

CHAPTER I

INTRODUCTION

Renewable energy, which comes from natural sources that can be replenished, such as solar, wind, hydro, geothermal, and biomass, is seen as a viable alternative for achieving development of sustainable society. Rechargeable battery technology has become a key research area in recent decades, as it enables the storage and utilization of sustainable energy sources. Presently, Li-ion batteries are used in various applications from portable electronics to electric vehicles. Nevertheless, Li-ion batteries have limitations in terms of the theoretical specific capacities and energy density ($387 \text{ Wh}\cdot\text{kg}^{-1}$, $155 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$) (Chen et al., 2021; Van der Ven et al., 2020).

Battery technologies include solid-state batteries, which offer enhanced safety and energy density, and sodium-ion batteries, noted for their abundance and cost-effectiveness. Among these, metal-sulfur batteries, such as lithium-sulfur (Li-S), sodium-sulfur (Na-S), and aluminum-sulfur (Al-S), stand out for their exceptionally high theoretical capacities and potential for low-cost manufacturing, given the global abundance of sulfur (Klimpel et al., 2022; Liu et al., 2021).

In particular, Al-S batteries have attracted attention because of the high abundance of Al in the earth's crust as well as aluminum's high theoretical gravimetric ($2980 \text{ mAh}\cdot\text{g}^{-1}$) and volumetric ($8046 \text{ mAh}\cdot\text{cm}^{-3}$) capacities. Furthermore, sulfur ($1675 \text{ mAh}\cdot\text{g}^{-1}$) as the cathode material offers environmentally friendly and inexpensive (Akgenc et al., 2021; Klimpel et al., 2022; Smajic et al., 2020).

An Al-S battery typically consists of an aluminum metal anode, a sulfur-based cathode, and an ionic liquid electrolyte, such as a mixture of aluminum chloride

(AlCl_3) and 1-ethyl-3-methylimidazolium chloride (EMIM) (Appiah et al., 2022; Gao et al., 2016; Xia et al., 2015). This electrolyte is crucial for enabling the electrochemical reaction while managing the interaction of Al^{3+} ions with host materials (Yang et al., 2018).

Despite this promising potential, the practical application of high-performance Al-S batteries is hindered by several critical challenges that impede performance and cyclability (Bhauriyal et al., 2020; Klimpel et al., 2022; Tu et al., 2021; F. Wang et al., 2020). Three major issues must be addressed: (1) The "shuttle effect," where soluble intermediate aluminum-polysulfides (Al_2S_n , such as Al_2S_{18} , Al_2S_{12} , Al_2S_6 , and Al_2S_3) diffuse from the cathode to the anode. This continuous loss of active material results in poor coulombic efficiency and rapid capacity fading. (2) Sluggish reaction: The multi-step Sulfur Reduction Reaction (SRR) involves complex electrochemical conversions with high energy barriers. These barriers restrict the battery's rate capability, leading to low power density. (3) Difficult conversion of Al_2S_3 , as the complete reduction to final, insulating discharge products and their re-oxidation are often incomplete. These insulating products can passivate the electrode surface, blocking active sites and leading to poor reversibility.

Designing suitable hosts for sulfur to address these issues has been the focus of many experimental studies. Early cathodes based on porous carbons like Ketjen black demonstrated high initial specific capacities (over $1400 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$) but suffered by the rapid dissolution of discharged products, highlighting the need for functional hosts, not just physical confinement (Cohn et al., 2015). Performance improved with the introduction of 2D materials; for instance, a 2D-BN nanosheet composite retained over $300 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 250 cycles (Zhang et al., 2019). More recently, functionalized MXenes (e.g., $\text{S}@ \text{Ti}_3\text{C}_2\text{O}_2$) and single-atom catalysts (e.g., Fe-SAs-NCF) have shown improved stability and polysulfide retention, demonstrating the potential of engineering materials with specific catalytic and anchoring properties (Luo et al., 2023; Zheng et al., 2022).

Alongside experimental work, computational studies based on Density Functional Theory (DFT) have been employed to screen suitable anchoring materials and calculate SRR energy barriers. However, current computational efforts are limited.

Most studies rely on strategies from the more established Li-S batteries field, often overlooking the properties of aluminum species, such as their larger ionic radii and complex solvation behavior. While specific studies have identified promising hosts, such as Cu-benzenehexathial (Cu-BHT) MOFs (Bhauriyal & Pathak, 2020) and single-atom supported $\text{Ti}_3\text{C}_2\text{O}_2$ MXene (Z. Wang et al., 2022). The field remains underexplored. There is a critical need for systematic investigations into transition metal catalysts and host materials tailored specifically for the unique chemistry of Al-S batteries

To address these challenges, our strategy focuses on O-functionalized vanadium carbide MXene (V_2CO_2). First-principles calculations in Li-S systems indicated that V_2CO_2 binds polysulfides very strongly (Zhu et al., 2023). While such strong binding can be an obstacle in Li-S systems by impeding the decomposition and further reaction of smaller polysulfides, we hypothesize this same characteristic is exceptionally promising for Al-S batteries. The high orders of Al_2S_n species are expected to likely require stronger adsorption strength for effective immobilization. However, because strong anchoring can restrict SRR. Therefore, we further propose a 3d-transition metal decorated design: the V_2CO_2 substrate will provide the powerful anchoring required to trap Al_2S_n species, while 3d-transition metal anchored to its surface will function as distinct catalytic centers to accelerate the sluggish sulfur reduction reaction. This design aims to create a host that actively manages the electrochemical conversion pathway, rather than just passively containing sulfur.

This study utilizes first-principles study to evaluate 3d-TMs decorated V_2CO_2 MXenes as cathode hosts for Al-S batteries. We examined the adsorption of S_8 and various Al_2S_n species then constructed free energy diagram for the sulfur reduction reaction, and the decomposition of Al_2S_3 . Specifically, we investigated the material's ability to suppress the shuttle effect through anchoring while simultaneously catalyzing the conversion of Al_2S_3 . This systematic evaluation provides guidelines for the rational design of high-performance cathode materials tailored to the Al-S system.

1.1 Research objectives

The first-principles calculations are carried out to systematically investigate 3d-transition metals decorated on V_2CO_2 cathodes as anchoring materials for Al-S batteries. This study examines the structural and electronic properties of various single atom (SA) and dual atom (DA) configurations to evaluate their stability and effectiveness. Special emphasis is placed on understanding these following objectives:

(1) To evaluate the material's efficiency in suppressing the shuttle effect. This will be achieved by systematically calculating the adsorption strength of key Al_2S_n on the V_2CO_2 , the SA and DA systems, thereby quantifying the anchoring strength of the host material.

(2) To investigate the catalytic enhancement of the Sulfur Reduction Reaction (SRR) kinetics. This involves constructing the Gibbs free energy profiles for the multi-step sulfur reduction pathway on the surfaces. This analysis will identify the rate-determining steps and quantify the energy barriers, providing a direct measure of the material's ability to overcome the sluggish kinetics inherent to the SRR.

(3) To assess the material's ability to promote the complete conversion of polysulfides and enhance reversibility. This objective focuses on analyzing the energy barriers for the decomposition of the final, insulating discharge product (Al_2S_3), a critical step for re-oxidation during charging. This will elucidate the material's potential to mitigate electrode passivation and the difficult conversion of low-order polysulfides.

1.2 Scope and limitation of the study

The scope of this study is focused on a systematic first principles investigation of single 3d-transition metal atoms decorated on V_2CO_2 MXenes as potential cathode host materials for Al-S batteries, employing spin-polarized Density Functional Theory (DFT) (Kohn & Sham, 1965) as implemented in the Vienna ab initio Simulation Package (VASP 6.3). The methodology uses the projector augmented wave (PAW) method for electron-ion interactions and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional (Blöchl, 1994; Kresse & Joubert, 1999; Perdew et al., 1996). Weak van der Waals interactions, critical for the adsorption of S_8 and Al_2S_n species, are accounted for using the Grimme DFT-D3 correction (Grimme et al., 2010,

2011). A plane-wave cutoff energy of 500 eV is used, with structural optimizations converged until the total energy difference is within 10^{-6} eV and all residual forces are below 0.02 eV/Å. The Brillouin zone is sampled using a 3x3x1 Monkhorst-Pack k-point mesh for structural relaxations and a denser 5x5x1 grid for static energy calculations, with a 20 Å vacuum applied in the z-direction (Monkhorst & Pack, 1976). The investigation includes screening 3d-transition metal (Sc-Zn except V), considering their valence electrons (V 3d4s, C 2s2p, O 2s2p, Al 3s3p, S 3s3p). The study first determines the most stable SA@V₂CO₂ structures, then systematically investigates the adsorption behaviors of Al₂S_n species and SRR. Then, selected the candidate 3d-TM atoms for DA@V₂CO₂. Finally, the energy barriers for Al₂S₃ decomposition on the most promising candidates are simulated using the climbing-image nudged elastic band (CI-NEB) method (Smidstrup et al., 2014).

This theoretical study has several inherent limitations: the GGA-PBE functional is an approximation; the calculations are performed in an idealized vacuum, neglecting the explicit, complex role of the AlCl₃-EMIM ionic liquid electrolyte, solvation effects, and the electrochemical double layer; the 0 K ground-state calculations do not capture full dynamic and thermal effects; and the supercell models represent an idealized, low concentration of single atoms and adsorbates. The scope is therefore focused on elucidating intrinsic material properties and catalytic mechanisms, providing a foundational screening for experimental design rather than a quantitative prediction of full-cell device performance.

1.3 References

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