

CHAPTER V

CONCLUSIONS

In this study, we employed first-principles DFT calculations to systematically investigate the potential of 3d-transition metal atoms, as both SA and DA, decorated on V_2CO_2 as cathode materials for Al-S batteries. Our findings demonstrate that modifying the V_2CO_2 surface with these atomic catalysts is a crucial and highly effective strategy for addressing the critical challenges that hinder Al-S battery performance, including the shuttle effect, sluggish sulfur reduction reaction (SRR), and the decomposition of Al_2S_3 .

Our analysis of adsorption strength reveals a clear performance for anchoring the soluble, high-order Al_2S_n species: Bare $V_2CO_2 < SA@V_2CO_2 < DA@V_2CO_2$. The bare surface exhibits only weak adsorption strength for Al_2S_{18} , which is insufficient to prevent polysulfide dissolution into the electrolyte. In contrast, the DA systems with V_O like d-Cr-vo@ V_2CO_2 , show strong adsorption strength. We observed that strong interaction is accompanied by a high energetic penalty. This interaction is governed by significant charge transfer, as quantified by Bader analysis, and results in structural deformation of the Al_2S_n species, confirmed by low similarity scores.

Furthermore, the Gibbs free energy profiles for the SRR show that DA systems show a better catalytic performance. The bare surface and most SA systems suffer from high overpotentials because the critical liquid-to-solid transition ($Al_2S_{12} \rightarrow Al_2S_6$) is thermodynamically challenging. We identified a strong linear correlation across all systems: catalysts with stronger interaction energies for Al_2S_{12} and Al_2S_6 relate with lower SRR overpotentials, suggesting strong adsorption is key to catalysis.

However, this adsorption strength in DA systems presents a critical trade-off for Al_2S_3 desorption. However, CI-NEB analysis of the Al_2S_3 decomposition shows that DA systems like d-Cr- $V_O@V_2CO_2$ significantly lower the energy barrier for the cleavage of Al-S bonds. The results show BEP relation between reaction energy and barriers. This

suggests DA system is highly effective at decomposing Al_2S_3 , which is the important step for the reversibility process.

In summary, $\text{d-Cr@V}_2\text{CO}_2$ and $\text{d-Cr-V}_\text{O}@\text{V}_2\text{CO}_2$, are identified as the most promising candidates, solving both the shuttle effect via strong anchoring and the sluggish via superior catalysis. The primary remaining challenge is balancing this high activity with the need for efficient product desorption to ensure long-term reversibility