

## CHAPTER IV

### INVESTIGATION OF CATHODE PERFORMANCE IN ALUMINUM-SULFUR BATTERIES: DFT, AND COMPUTATIONAL STUDY

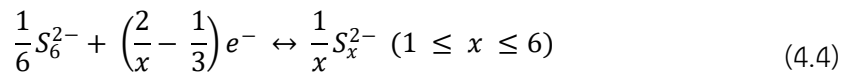
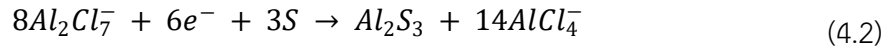
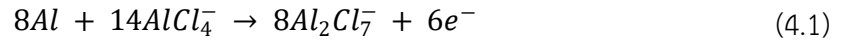
In the previous chapter, we established the theoretical and computational framework for this study. We began with an overview of the theoretical and computational methods, focusing on the Schrödinger equation and its approximate solutions through the variational principle. Key developments in computational materials science were highlighted, followed by an overview of density functional theory (DFT), the foundation of our calculations. Methods for structural optimization and error correction in DFT were also discussed, along with the climbing image-nudged elastic band (CI-NEB) method for the decomposition of  $\text{Al}_2\text{S}_3$ . Finally, computational details implemented using the Vienna Ab initio Simulation Package (VASP) were summarized.

In this chapter, we investigated the structural and electronic properties of 3d-transition metals decorated  $\text{V}_2\text{CO}_2$  cathode materials. We assess the stability of  $\text{Al}_2\text{S}_n$  species on  $\text{SA@V}_2\text{CO}_2$  and  $\text{DA@V}_2\text{CO}_2$  using advanced structural analysis techniques, including Bader charge and Smooth Overlap of Atomic Positions) analyses. The chapter further explores the sulfur reduction reaction to evaluate cathode performance and examines the decomposition of  $\text{Al}_2\text{S}_3$  to understand the reversibility and efficiency of aluminum-sulfur batteries. These investigations provide critical insights into the design of high-performance cathode materials.

#### 4.1 The structural and electronic properties for $\text{V}_2\text{CO}_2$ MXene

According to previous study, the redox process of Al-S batteries with the electrolyte of 1-ethyl-3-methylimidazolium chloride ( $[\text{EMIM}]^+\text{Cl}^-$ ) as electrolyte can be summarized as given equations (4.1) and (4.2) The charge-discharge process of Al-S

batteries involved the formation of  $S_8$  and  $Al_2S_n$  species as equations (4.3) and (4.4). The sulfur reduction reactions initially start from  $S_8$ ,  $Al_2S_{18}$ ,  $Al_2S_{12}$ ,  $Al_2S_6$  to  $Al_2S_3$ .



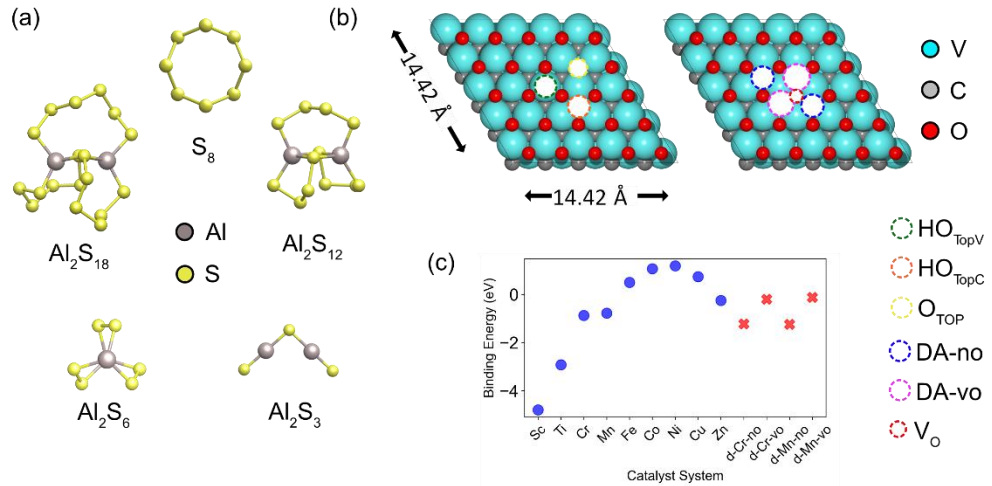
The optimized structures of  $S_8$  and  $Al_2S_n$  species show the most stable structures among all the possible structures in Figure 4.1a. The morphology of  $S_8$  is a crownlike orthorhombic structure.  $Al_2S_3$  presents a planar bent. For the structure of  $Al_2S_6$ ,  $Al_2S_{12}$ , and  $Al_2S_{18}$ , they form 3D cluster shapes without overhanging bonds which results were consistent with other computational studies (Bhauriyal & Pathak, 2020; Z. Wang et al., 2022; Zheng et al., 2022). The side views of the surfaces are presented in Figure 4.1b, where  $V_2CO_2$  with a terminal group of O atoms has the V–O bond with length of 1.95 Å, and V–C bond with length of 2.05 Å. In this study, 3d-TMs excluding V were decorated on the bare  $V_2CO_2$  due to their unique catalytic properties, specifically their ability to improve polysulfide conversions by facilitating electron transfer and promoting adsorption. Additionally, the choice of 3d-TMs (like Cr, Mn, and Fe) is driven by their distinct properties, such as better catalytic activity, structural stability, and flexibility in designing materials with tunable electronic characteristics, which improves their performance in energy storage applications such as Li-S, and Al-S batteries (Andritsos et al., 2021; Chen et al., 2021; Gu et al., 2020; Ju et al., 2022; Yang et al., 2013).

For the binding site of SA, there are four possible binding sites including  $bridge_{VO}$ , Hollow  $O_{TopV}$ , Hollow  $O_{TopC}$ , and  $O_{Top}$  shown in Figure 4.1b. We find that  $O_{Top}$  is unstable site for all decorated SAs. As well as  $bridge_{VO}$  site, the decorated SAs change into Hollow  $O_{TopV}$  site for all surfaces. These suggest that there are two

preferential sites where Sc, Ti, Cr, Mn, and Cu prefer to bind on Hollow  $O_{\text{TopC}}$  site, and Fe, Co, Ni, and Zn as decorated SAs prefer to bind on Hollow  $O_{\text{TopV}}$  site shown in Figure 4.1c. Similarly, the DA binding site including Cr and Mn follows the same strategy in both the no-oxygen vacancy and oxygen vacancy systems ( $V_O$ ). A detailed analysis of all tested configurations for both SA and DA systems is provided in Figure A1. To assess the viability of these materials, we determined their relative stability. For the SA and d-DA-no systems, where dopants are decorated on the surface, we calculated the binding energy ( $E_b$ ) to quantify the strength of the anchor using the formula:

$$E_b = E_{\text{decorated}} - E_{\text{surface}} - nE_{\text{metal}} \quad (4.5)$$

where  $E_{\text{decorated}}$  and  $E_{V_2CO_2}$  are the total energy of the decorated  $V_2CO_2$  for SA and DA systems and  $V_2CO_2$  or with an oxygen vacancy for d-DA- $V_O@V_2CO_2$ , respectively.  $n$  is the number of decorated atoms, and  $E_{\text{metal}}$  is the energy of the single atom metal.

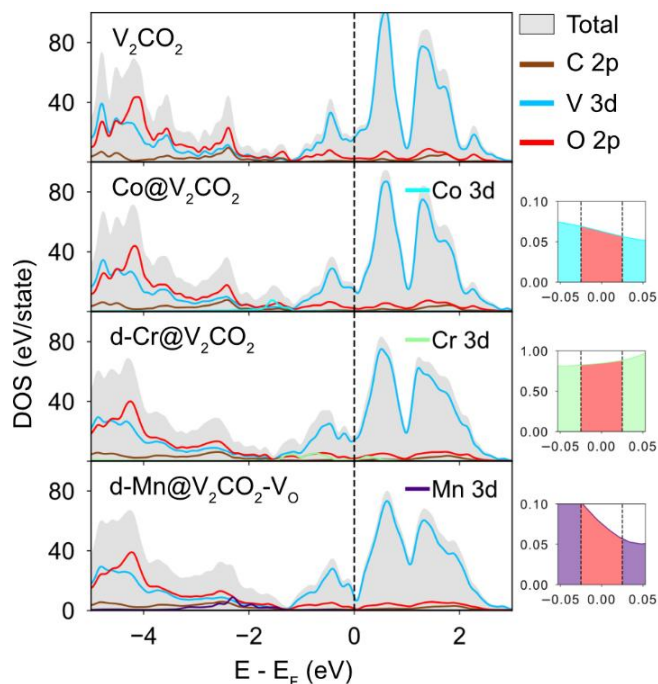


**Figure 4.1** Optimized structures of  $V_2CO_2$  and adsorption configurations: (a) Top views of the optimized  $3 \times 3 \times 1$   $V_2CO_2$ . (b) Possible binding sites for  $SA@V_2CO_2$ . (c)  $DA@V_2CO_2$  configurations:  $d$ -DA (left) without oxygen vacancy and  $d$ -DA-vo (right) with surface oxygen vacancy. (c) Binding energy of SA and DA on  $V_2CO_2$  surfaces for various transition metal.

We find that the 3d-TM, Zn and DAs have negative  $E_b$  values, indicating the possibility of successful fabrication, providing a reference for experimental preparation. To further examine their stability under operating conditions, we performed ab initio molecular dynamics (AIMD) simulations, a method used in similar a computational study (Singsen et al., 2022). The simulations, performed at e.g., 300 K for 10 ps, revealed that the structures remain intact with no significant degradation, thus suggesting their excellent thermal stability (see Figure A2 for details).

To understand how SAs and DAs affect the material's electronic properties, we analyzed the projected density of states (PDOS) for each system (see Figure A3 for all systems). Figure 4.2 presents the DOS for representative cases: bare, Co@V<sub>2</sub>CO<sub>2</sub>, d-Cr@V<sub>2</sub>CO<sub>2</sub>, and d-Cr-V<sub>O</sub>@V<sub>2</sub>CO<sub>2</sub>. We find that the bare exhibits metallic character. The states near the Fermi level are dominated by V 3d orbitals, with non-negligible contributions from C 2p and O 2p orbitals, consistent with previous computational studies (Gao et al., 2022; Zou et al., 2024). Both SA and DA@V<sub>2</sub>CO<sub>2</sub> preserves this essential metallic nature. The SA systems, represented by Co@V<sub>2</sub>CO<sub>2</sub>, introduces additional states near the Fermi level originating from the Co atom, though these are less dominant than the V 3d states. Similarly, the DA systems maintain conductivity, where the interaction between the dual 3d-TMs and the substrate further modulates the states around the Fermi level.

The impact of these tuned structural and electronic properties on the material's performance as a cathode host will be systematically investigated in the following sections.



**Figure 4.2** Projected Density of States (PDOS) for the bare  $V_2CO_2$  surface, SA (Co), and DA (d-Cr and d-Mn- $V_O$ ). Fermi level ( $E_F$ ) is adjusted to 0 eV. Light blue, V; brown, C; red, O; sky blue, Co; neon, d-Cr; violet, d-Mn- $V_O$ .

## 4.2 Adsorption energy of sulfur species ( $S_8$ , $Al_2S_n$ )

A critical challenge hindering the practical application of Al-S batteries is the dissolution of  $Al_2S_n$  species into the electrolyte. This phenomenon, known as the shuttle effect, is primarily caused by the high solubility of large, higher order  $Al_2S_n$  species such as  $S_8$ ,  $Al_2S_{18}$ , and  $Al_2S_{12}$ . To mitigate this issue, the  $V_2CO_2$ ,  $SA@V_2CO_2$  and  $DA@V_2CO_2$  must be capable of strongly anchoring these  $S_8$  and  $Al_2S_n$  species to confine them within the cathode region. Firstly, we investigated for the most stable adsorbed configurations and adsorption sites. The optimized structures of  $S_8$  and  $Al_2S_n$  species are detailed in Figure A4-A8. To understand the anchoring performance, we deconstructed the adsorption process into its fundamental energetic components: the net adsorption energy ( $E_{ads}$ ), the intrinsic interaction energy ( $E_{int}$ ),

and the energetic penalty from structural deformation ( $E_{def}$ ). The adsorption energy,  $E_{ads}$ , can be calculated using the following equation:

$$E_{ads} = E_{total} - E_{surface} - E_{S_8 \text{ or } Al_2S_n} \quad (4.6)$$

where  $E_{total}$ ,  $E_{surface}$ , and  $E_{S_8 \text{ or } Al_2S_n}$  are the total energy of the fully relaxed adsorbed system, the isolated catalyst-decorated surface, and the isolated sulfur species in a vacuum, respectively. A more negative  $E_{ads}$  value indicates a stronger, more favorable adsorption strength.

This adsorption energy is a balance between the intrinsic interaction and the deformation penalty, as defined by the relationship  $E_{ads} = E_{int} + E_{def}$ . These components are calculated as:

$$E_{int} = E_{total} - E_{surface (distorted)} - E_{S_8 \text{ or } Al_2S_n (distorted)} \quad (4.7)$$

$$E_{def} = (E_{surface (distorted)} - E_{surface}) + (E_{S_8 \text{ or } Al_2S_n (distorted)} - E_{S_8 \text{ or } Al_2S_n}) \quad (4.8)$$

Here,  $E_{int}$  quantifies the interaction between the species and the surface in their final ( $E_{total}$ ) by subtracting the single-point energy of the surface ( $E_{surface (distorted)}$ ) and the  $S_8$  or  $Al_2S_n$  species ( $E_{S_8 \text{ or } Al_2S_n (distorted)}$ ) in their final, distorted geometries. This isolates the interaction, separate from the energy cost of deformation. The deformation energy,  $E_{def}$ , is the sum of the energy required to distort the surface from its relaxed state ( $E_{surface}$ ) to its final adsorbed geometry ( $E_{S_8 \text{ or } Al_2S_n (distorted)}$ ) and to distort the polysulfide from its relaxed state ( $E_{S_8 \text{ or } Al_2S_n}$ ) to its final adsorbed geometry ( $E_{S_8 \text{ or } Al_2S_n (distorted)}$ ).

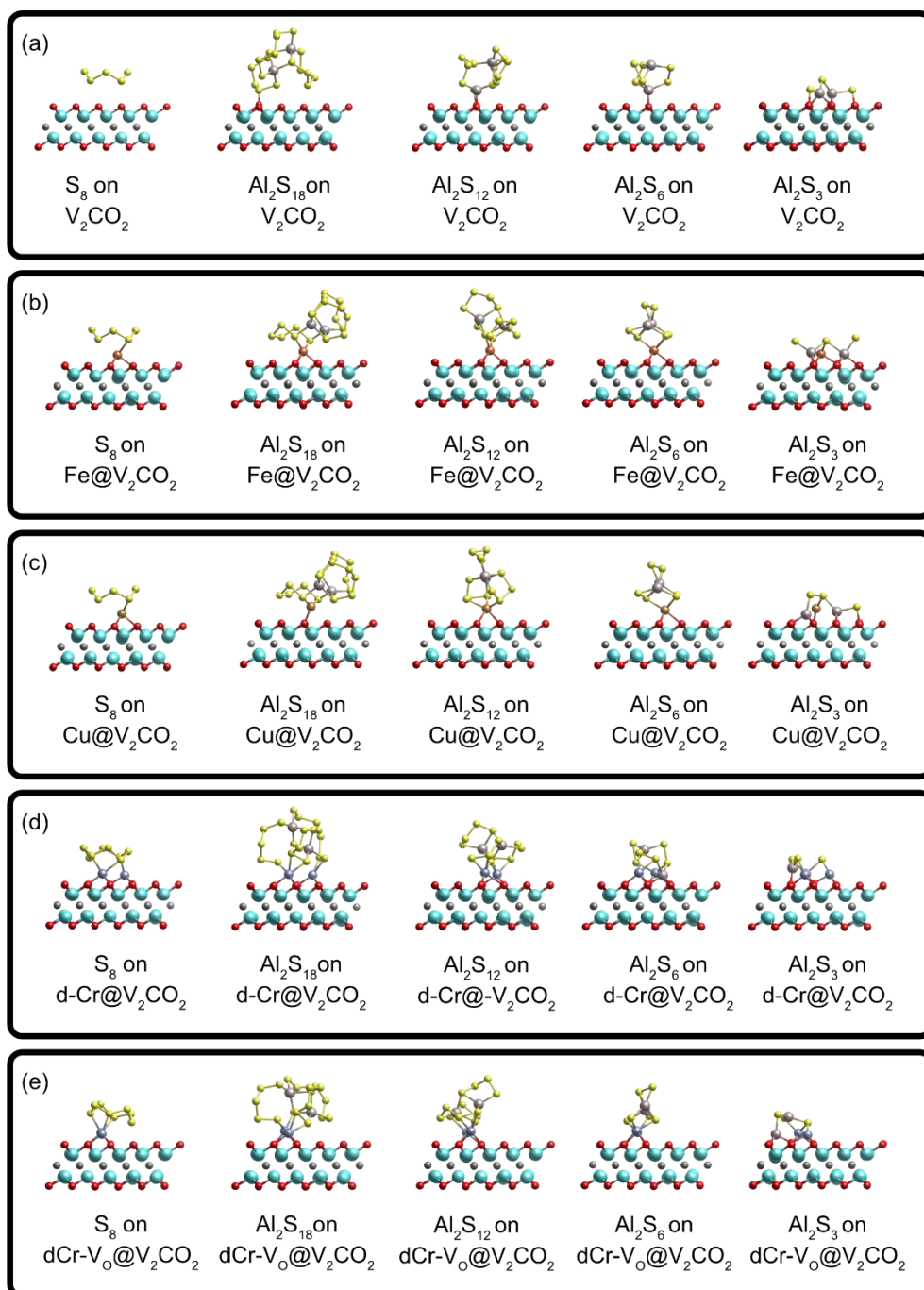
On the bare  $V_2CO_2$ , Al-O bonds form easily during  $Al_2S_n$  species adsorption. Species like  $Al_2S_3$ ,  $Al_2S_6$ , and  $Al_2S_{12}$  strongly adsorb due to the formation of Al-O bonds. In contrast,  $S_8$  and  $Al_2S_{18}$  show weak adsorption.  $S_8$  lacks Al atoms, preventing Al-O bond formation, while  $Al_2S_{18}$  is a large cluster where S atoms obstruct bonding shown in Figure 4.3a.

For the  $SA@V_2CO_2$ , S atoms from  $S_8$  and  $Al_2S_n$  species form bonds with the TMs. Depending on the adsorption site,  $Al_2S_n$  species adopt different configurations on the surface. For example,  $Fe@V_2CO_2$ , where Fe binds to the Hollow  $O_{TopV}$  site, the

Fe atom forms multiple bonds with S atoms in higher-order  $\text{Al}_2\text{S}_n$  species.  $\text{Al}_2\text{S}_3$  prefers Al–O bonds, while S atoms favor Fe–S bonds in Figure 4.3b.  $\text{Cu@V}_2\text{CO}_2$  behaves similarly, but the  $\text{Al}_2\text{S}_n$  configuration varies depending on the TM atom in Figure 4.3c.

On  $\text{DA@V}_2\text{CO}_2$ , S atoms of  $\text{S}_8$ , and high orders of  $\text{Al}_2\text{S}_n$  interact form bonds with both TMs. For high orders of  $\text{Al}_2\text{S}_n$ , several S atoms can bond with dual atoms resulting the different configurations comparing to  $\text{SA@V}_2\text{CO}_2$ . While Low orders of  $\text{Al}_2\text{S}_n$  species also bond with both TMs, but their size and fewer S atoms cause structural distortion shown in Figure 4.3d and Figure 4.3e. Furthermore, the adsorption of  $\text{Al}_2\text{S}_n$  species on  $\text{DA@V}_2\text{CO}_2$  for example, with and without oxygen vacancies ( $\text{dCr@V}_2\text{CO}_2$  and  $\text{dCr-V}_\text{O@V}_2\text{CO}_2$ ) represent the different configurations suggested the effect of vacancies on the adsorption. These might be discussed in the further section.

The calculated interaction energy for  $\text{S}_8$  and large soluble  $\text{Al}_2\text{S}_n$  species are presented in Figure 4.4a. The solid bars represent the final, net adsorption energy ( $E_{\text{ads}}$ ), while the hatched bars stacked on top represent the positive deformation energy penalty ( $E_{\text{def}}$ ). Therefore, the total height of each stacked bar (solid plus hatched) represents the total intrinsic interaction energy ( $E_{\text{int}}$ ). On the bare  $\text{V}_2\text{CO}_2$  surface, the adsorption of these species is weak, with  $E_{\text{ads}}$  values of -0.96 eV for  $\text{S}_8$ , -1.02 eV for  $\text{Al}_2\text{S}_{18}$ , and -2.15 eV for  $\text{Al}_2\text{S}_{12}$ . According to previous computational study, we find that the  $E_{\text{ads}}$  of  $\text{Al}_2\text{S}_{18}$ ,  $\text{Al}_2\text{S}_{12}$  with the ionic liquid electrolyte are -1.49, and -1.34 eV, respectively. This refers to the weak adsorption strength that might be insufficient to overcome the strong adsorption strength of the high orders of  $\text{Al}_2\text{S}_n$  species with ionic liquid in the electrolyte, indicating that the bare might be an ineffective anchor and would suffer from a severe shuttle effect. Critically, the hatched bars ( $E_{\text{def}}$ ) for the bare surface are almost the same portion as adsorption energy, meaning the total interaction energy ( $E_{\text{int}}$ ) is nearly identical to the final adsorption energy. This lack of deformation is characteristic of weak physisorption. Critically, the hatched bars ( $E_{\text{def}}$ ) for the bare surface are a significant portion of the  $E_{\text{ads}}$ , indicating that a deformation penalty is paid even for this weak interaction.



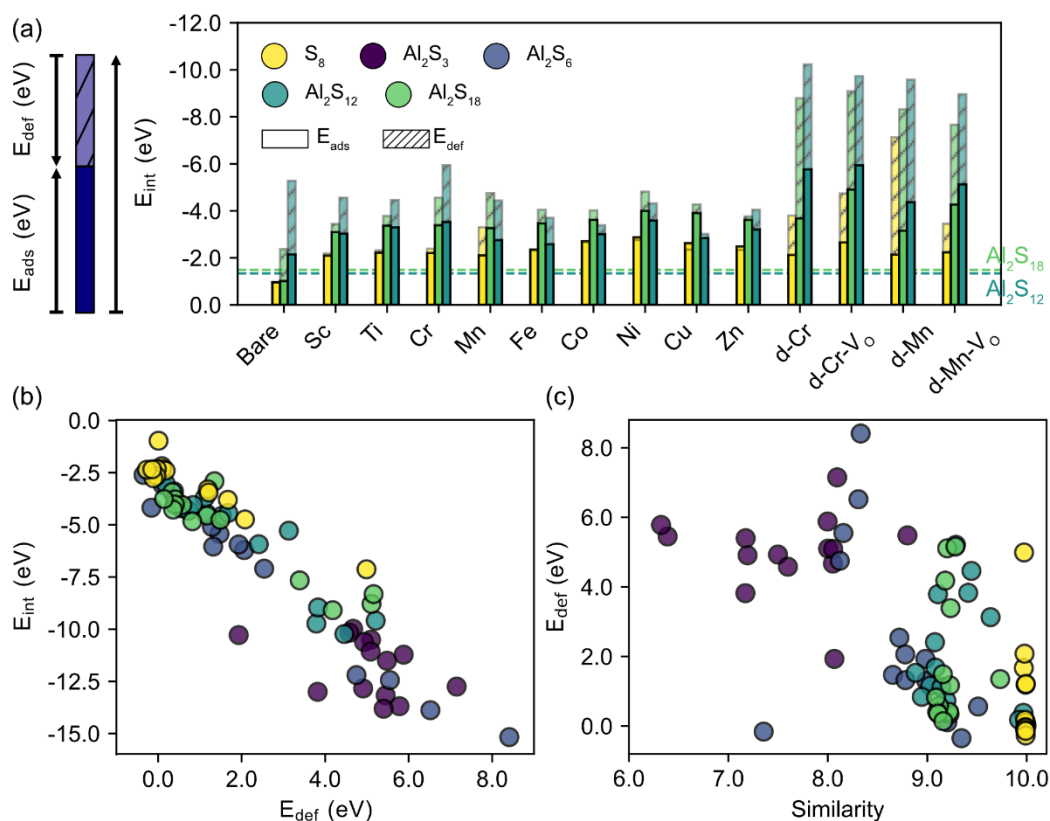
**Figure 4.3** (a) Adsorption of  $S_8$ , and  $Al_2S_n$  species on the bare  $V_2CO_2$  surface, showcasing side views of each configuration. (b) and (c) Adsorption of the same species on  $Fe@V_2CO_2$ , and  $Cu@V_2CO_2$  with the SA positioned at the hollow  $O_{topV}$  site and the hollow  $O_{topC}$  site respectively (d) and (e) Adsorption of the species on  $V_2CO_2$  surfaces modified with DA configurations, both with and without oxygen vacancies ( $dCr@V_2CO_2$  and  $dCr-V_o@V_2CO_2$ ).

The introduction of SAs significantly enhances the adsorption strength since the interaction between the high orders of  $\text{Al}_2\text{S}_n$  and  $\text{SA@V}_2\text{CO}_2$  become stronger. For example, the  $E_{ads}$  of  $\text{Al}_2\text{S}_{12}$  is strengthened to -3.30 eV on  $\text{Ti@V}_2\text{CO}_2$  and -3.53 eV on  $\text{Cr@V}_2\text{CO}_2$ , values which are stronger than that of the bare. Furthermore,  $E_{def}$  of  $\text{SA@V}_2\text{CO}_2$  is less than that of the bare indicating the interaction between TMs and S atoms of  $\text{Al}_2\text{S}_n$  species did not break the structure of high orders  $\text{Al}_2\text{S}_n$  species. This trend holds across the various TMs, indicating that SAs are a viable strategy for effectively capturing or suppressing the high orders of  $\text{Al}_2\text{S}_n$  species. Furthermore, the early 3d-TMs including Sc, Ti, Cr, Mn show the negligible difference of the adsorption energy. While the late 3d-TMs like Co, Ni, Cu, and Zn show excessive adsorption strength especially Ni.

The anchoring effect is further amplified in DAs. These surfaces exhibit the strongest interaction (total bar height) compared to the other systems. This strong interaction comes with a significant penalty, as DAs also show the largest  $E_{def}$ . Despite this high energetic penalty, the resulting strongest adsorption strength, consistently surpassing both the bare and SA systems. For instance, the adsorption of  $\text{Al}_2\text{S}_{12}$  on the d-Cr-vo@ $\text{V}_2\text{CO}_2$  system reaches -5.94 eV. These results clearly establish a performance hierarchy (Bare < SA < DA) and demonstrate that DA systems are a highly effective strategy for capturing the high orders of  $\text{Al}_2\text{S}_n$  species responsible for the shuttle effect.

To further understand this energetic trade-off, we analyzed the correlations between these energy components and the resulting structural changes, as shown in Figure 4.4b. The left panel, which plots  $E_{int}$  versus  $E_{def}$ , reveals a clear trade-off: stronger interactions (more negative  $E_{int}$ ) force the system to pay a higher energetic penalty (more positive  $E_{def}$ ). For instance, the adsorption of  $\text{S}_8$  on the bare surface involves weak interaction and deformation. In contrast, the adsorption of  $\text{Al}_2\text{S}_n$  species on the decorated surfaces results in highly strong interaction and correspondingly large deformation. In Figure 4.4c, we examined this structural change using the similarity, where a score close to 10 indicates high structural integrity, while lower scores signify greater deformation. The right panel of Figure 3c plots this energetic penalty ( $E_{def}$ ) against the similarity, a measure of structural distortion.

Interestingly, the plot does not show a simple linear correlation. Instead, it reveals a complex relationship, indicating that the energetic cost of deformation is not directly proportional to the magnitude of the structural distortion. This suggests that the cost of deforming a polysulfide is highly dependent on the specific nature of the interaction and not just the final degree of structural change.



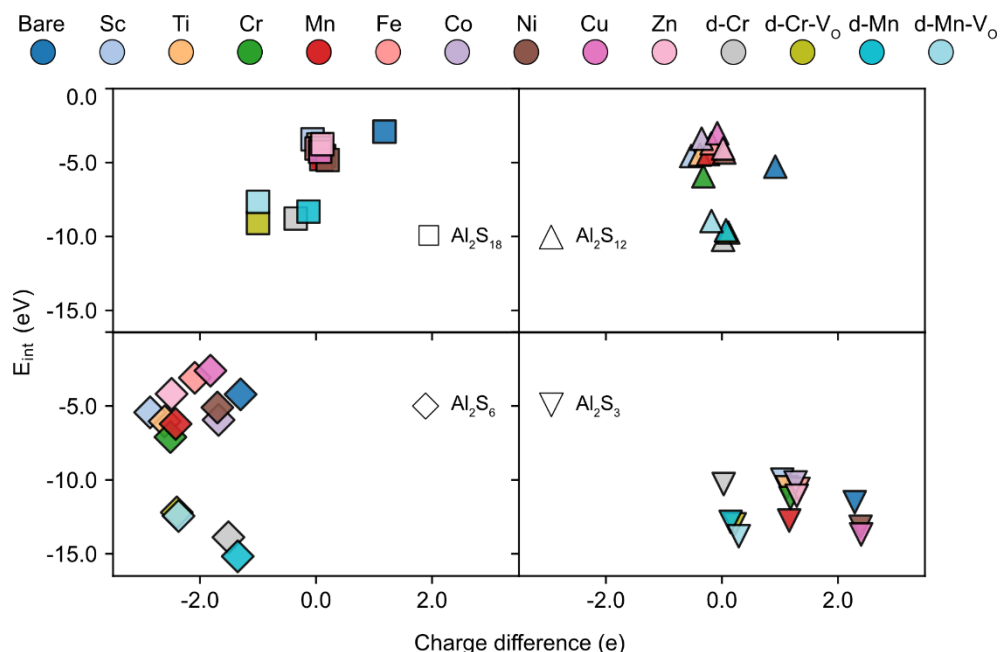
**Figure 4.4** Analysis of polysulfide adsorption on bare and SA and DA systems. (a) Interaction energy ( $E_{int}$ ) of large, soluble sulfur species ( $S_8$ ,  $Al_2S_{18}$ , and  $Al_2S_{12}$ ) on bare, SA, and DA@V<sub>2</sub>CO<sub>2</sub>. (b) Correlation between the interaction energy ( $E_{int}$ ) and the corresponding adsorption energy ( $E_{ads}$ ) and deformation energy ( $E_{def}$ ) for all sulfur species across all surfaces. The species are color-coded as follows:  $S_8$  (dark purple),  $Al_2S_{18}$  (medium blue),  $Al_2S_{12}$  (light green),  $Al_2S_6$  (yellow-green), and  $Al_2S_3$  (yellow).

Next, we investigated the electronic properties of the strong interaction. To quantify the charge difference upon adsorption, we performed a Bader charge

analysis. In this study, we calculated the charge transfer as the difference in the summed Bader charge of the three S atoms nearest the adsorption site between the adsorbed and isolated states. A positive value indicates that the  $S_8$  or  $Al_2S_n$  species have lost electrons to the surface, while a negative value signifies that it has gained (or accepted) donated electrons from the surface.

The relationship between this charge transfer and the interaction energy ( $E_{int}$ ) is plotted in Figure 4.5. An interesting behavior is observed for the bare surface. For higher-order species like  $Al_2S_{18}$  and  $Al_2S_{12}$ , there appears to be a significant charge transfer from the polysulfide to the surface (1.18 e and 0.92 e, respectively). However, this does not translate into strong interaction energy. This might suggest that the charge redistribution does not lead to the formation of a stable chemical bond, which is likely because the O-terminated  $V_2CO_2$  surface is chemically unfavorable for forming strong bonds with the S atoms in the  $Al_2S_n$  species.

For the SA and DA systems, a clear correlation between the magnitude of charge transfer and interaction strength emerges. As seen in Figure 4.5, the higher-order species  $Al_2S_{18}$  and  $Al_2S_{12}$  (top panels) generally show a smaller magnitude of charge difference compared to the lower-order species  $Al_2S_6$  and  $Al_2S_3$  (bottom panels). For  $Al_2S_{18}$  and  $Al_2S_{12}$ , stronger interaction generally correlates with a greater loss of electrons to the surface. This trend is even more pronounced for the smallest species,  $Al_2S_3$ , which shows a large loss of electrons (up to  $\sim 2.4$  e) on the decorated surfaces. This suggests a bonding mechanism where the catalyst atom withdraws electron density from these polysulfides. A notable exception is seen for the DA- $V_O$  systems, which exhibit the strongest interaction for these species while showing a significant gain of electrons, indicating a different and highly effective anchoring mechanism enhanced by the  $V_O$ .



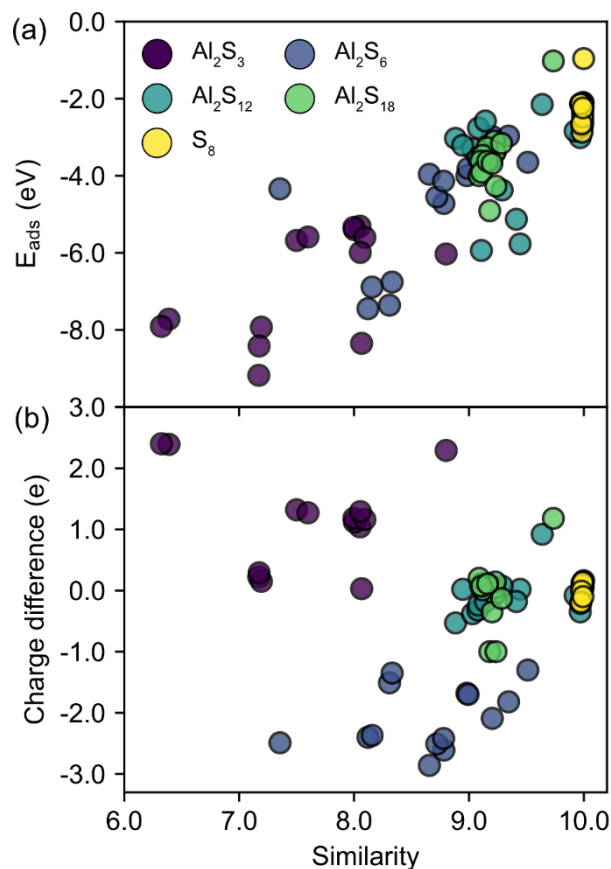
**Figure 4.5** The relationship between charge transfer and interaction energy for  $\text{Al}_2\text{S}_n$  species. The plot shows the relationship between the calculated charge difference on the  $\text{Al}_2\text{S}_n$  species and the corresponding interaction energy ( $E_{\text{int}}$ ) on the bare, SA, and DA@ $\text{V}_2\text{CO}_2$ . Each system is represented by a unique color, and each  $\text{Al}_2\text{S}_n$  species is represented by a unique marker shape, as defined in the legend.

In contrast,  $\text{Al}_2\text{S}_6$  exhibits unique and opposite behavior. For this species, stronger interaction energy is directly correlated with a greater gain of electrons from the surface. This remarkable trend, with charge difference values reaching  $-2.86$  e on  $\text{Sc@V}_2\text{CO}_2$  and  $-2.37$  e on  $\text{d-Mn-V}_0\text{@V}_2\text{CO}_2$ , suggests a mechanism dominated by electron donation from the surface to the  $\text{Al}_2\text{S}_6$ . This donation likely creates a powerful electrostatic and covalent interaction responsible for the strong binding. Overall, these results indicate that charge transfer, regardless of its direction, is a key electronic origin of the strong adsorption necessary for effective anchoring on the decorated surfaces.

This adsorption and the electronic properties appear to have a direct and measurable impact on the structure of the adsorbed  $\text{S}_8$  and  $\text{Al}_2\text{S}_n$  species. The correlation between the similarity score and adsorption energy, presented in Figure 4.6a reveals a distinct trend: the stronger the adsorption energy, the more the  $\text{S}_8$  and

$\text{Al}_2\text{S}_n$  species' structure is deformed, resulting in a lower similarity score. For example, on the bare surface, the  $\text{S}_8$  molecule has a similarity score of 9.99, indicating it is almost completely undeformed, which is consistent with weak physisorption. However, upon adsorption on the  $\text{SA@V}_2\text{CO}_2$ , the similarity scores for the  $\text{Al}_2\text{S}_n$  species decrease significantly. Furthermore, we can clearly see the separation of each  $\text{S}_8$ ,  $\text{Al}_2\text{S}_6$ ,  $\text{Al}_2\text{S}_3$  species depending on the correlation of  $E_{\text{ads}}$  and similarity value. While  $\text{Al}_2\text{S}_{18}$  and  $\text{Al}_2\text{S}_{12}$  seem difficult to separate from each other since both are the large cluster. These indicate a direct structural consequence of strong anchoring.

Finally, to create a unified picture of the adsorption of  $\text{S}_8$  and  $\text{Al}_2\text{S}_n$  species, we directly correlated the electronic cause with the structural effect. As shown in Figure 4.6b, there is a relationship between the bader charge transfer and the similarity score. For instance, the  $\text{Al}_2\text{S}_3$  species on Ni and Cu catalysts, which exhibit the largest charge loss (2.39 e and 2.40 e), also show the most significant deformation with the lowest similarity scores (6.38 and 6.32, respectively). Conversely, the  $\text{Al}_2\text{S}_6$  species on Sc and Ti, which show the largest charge gain (-2.86 e and -2.61 e), also display considerable deformation with similarity scores of 8.65 and 8.78. This suggests that a large magnitude of charge transfer, regardless of direction, leads to the formation of strong chemical bonds that physically rearrange the structure of the adsorbed  $\text{Al}_2\text{S}_n$  species.



**Figure 4.6** Correlation between the similarity value and the corresponding adsorption energy ( $E_{ads}$ ) and charge difference for  $S_8$  and  $Al_2S_n$  species across all surfaces. The species are color-coded as follows:  $S_8$  (dark purple),  $Al_2S_{18}$  (medium blue),  $Al_2S_{12}$  (light green),  $Al_2S_6$  (yellow-green), and  $Al_2S_3$  (yellow).

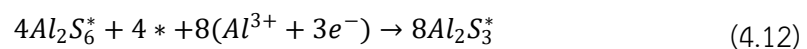
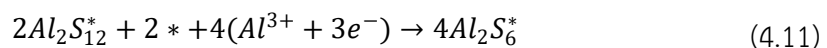
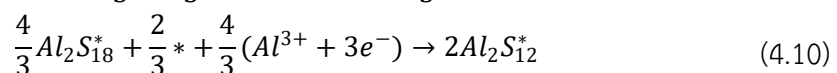
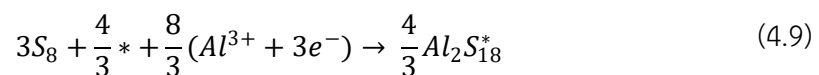
In summary, this analysis suggests a logical narrative for the enhanced anchoring performance of the 3d-TM decorated  $V_2CO_2$  surfaces. The bare suffers from a severe shuttle effect due to the weak adsorption strength. The 3d-TMs decorated systems with SA and DA catalysts show to be highly effective anchors for large, soluble polysulfides (Figure 4.4a). This superior performance seems to be driven by a strong intrinsic interaction (Figure 4.4b), which has a clear electronic origin in the form of significant charge transfer between the catalyst and the polysulfide (Figure 4.5). This adsorption strength comes with an energetic cost in the form of structural distortion, as indicated by the deformation energy analysis and directly causes a quantifiable physical deformation using similarity (Figure 4.6a). The adsorption of

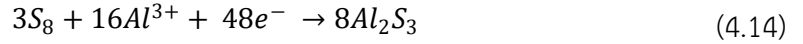
$Al_2S_n$  species tends to correlate charge transfer for several  $Al_2S_n$  species (Figure 4.6b). Next further step is to determine if they can also efficiently catalyze the electrochemical conversion of these  $S_8$  and  $Al_2S_n$  species.

### 4.3 Gibbs free energy profiles of sulfur reduction reactions

The sulfur reduction reaction (SRR) in Al-S batteries plays a crucial role in determining the overall performance and efficiency of the batteries. To better understand the electrochemical behavior of Al-S batteries, we investigated the SRR mechanism by referencing analogous studies in Li-S batteries (L. Wang et al., 2022). In all systems, the catalytic properties of the electrode materials are critical for promoting the conversion of polysulfides during the charge-discharge process. Our previous analysis of adsorption and interaction energy highlighted the significant influence of  $V_2CO_2$  surfaces, especially when modified with SA or DA, on facilitating polysulfide conversions.

The SRR in Al-S batteries involves a sequence of electron-transfer reactions, wherein high orders of  $Al_2S_n$  are reduced stepwise to low order of  $Al_2S_n$  species with  $Al_2S_3$  being the final discharge product. This multistep reduction process can be represented as a series of electron-transfer reactions, analogous to the mechanism in Li-S batteries. Each reaction step is accompanied by Gibbs free energy changes, which play a critical role in determining the overall kinetics and overpotential of the SRR. The mechanism and the overall SRR for Al-S batteries can be expressed through the following reaction steps:





The overpotential for SRR ( $\eta^{SRR}$ ) is derived from the Gibbs free energy changes and the electron transfer involved in each step. The overpotential is calculated using the following expression:

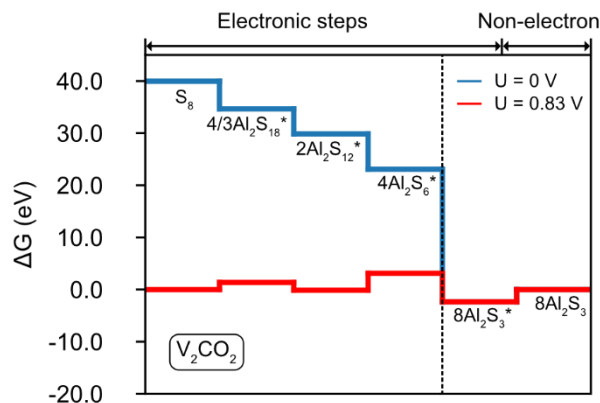
$$\eta^{SRR} = -\max\left(\frac{\Delta G_i}{N_i \cdot e}\right) + U_{eq} \quad (4.15)$$

where  $\Delta G_i$  the Gibbs free energy change associated with step  $i$ ,  $N_i$  is the number of electrons transferred in that step,  $e$  is the elementary charge, and  $U_{eq}$  is the theoretical equilibrium potential. In contrast to Li-S batteries, the theoretical equilibrium potential for SRR in Al-S systems is less straightforward to pinpoint due to the multiple discharge steps. We estimated the equilibrium potential to be approximately 0.83 V, based on this number divided by the standard Gibbs free energy (-39.96 eV) of  $Al_2S_3$  formation, and used this value in our overpotential calculations.

$$\Delta G_f^0 = 8G(Al_2S_3_{bulk})^0 - 3G(S_8_{bulk})^0 - 3G(Al_{atom})^0 \quad (4.16)$$

We computed the Gibbs free energy profiles for SRR including bare, SA@V<sub>2</sub>CO<sub>2</sub>, and DA@V<sub>2</sub>CO<sub>2</sub>. At  $U = 0$  V and  $U = 0.83$  V (equilibrium potential), the Gibbs free energy values for the reduction of  $Al_2S_n$  species are summarized in Table A1.

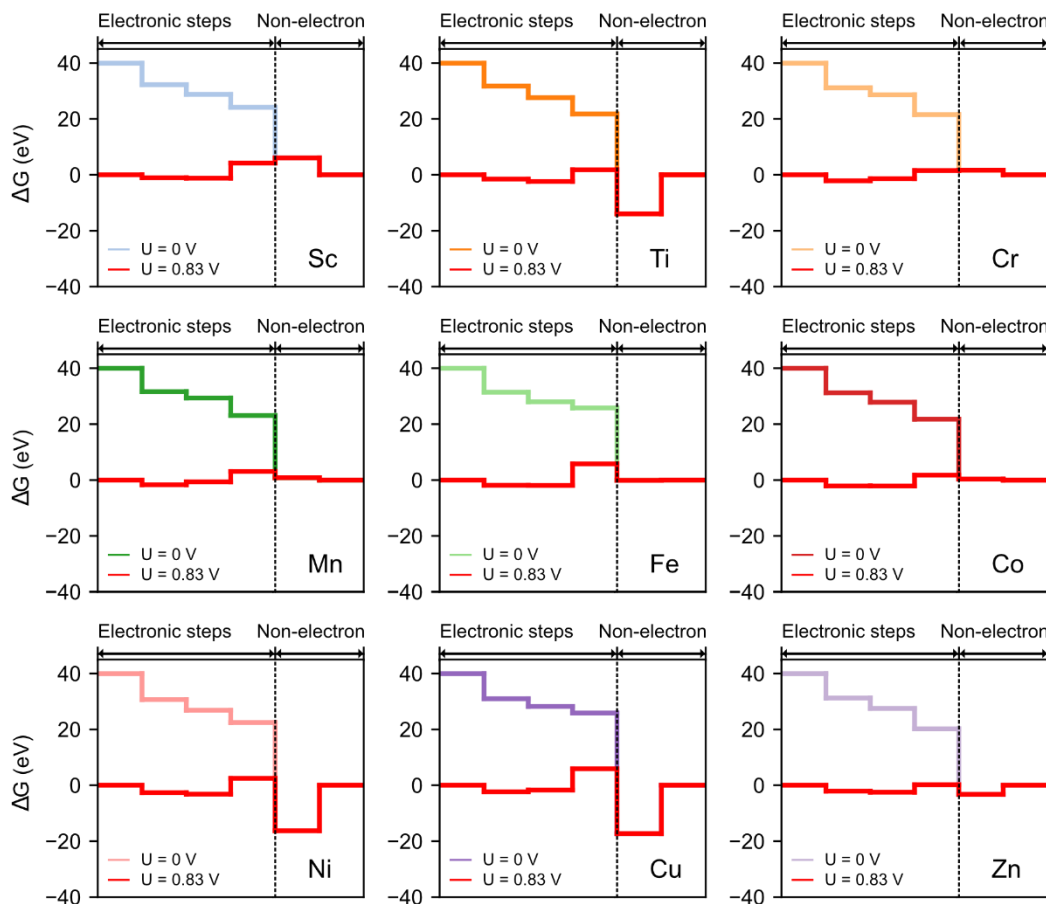
On the bare V<sub>2</sub>CO<sub>2</sub> surface, there are some endothermic steps at equilibrium potential as shown in Figure 4.7. It indicates that the bare surface struggles to convert from the solid  $S_8$  to the liquid  $Al_2S_{18}$  and liquid  $Al_2S_{12}$  to solid  $Al_2S_6$ . Furthermore, the negative Gibbs free energy for the non-electron step (-2.35 eV) is thermodynamically unfavorable while the overall SRR is thermodynamically favorable. The non-electron step, which is the  $Al_2S_3$  desorption, faces significant energy barriers that slow down the overall reaction kinetics.



**Figure 4.7** Sulfur reduction reaction (SRR) performance of the bare  $V_2CO_2$ . Gibbs free energy diagram of SRR for  $V_2CO_2$ . at  $U = 0$  V and equilibrium potential ( $U = 0.83$  V).

When SA are introduced on the  $V_2CO_2$  surface, we observed notable improvements in SRR process in Figure 4.8. The conversion from the solid  $S_8$  to the liquid  $Al_2S_{18}$  becomes more thermodynamically stable. Some SAs reduce the thermodynamic barriers associated with the conversion from the liquid  $Al_2S_{12}$  to the solid  $Al_2S_6$  and promote the  $Al_2S_3$  desorption. For example, in  $Cr@V_2CO_2$ , the liquid  $Al_2S_{18}$  to the solid  $Al_2S_6$  has lower thermodynamic barrier (2.91 eV) compared to the bare (3.24 eV). While the  $Al_2S_3$  desorption is thermodynamically favorable.

For the  $Sc@V_2CO_2$ , the Gibbs free energy for the conversion from the solid  $S_8$  to the liquid  $Al_2S_{18}$  decreases to -1.21 eV. However, the conversion from liquid  $Al_2S_{12}$  to solid  $Al_2S_6$  remains thermodynamically unfavorable. In the  $Sc@V_2CO_2$ , the Gibbs free energy for from liquid  $Al_2S_{12}$  to solid  $Al_2S_6$  is reduced to 4.17 eV. The  $Al_2S_3$  desorption, however, shows a positive Gibbs free energy (6.03 eV), which could hinder the complete SRR of sulfur species at the equilibrium potential. The  $Ti@V_2CO_2$  also shows reduced energy barriers, with a Gibbs free energy of -2.38 eV for  $Al_2S_{12}$  and 1.78 eV for  $Al_2S_6$ , indicating better catalytic activity than the bare surface.



**Figure 4.8** SRR performance of 3d-TMs as SA@V<sub>2</sub>CO<sub>2</sub>. Gibbs free energy diagram of the sulfur reduction reaction (SRR) for SA@V<sub>2</sub>CO<sub>2</sub> at U = 0 V and at the equilibrium potential (U = 0.83 V). The diagram illustrates the energy profiles and highlights the impact of different 3d-transition metals on SRR performance.

Our results show that DA@V<sub>2</sub>CO<sub>2</sub> significantly improved the conversion of S<sub>8</sub> and higher order of Al<sub>2</sub>S<sub>n</sub> compared the bare and SA systems. For instance, in the d-Cr-no@V<sub>2</sub>CO<sub>2</sub>, the Gibbs free energy for the conversion from solid S<sub>8</sub> to liquid Al<sub>2</sub>S<sub>18</sub> is reduced to -4.36 eV, while for liquid Al<sub>2</sub>S<sub>12</sub> to solid Al<sub>2</sub>S<sub>6</sub> is -14.67 eV, indicating a highly favorable reaction shown in Figure 4.9. Similarly, in the d-Mn-vo@V<sub>2</sub>CO<sub>2</sub>, the conversion from solid S<sub>8</sub> to liquid Al<sub>2</sub>S<sub>18</sub> and liquid Al<sub>2</sub>S<sub>12</sub> to solid Al<sub>2</sub>S<sub>6</sub> are -5.15 eV and -12.67 eV, respectively. These results demonstrate that DA systems offer superior performance in promoting the electronic steps during the SRR process.

Despite their excellent performance in polysulfide conversion, DA@V<sub>2</sub>CO<sub>2</sub> encounter significant challenges in the Al<sub>2</sub>S<sub>3</sub> desorption. The Gibbs free energy for

$\text{Al}_2\text{S}_3$  desorption in DA systems is highly negative, such as -26.12 eV in the d-Mn-vo@ $\text{V}_2\text{CO}_2$ , suggesting that  $\text{Al}_2\text{S}_3$  is too strongly adsorbed to the DA-modified surface. Furthermore, the  $\text{V}_\text{O}$  in DA systems including d-Cr- $\text{V}_\text{O}$  and d-Mn- $\text{V}_\text{O}$  provide stronger adsorption strength compared to non-vacancy systems. This excessive adsorption strength leads to thermodynamically unfavorable desorption, which can hinder the overall reversibility of the battery.

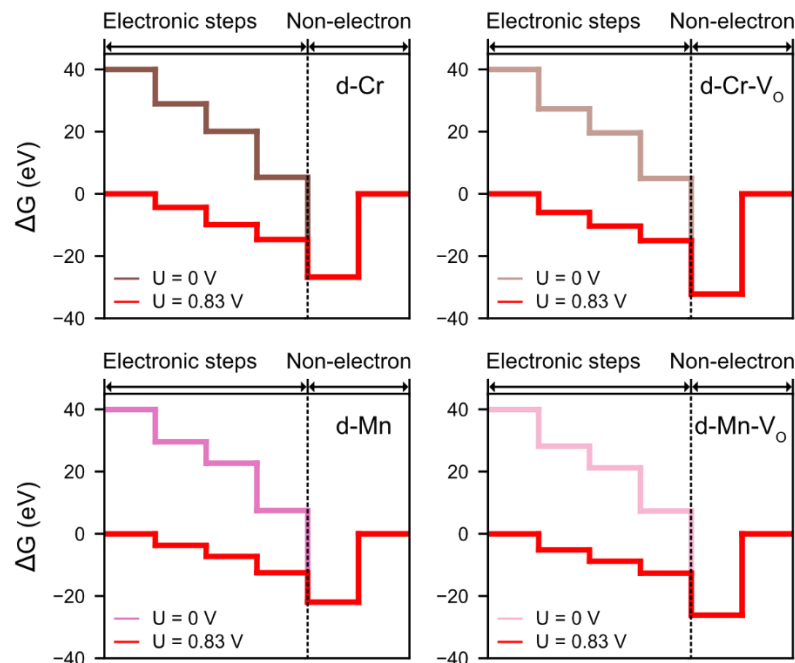
Our similarity analysis and deformation energy calculations indicate significant structural changes in the adsorbed  $\text{Al}_2\text{S}_3$  species, exacerbating the desorption issue. The distortion arises from the strong interaction between  $\text{Al}_2\text{S}_3$  and the dual active sites provided by the DA catalysts, which stabilizes the polysulfides but hinders the desorption of the final sulfur product.

In contrast, the SA@ $\text{V}_2\text{CO}_2$  and the bare  $\text{V}_2\text{CO}_2$  surface do not perform as well in the conversion of higher orders of  $\text{Al}_2\text{S}_n$ . However, these systems show more favorable desorption for  $\text{Al}_2\text{S}_3$ . This implies to the weaker adsorption strength in SA and bare systems allows for easier desorption of  $\text{Al}_2\text{S}_3$ .

We also considered the limiting potential and overpotential, following the methodology used for ORR and other metal–sulfur batteries. Despite improvements in the phase transition steps for SA systems, we observed high overpotentials in several cases, as shown in Figure 4.10a. This finding suggests that the conversion of liquid  $\text{Al}_2\text{S}_{12}$  to solid  $\text{Al}_2\text{S}_6$  is the critical step for evaluating catalytic performance. In contrast, DA systems display the highest limiting potential.

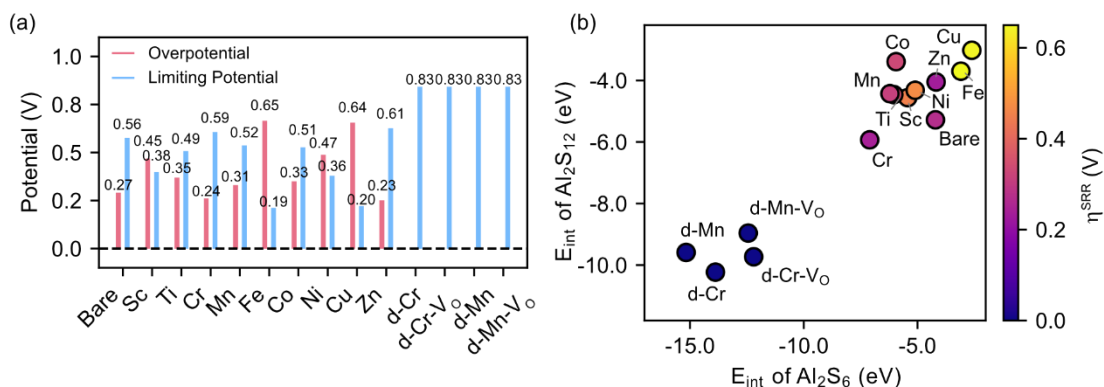
Recognizing the importance of the liquid  $\text{Al}_2\text{S}_{12}$  to solid  $\text{Al}_2\text{S}_6$  transition, we further investigated the stronger interactions lead to better SRR catalytic performance, as these species act as bridges for the liquid–solid transition during SRR. Our findings emphasize the importance of the relationship between the adsorption strength of  $\text{Al}_2\text{S}_n$  ( $n = 12$  and  $6$ ) species and the SRR overpotential. Our results show a linear correlation between the interaction energy of  $\text{Al}_2\text{S}_{12}/\text{Al}_2\text{S}_6$  and the SRR overpotential, as illustrated in Figure 4.10b. Clearly accelerating the conversion from liquid  $\text{Al}_2\text{S}_{12}$  to solid  $\text{Al}_2\text{S}_6$  throughout the entire reaction process. Overall, our study reveals the dominant role of  $\text{Al}_2\text{S}_6$  adsorption strength in determining SRR catalytic

performance, providing theoretical guidance for the rapid screening of efficient SRR catalysts.



**Figure 4.9** SRR performance of 3d-TMs as DA@V<sub>2</sub>CO<sub>2</sub> surfaces. Gibbs free energy diagram of the sulfur SRR for DA@V<sub>2</sub>CO<sub>2</sub> at U = 0 V and at the equilibrium potential (U = 0.83 V).

In summary, this analysis suggests that the bare surface struggles to convert from the solid S<sub>8</sub> to the liquid Al<sub>2</sub>S<sub>18</sub> and from liquid Al<sub>2</sub>S<sub>12</sub> to solid Al<sub>2</sub>S<sub>6</sub>, and is thermodynamically unfavorable for Al<sub>2</sub>S<sub>3</sub> desorption. The 3d-TM decorated systems with SAs show improvement in the S<sub>8</sub> to liquid Al<sub>2</sub>S<sub>18</sub> step due to the stronger adsorption strength for Al<sub>2</sub>S<sub>18</sub>. However, we find that SAs still struggle to convert liquid Al<sub>2</sub>S<sub>12</sub> to solid Al<sub>2</sub>S<sub>6</sub>, despite thermodynamically favorable Al<sub>2</sub>S<sub>3</sub> desorption. Among SA@V<sub>2</sub>CO<sub>2</sub>, only Cr@V<sub>2</sub>CO<sub>2</sub> shows a lower overpotential than that of the bare surface. In the case of DAs, there are no energy barriers for electronic steps, indicating no overpotential. Unfortunately, DAs face a critical challenge in Al<sub>2</sub>S<sub>3</sub> desorption. Thus, we need to further investigate the decomposition of Al<sub>2</sub>S<sub>3</sub>, since this is an important step for the reversible process of Al-S batteries.



**Figure 4.10** (a) A comparison of the calculated limiting potential and overpotential ( $\eta^{SRR}$ ) across all catalyst systems. (b) The relationship between the interaction energy ( $E_{int}$ ) of  $Al_2S_{12}$  and  $Al_2S_6$  and the calculated  $\eta^{SRR}$  on the bare, SA, and DA systems.

#### 4.4 Decomposition of $Al_2S_3$

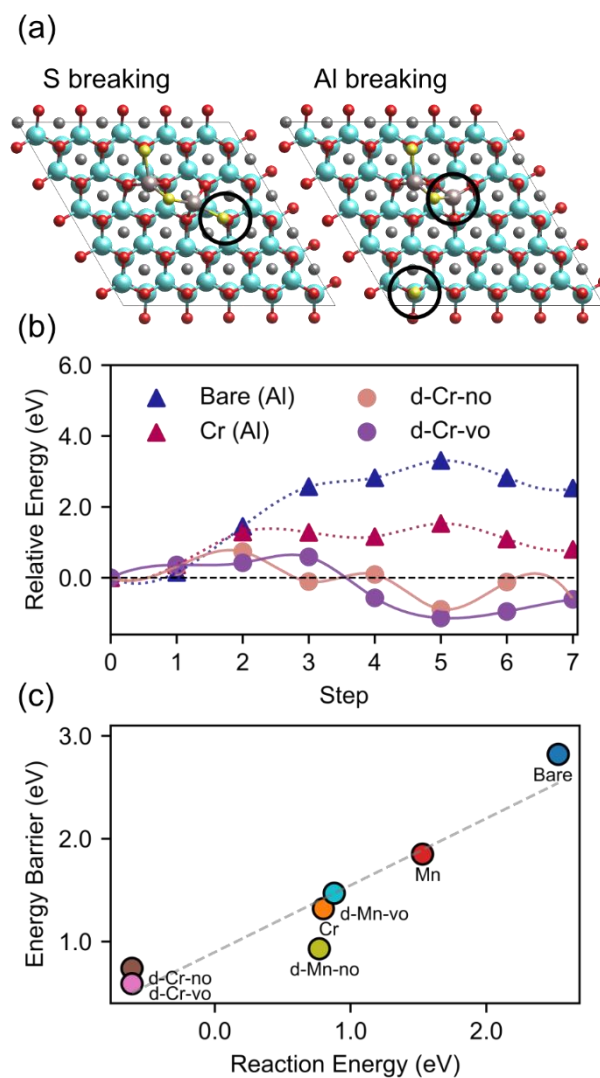
The decomposition of  $Al_2S_3$  is a crucial step in the SRR and the overall charge-discharge process of Al-S batteries. Effective decomposition ensures the battery's reversibility and directly affects the stability and efficiency of the electrochemical cycle. In this study, we investigated the breaking of S and Al atoms (only Al for DA systems), as the decomposition of  $Al_2S_3$  requires the cleavage of both elements. This process begins with the dissociation of the S atom from  $Al_2S_3$ . Subsequently, the remaining Al atom is released from  $Al_2S_2$  once the S atom has fully dissociated, as illustrated in Figure 4.11a.

The all-decomposition pathway of  $Al_2S_3$  is presented in Figure A9. We found that S breaking in  $Al_2S_3$  occurs rapidly, making it difficult to identify a transition state due to the swift nature of the reaction pathway. On  $V_2CO_2$ , the decomposition of  $Al_2S_3$  is endothermic, with a high energy barrier indicating that both Al and S atoms struggle to dissociate from  $Al_2S_3$ . In Figure 4.11b, we found that Al breaking is a less favorable step than S breaking. For SA systems, we focused on Cr and Mn, as these single atoms exhibited the best SRR performance.

The introduction of Cr and Mn significantly enhances the decomposition process of  $Al_2S_3$ . The presence of SAs lowers the energy barrier for Al breaking, even

though the barrier for S breaking in Mn and Cr is slightly higher than that of the bare surface. For DA systems, both Cr and Mn significantly enhance the decomposition of  $\text{Al}_2\text{S}_3$ , with the most favorable reaction pathways observed in d-Cr-no and d-Cr-vo. We also observed Brønsted-Evans-Polanyi (BEP) relation between the reaction energy and the energy barrier, as shown in Figure 4.11c. Notably, Cr demonstrates impressive performance in both SA and DA systems.

We also analyzed the Integrated Crystal Orbital Hamilton Population (ICOHP) values of key bonds involved in the  $\text{Al}_2\text{S}_3$  decomposition pathway in Figure A10. ICOHP provides a quantitative measure of bonding interactions, where more negative values indicate stronger bonds. We found out that the quantitative measure cannot directly examine the key bonds in the decomposition of  $\text{Al}_2\text{S}_3$  since the complexity of optimized  $\text{Al}_2\text{S}_3$  configuration on the different systems.



**Figure 4.11** The decomposition of  $\text{Al}_2\text{S}_3$  on bare,  $\text{Cr@V}_2\text{CO}_2$ , and Mn and Cr- $\text{@V}_2\text{CO}_2$  with and without  $\text{V}_\text{O}$ . (a) Schematic of S breaking and Al breaking. (b) The relative corresponding of energy with the decomposition step of  $\text{Al}_2\text{S}_3$  in each system. (c) The correlation between energy barrier and reaction energy.

## 4.5 References

- Andritsos, E. I., Lekakou, C., & Cai, Q. (2021). Single-Atom Catalysts as Promising Cathode Materials for Lithium–Sulfur Batteries. *The Journal of Physical Chemistry C*, 125(33), 18108–18118.
- Bhauriyal, P., & Pathak, B. (2020). Superior anchoring effect of a Cu-benzenehexathial MOF as an aluminium–sulfur battery cathode host. *Materials Advances*, 1(9), 3572–3581.
- Chen, Y.-H., Qi, M.-Y., Li, Y.-H., Tang, Z.-R., Wang, T., Gong, J., & Xu, Y.-J. (2021). Activating two-dimensional  $\text{Ti}_3\text{C}_2\text{T}_x$ -MXene with single-atom cobalt for efficient  $\text{CO}_2$  photoreduction. *Cell Reports Physical Science*, 2(3), 100371.
- Gao, P., Song, M., Wang, X., Liu, Q., He, S., Su, Y., & Qian, P. (2022). Theoretical Study on the Electronic Structure and Magnetic Properties Regulation of Janus Structure of  $\text{M}'\text{MCO}_2$  2D MXenes. *Nanomaterials*, 12(3).
- Gu, J., Zhu, Q., Shi, Y., Chen, H., Zhang, D., Du, Z., & Yang, S. (2020). Single Zinc Atoms Immobilized on MXene ( $\text{Ti}_3\text{C}_2\text{Cl}_x$ ) Layers toward Dendrite-Free Lithium Metal Anodes. *ACS Nano*, 14(1), 891–898.
- Ju, S., Yuan, C., Zheng, J., Yao, L., Zhang, T., Xia, G., & Yu, X. (2022). Identifying single-atom catalysts for boosted Al–S conversion reactions. *Energy Storage Materials*, 52, 524–533.
- Singsen, S., Fongkaew, I., Hirunsit, P., & Suthirakun, S. (2022). Suppressing Polysulfides Shuttling and Promoting Sulfur Utilization via Transition Metal and Nitrogen Co-Doping on Graphdiyne Cathodes of Lithium-Sulfur Batteries: A First-Principles Modeling. *ACS Applied Energy Materials*, 5(8), 9722–9732.
- Wang, L., Hu, Z., Wan, X., Hua, W., Li, H., Yang, Q. H., & Wang, W. (2022).  $\text{Li}_2\text{S}_4$  Anchoring Governs the Catalytic Sulfur Reduction on Defective  $\text{SmMn}_2\text{O}_5$  in Lithium–Sulfur Battery. *Advanced Energy Materials*, 12(20).
- Wang, Z., Zheng, X., Chen, A., Han, Y., Wei, L., & Li, J. (2022). Unraveling the Anchoring Effect of MXene-Supported Single Atoms as Cathodes for Aluminum–Sulfur Batteries. *ACS Materials Letters*, 4(8), 1436–1445.

- Yang, X.-F., Wang, A., Qiao, B., Li, J., Liu, J., & Zhang, T. (2013). Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis. *Accounts of Chemical Research*, 46(8), 1740–1748.
- Zheng, X., Wang, Z., Li, J., & Wei, L. (2022). Binder-free S@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> sandwich structure film as a high-capacity cathode for a stable aluminum-sulfur battery. *Science China Materials*, 65(6), 1463–1475.
- Zou, F., Cong, Y., Song, W., Liu, H., Li, Y., Zhu, Y., Zhao, Y., Pan, Y., & Li, Q. (2024). Interfacial Properties of Anisotropic Monolayer SiAs Transistors. *Nanomaterials*, 14(3).