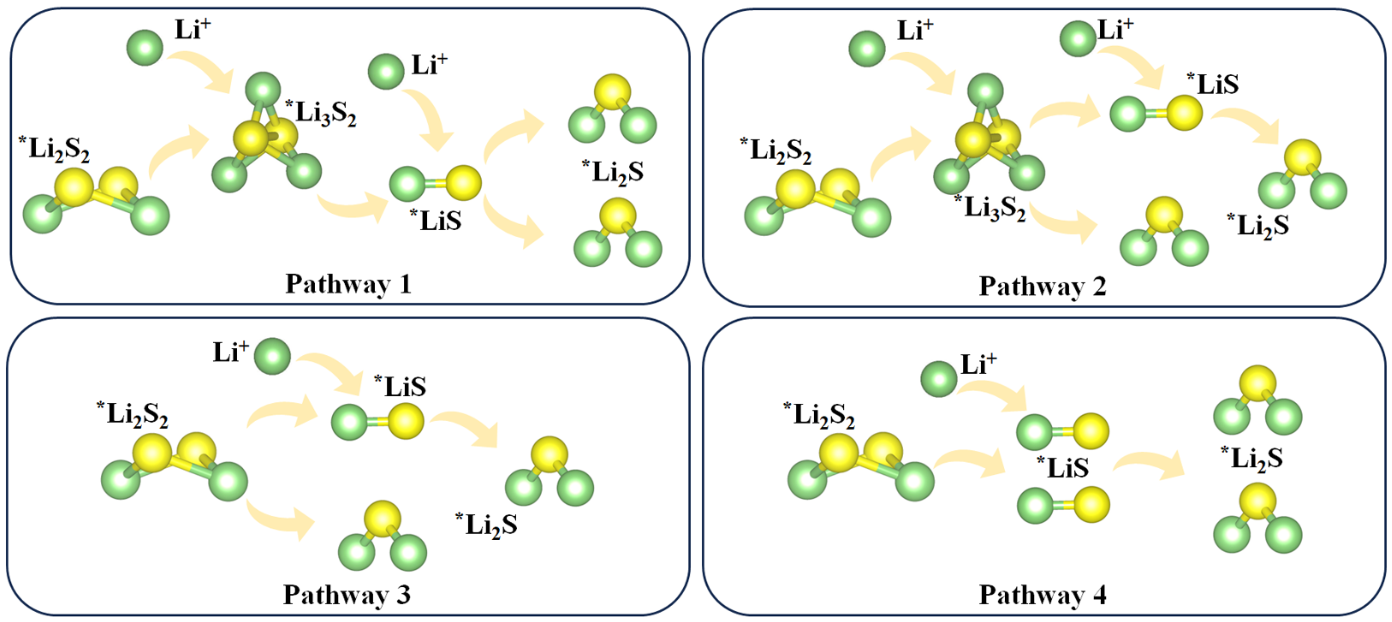
We also calculated the charge difference and Bader charges of Li2S2 and Li2S adsorbed on the surface of the VO(1-x)S(1+x) alloy. As illustrated in Figure 4(a) and (b), for all alloy surfaces, the site of charge accumulation is situated between the O of the substrate and the Li of Li2S2 and Li2S, which indicates that Li-O bonds are formed. The charge depletion occurred exclusively on Li2S2 and Li2S molecules, indicating that these species produced charge transfer to the substrate. This transfer facilitated the breakage of the Li-S bond and further catalyzed the conversion of LiPSs. Furthermore, as demonstrated in Figure 4(c) and Table S1, the Bader charge indicates that all VO(1-x)S(1+x) alloys exhibit significant variations in Li2S2 charge transfer. This suggests that when the alloys adsorb Li2S2, the alteration of O concentration influences the capacity and extent of Li2S2 electron transfer, thereby resulting in evident disparities in the charge transfer amount. For Li2S, the charge transfer difference is smaller, indicating that the electronic interaction mechanism between the alloyed structure and Li2S has not been fundamentally changed, resulting in a less pronounced change in charge transfer during adsorption compared to Li2S2.



**Figure 4:** **Charge difference between (a) Li2S2 and (b) Li2S adsorbed on a partial VO(1-x)S(1+x) monolayers. The same isosurface value of 0.003 e Å-3 is used in the plots. pink shading indicates charge deficiency. Purple shading indicates charge accumulation.(c) Charge transfer (|*e*|) from Li2S2 and Li2S to VO(1-x)S(1+x) monolayers.**

**3.4 Catalytic capacity of VO(1-x)S(1+x) alloys for the rate-limiting step of lithium-sulfur batteries**

Four possible conversion pathway i (i = 1, 2, 3, or 4) are proposed to investigate the conversion of Li2S2 to Li2S, as shown in Figure 5. The transformation pathways are as follows (where the symbol “\*” represents the VO(1-x)S(1+x) alloy catalyst substrate):



**Figure 5: Predicted reaction pathway of Li2S2RR including ∗Li3S2, and ∗LiS.**

In pathway 1, adsorbed Li2S2 combines spontaneously with a Li atom to form a Li3S2 intermediate, which then combines with a Li atom to form Li2S. Pathway 1 is as follows:

\*Li2S2 + Li+ + e- → \*Li3S2  (5a)

\*Li3S2 + Li+ + \* → 2\*Li2S (5b)

In pathway 2, adsorbed Li2S2 combines with a Li atom to form a Li3S2 cluster, which then decomposes into a Li2S product and a LiS intermediate. The latter is subsequently converted to Li2S by combining with a Li atom. Pathway 2 is as follows:

\*Li2S2 + Li+ + e- → \*Li3S2 (6a)

\*Li3S2 + \* → 2\*LiS + \*Li2S (6b)

\*LiS + Li+ + e- → \*Li2S (6c)

In contrast to pathway 2, in pathway 3, adsorbed Li2S2 reacts directly with a Li atom to form a LiS intermediate and a Li2S product, after which the intermediate bonds with a Li atom to form a Li2S product. Pathway 3 is as follows:

\*Li2S2 + Li+ + e- → \*LiS + Li2S (7a)

\*LiS + Li+ + e- → \*Li2S (7b)

In pathway 4, adsorbed Li2S2 first decomposes into two LiS intermediates, which then combine with a Li atom to form Li2S. Pathway 4 is as follows:

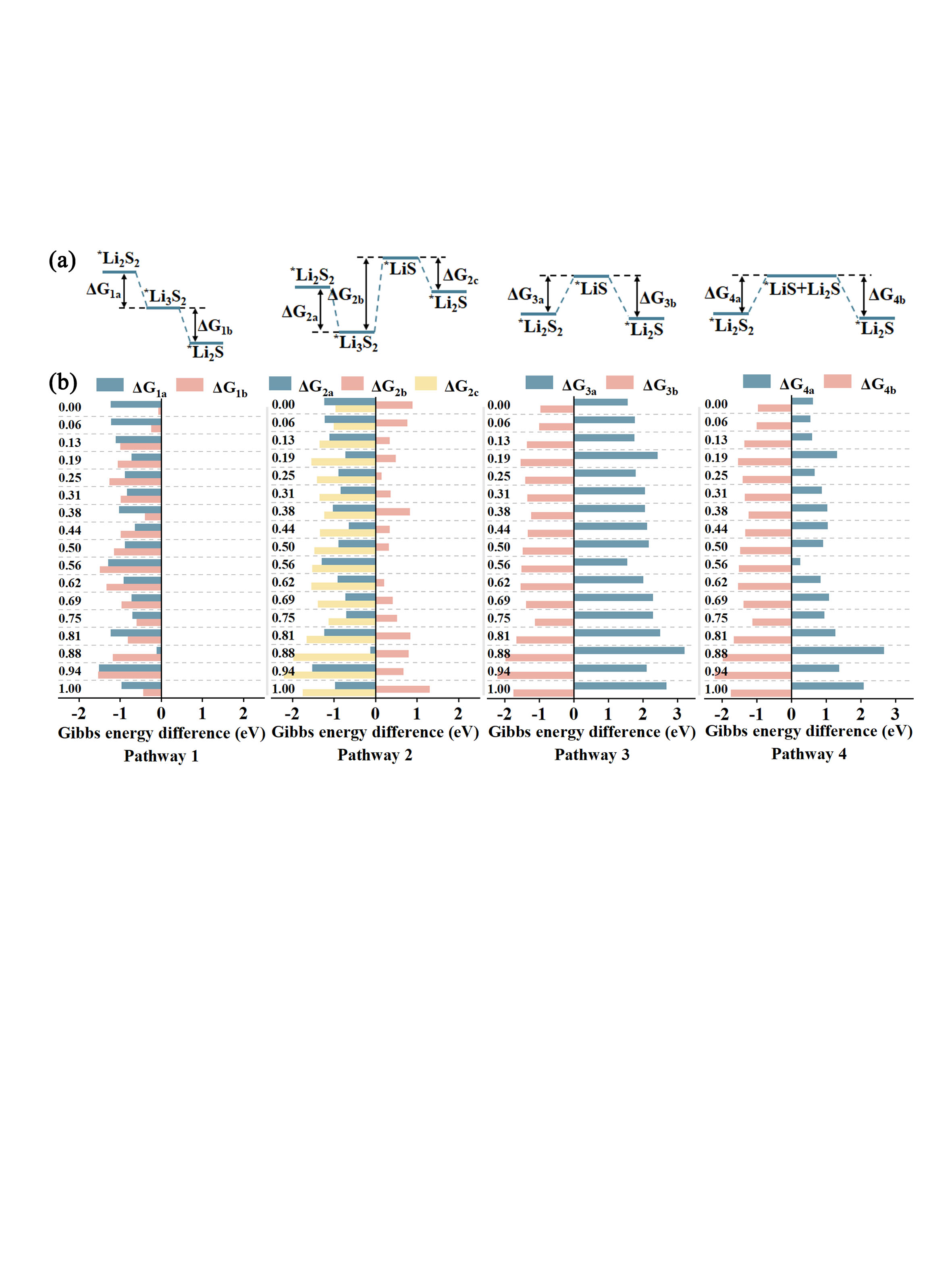
\*Li2S2 + \* → 2\*LiS (8a)

\*LiS + Li+ + e- → \*Li2S (8b)

In order to evaluate the thermodynamic properties of VO(1-x)S(1+x) alloys during the conversion of Li2S2 to Li2S, we calculated the Gibbs free energy for each conversion pathway[55, 56]:

(9)

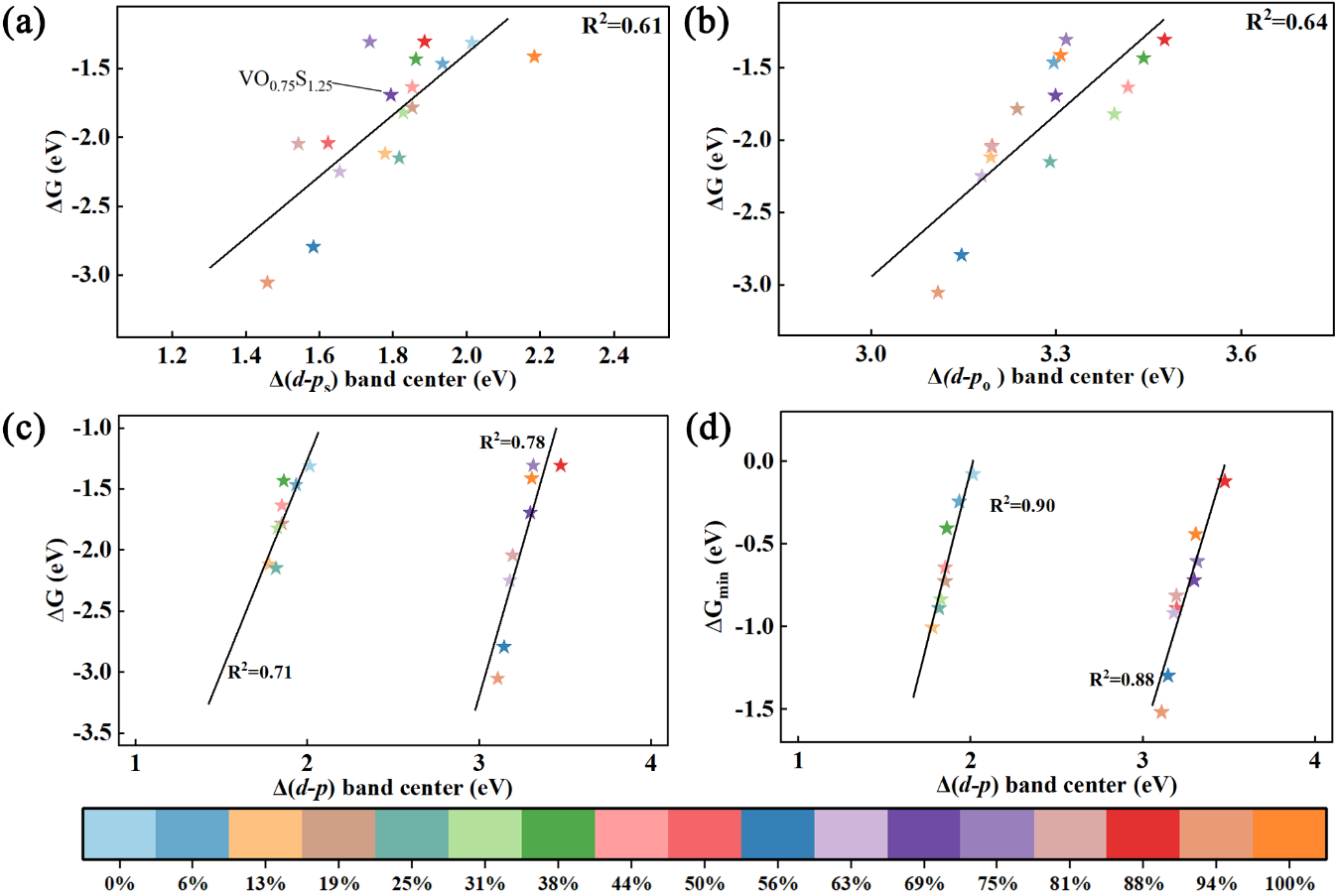
where is the energy of the product minus the energy of the reactant, here is denoted as the difference in energy of the adsorption systems of Li2S2 and Li2S on the surface of the VO(1-x)S(1+x) alloy (). and are the zero-point energy and entropy contributions to the free energy at standard temperature and pressure, respectively. represents the temperature. The contribution of zero-point energy and entropy () to the Gibbs energy is significantly smaller than the total energy difference (). Accordingly, the effects of and are excluded from the calculation of . The trends of calculated for the four pathways are shown in Figure 6(a). In order to analyze the reaction path-dependent activity in the conversion of Li2S2 to Li2S, we calculated the Gibbs free energy difference ( for each step involved in the pathways. The “i” represents the four pathways mentioned above, while the “j” (j = a, b, or c) represents the corresponding step in pathway (see Figure 6(a)). The for all potential conversion stages on the surface of the VO(1-x)S(1+x) alloy have been accurately recorded in Figure 6(b) and Table S2. From a thermodynamic perspective, the most probable reaction pathways for different VO(1-x)S(1+x) alloys can be derived from the value of , which represents the smallest Gibbs free energy difference among , and . These reactions may involve the decomposition of the Li-S bond. As illustrated in Figure 6, the conversion step in pathway 1 is exothermic for all VO(1-x)S(1+x) alloys, indicating that both steps in pathway 1 can be formed spontaneously. In pathway 2, an endothermic reaction is observed for the conversion of Li3S2 to LiS, and the remaining steps are exothermic. Both pathways 3 and 4 are endothermic reactions when the intermediate phase LiS is produced in step a, whereas it can be formed spontaneously in step b. For the three steps containing heat-absorbing reactions, we compared their Gibbs free energy differences. The free energies of pathway 2 are found to be generally smaller than those of pathways 3 and 4. One difference between pathway 2 and the other two pathways is that it generates the Li3S2 intermediate phase first and then the LiS intermediate phase. The remaining two pathways involve the direct generation of the LiS intermediate phase, which is then subjected to a reaction with Li, resulting in the formation of the final product, Li2S. From the above analysis, we can infer that the conversion of Li2S2 to Li2S prefers the pathway 1 process for the VO(1-x)S(1+x) alloy surface[45, 54].



**Figure 6:** **The four potential reaction pathways for converting Li2S2 to Li2S are illustrated schematically. The Gibbs energy difference for each fundamental step in each potential pathway is also presented in histogram form below.**

**3.5 Relationship between orbital energy level and free energy**

An analysis of the electronic effects can be achieved by examining the intrinsic electronic structure[57]. The central energy level of the *d*-band of the transition metal element determines the extent to which the antibonding orbitals can be filled with electrons, and thus determines the stability and strength of the adsorbed bonding. The *p*-band centers of nonmetals also significantly influence the adsorption of reaction intermediates, including protons[58]. Thus, for the VO(1-x)S(1+x) alloy, the *d*-band electrons of its metallic elements and the *p*-band electrons of its nonmetallic elements play an essential role in forming and breaking bonds. To gain further insight into the distinct behaviors exhibited by VO(1-x)S(1+x) alloys during the conversion of Li2S2 to Li2S, it is essential to undertake a detailed examination of their corresponding electronic structures. We calculated the *d*-band centers of transition metal elements and *p*-band centers of nonmetallic elements based on the PDOS results of VO(1-x)S(1+x) alloys and explored the synergistic effect between the *p*-orbitals and *d*-orbitals of the VO(1-x)S(1+x) alloy system by using the energy-gap Δ(*d*-*p*s) model. As shown in Figure 7(a), the value of is positively correlated with Δ(*d*-*p*s). Among them, the smaller the energy gaps at the centers of the *d* and *p* bands, the more hybridization between the *d* and *p* bands of the VO(1-x)S(1+x) alloy, which is favorable for charge transfer. this would promote the kinetics of the Li2S2 to Li2S conversion. Furthermore, the relationship between and the *d*- and *p*-orbital energy levels is examined separately, as illustrated in Figure S24(a) and (b). It is evident that exhibits a relatively weak correlation with both the *d*- and *p*-orbital energy levels. This indicates that the *d*- and *p*-orbital energy levels alone have little effect on the activity of VO(1-x)S(1+x) alloys, whereas combining both plays an important role in accelerating the reaction kinetics. Nevertheless, as the energy gap decreases gradually, its relationship with becomes increasingly divergent. For instance, on the VO0.75S1.25 surfaces with the lower , the energy gaps are relatively high.



**Figure 7: Relationships between** **and (a) Δ(*d*-*p*s); (b) Δ(*d*-*p*o); (c) Δ(*d*-*p*). (d) Relationships between and Δ(*d*-*p*).**

Given the role of the *p*-band of O in the overall electronic structure after O doping in VS2, we also calculated the *p*-band centers of doped non-metallic O atoms in VO(1-x)S(1+x) alloys at varying concentrations. We analyzed the relationship between the *p*-band centers of the non-metallic O element and (see Figure S24(c)). Nevertheless, the values are only loosely correlated with the scaling of the *p*-orbital energy levels of the non-metallic O element, with the lower coefficients of determination. Subsequently, as illustrated in Figure 7(b), we investigated the potential synergistic effect between the *d*-band centers of metallic elements and the *p*-band centers of non-metallic O elements. We focused on the relationship between “” and Δ(*d*-*p*o), where Δ(*d*-*p*o) is the energy gap between the *d*-band centers of metallic elements and the *p*-band centers of nonmetallic O elements. Although the coefficient of determination is greater for the relationship between Δ(*d*-*p*o) and than for that between O-*p* alone and , the correlation remains weak, indicating that Δ(*d*-*p*o) is unable to characterize SRR activity adequately. Both of these attempts have shown that a single Δ(*d*-*p*) model is not suitable for application to VO(1-x)S(1+x) alloy materials.

In order to ascertain the source of the Δ(*d*-*p*) model deviation, a detailed examination of the electronic structure of the VO(1-x)S(1+x) alloy has been conducted. As previously discussed in the analysis of the PDOS of the VO(1-x)S(1+x) alloy, the pristine VS2 exhibits a dominant contribution to its overall electronic state from the S-*p* orbitals. Following the incorporation of the O element, electronic states of the O element emerge near their Fermi energy levels in the PDOS of VO(1-x)S(1+x) alloys. At low concentrations of O doping, the S element remains the dominant factor influencing the overall electronic state action in VO(1-x)S(1+x) alloys. As the concentration of O increases gradually, particularly when the doping concentration is close to 50%, the intensity of the density of states peak corresponding to O-*p* increases accordingly. Meanwhile, the distribution range on the energy axis becomes more clearly defined. This suggests that the *p*-orbital electrons of the O atoms contribute an increasing proportion of the electronic density of states in the VO(1-x)S(1+x) alloy as the concentration of O doping increases. From the perspective of electronic structure, it is evident that doping with O elements results in significant orbital overlap between the O-*p* orbitals and the original S-*p* orbitals. This suggests an interaction between the two types of orbitals. As the O concentration increases, it has a more significant effect on the PDOS of the whole system, which makes the contributions of the O-*p* orbitals gradually dominate in the PDOS. Consequently, this could potentially alter the electronic structure characteristics of the material as a whole.

Therefore, we propose a combinational descriptor of S-*p* and O-*p* to characterize the Gibbs free energy difference of the rate-limiting step. The O concentration between 44% and 50% was identified as the dividing line. The VO(1-x)S(1+x) alloy with an O concentration content of 0% to 44% employs the Δ(*d*-*p*s) model to describe for this portion of the rate-limiting step. The VO(1-x)S(1+x) alloy with an O concentration content of between 50% and 100% employs the Δ(*d*-*p*o)model to describe for this portion of the rate-limiting step. A combined model with Δ(*d*-*p*s) and Δ(*d*-*p*o) on the x-axis and on the y-axis was constructed, as shown in Figure 7(c), where the data points of are distributed almost near the fitted curve. The coefficient of determination between Δ(*d*-*p*s) and is 0.71, and that between Δ(*d*-*p*o) and is 0.78, indicating a notable enhancement in the degree of correlation when compared to the correlation observed when Δ(*d*-*p*s) and Δ(*d*-*p*o) are employed to describe in isolation. This indicates that our combined descriptors are of high quality. Based on the combined descriptors, we can infer that the larger the Δ(*d*-*p*) in the corresponding range, the larger the reaction drives for its Li2S2 to Li2S conversion. To establish clearly defined screening criteria for VO(1-x)S(1+x) alloy materials based on the combinational descriptor Δ(*d*-*p*), we will further examine the relationship between the combinational descriptor Δ(*d*-*p*) and . As illustrated in Figure 7(d), there is a strong correlation between and the combined descriptor, with coefficients of determination 0.90 and 0.88, respectively. In all alloy systems, the value of is negative, indicating that Li2S2 can spontaneously generate intermediates and subsequently form Li2S. Therefore, we consider VO(1-x)S(1+x) alloy materials as potential catalysts for Li2S2 conversion.

1. **Conclusion**

In this study, we investigated the mechanism of alloyed VO(1-x)S(1+x) materials for the conversion of Li2S2 to Li2S in lithium-sulfur batteries and assessed the potential catalytic properties of various materials. Firstly, 845 VO(1-x)S(1+x) alloy materials were constructed in 17 ratios by ATAT. The formation energy of each alloy was obtained by using the cluster expansion method, and the reliability was verified by CV in combination with DFT calculations. A total of 17 VO(1-x)S(1+x) alloys with varying O concentrations were screened for the ground state structure. For their potential use as battery materials, it is crucial to ascertain their electrical conductivity. This was demonstrated through the examination of the energy band structure and PDOS, indicating that the alloys retain the metallic properties of the original VS2, while exhibiting good electrical conductivity. Subsequently, we proposed two reasonable intermediates among four possible reaction pathways for the conversion of Li2S2 to Li2S, based on the possibility of multiple conversion pathways for the conversion of Li2S2 to Li2S. We then calculated the adsorption energies of these 17 kinds of VO(1-x)S(1+x) alloy systems for Li2S2 to gain further insight. The adsorption energies of all systems are higher than that of pristine VS2, which may be due to the formation of new Li-O bonds. This is evidenced by the charge differential and Bader charges, which indicate that the formation of these bonds is a possible intermediate in the conversion of Li2S2 to Li2S. Finally, to evaluate the potential of VO(1-x)S(1+x) alloys as catalysts for lithium-sulfur batteries, we calculated the Gibbs free energies for each conversion pathway and modeled the Δ(*d*-*p*s) and Δ(*d*-*p*o) of VO(1-x)S(1+x) alloy materials with their performance in catalyzing the sulfur reduction reaction in Li-S batteries. The model was utilized for Gibbs free energy screening of the rate-limiting reaction from Li2S2 to Li2S. In addition, we established the relationship between and the surface properties of VO(1-x)S(1+x) alloys, which provides detailed design rules for VO(1-x)S(1+x) as cathode catalysts for Li-S batteries. Based on this model we identified VO(1-x)S(1+x) alloys as potential cathode electrocatalysts for lithium-sulfur batteries.

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