On an Alternative Active Site for VO_2^+ Adsorption on Graphene-based Electrodes

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Introduction

The vanadium redox flow battery (VRFB) is a low-cost energy storage solution on a grid-scale level. The VRFB consists of large electrolyte tanks and carbon-based electrodes to convert V(III) to V(II) at the negative electrode, while the sluggish positive electrode converts V(V) to V(IV) during the charging process (Figure 1)[1]. A fundamental understanding of the electron transfer mechanisms may lead to improved catalytic functionality of the carbon electrodes if we succeed in identifying the sites where the reduction of VO_2^+ to VO^{2+} occurs.

$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

$V^{3+} + e^- \rightarrow V^{2+}$
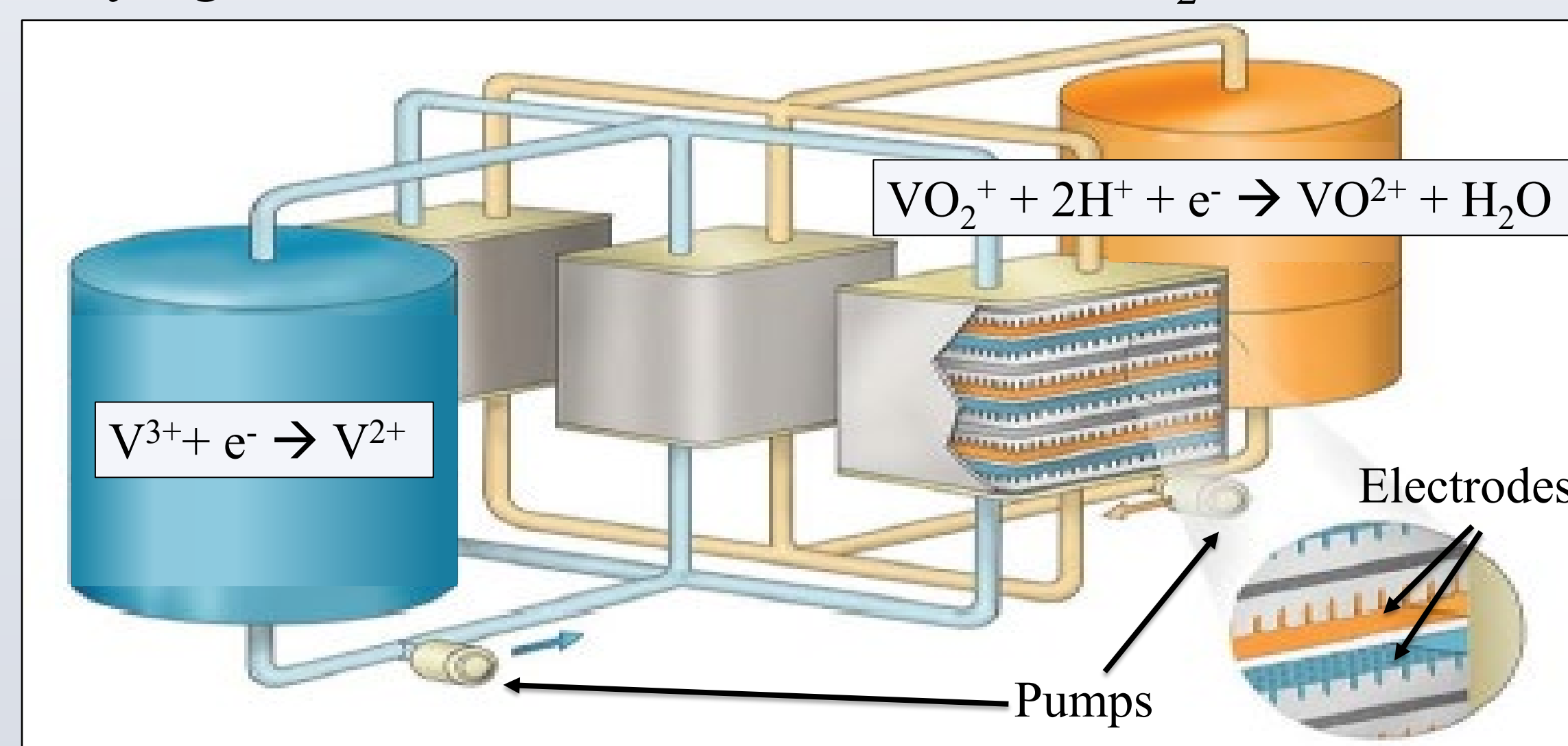
Electrodes

Pumps

Figure 1. Schematic of a traditional Vanadium Redox Flow Battery.

Density functional theory (DFT) is a quantum mechanical computational technique that applies Schrodinger's equation to allow an understanding of the electronic structure, in this case, of graphene-based electrodes and its interaction with VO_2^+ [2] By investigating the popular literature proposed –OH active site, DFT allows a theoretical view of this active site's interaction with VO_2^+ [3]. This study also aims to identify a new active site, such as the edge carbon active site (Figure 2).
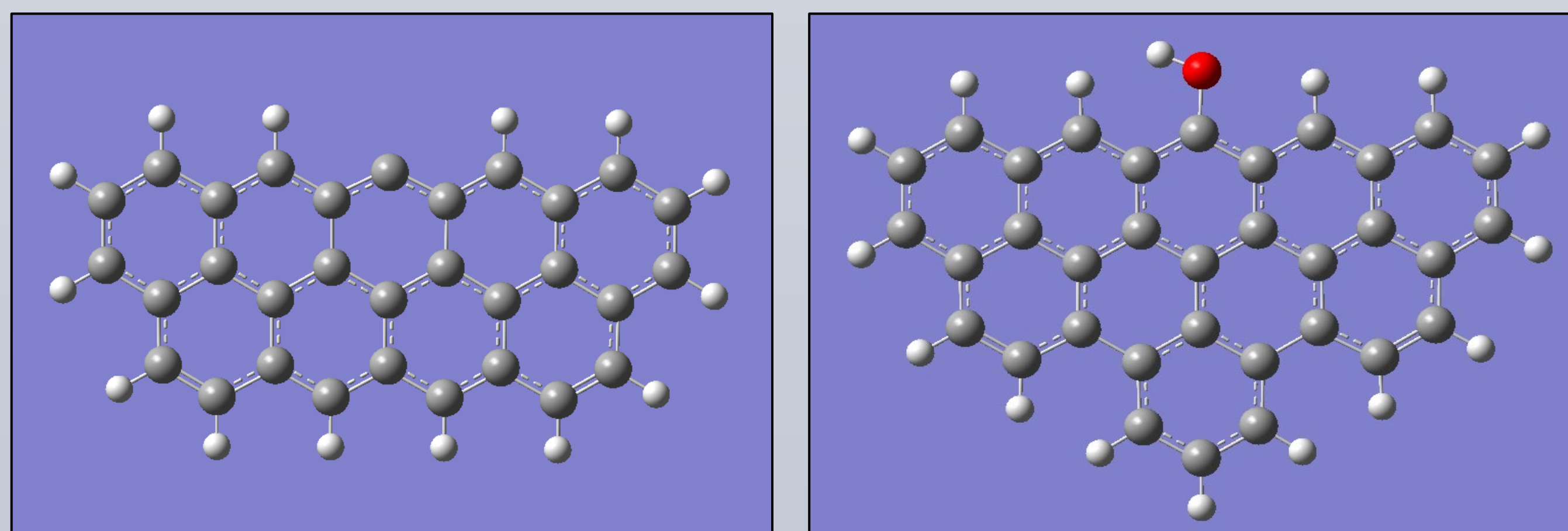

Figure 2. Representative graphene clusters with edge carbon active site and hydroxyl active site.

Objectives

☐ Investigate using density functional theory (DFT) the plausibility of the positive electrode reaction at a hydroxyl active site, as proposed in the dominant literature.

☐ Compare vanadium-down vs. oxygen-down adsorption to the edge carbon active site to determine their thermodynamic and kinetic feasibility.

☐ Identify the pathways of the critical mechanistic steps by finding transition states for VO_2^+ adsorption.

Methodology

The GaussView software was used generate the initial structures with OH and edge carbon active sites. Gaussian is the quantum chemistry software used to optimize the geometries and complete the vibrational frequency calculations at the B3LYP/6-31G(d) level of theory. By analyzing the approach of VO_2^+ to the proposed active sites, the distance between atoms is monitored to determine if electro(chemical) interaction is likely to occur or not. The Gibbs energy of the relevant transitions are evaluated to determine the outcomes with given combinations of charge (C) and spin multiplicity (M).
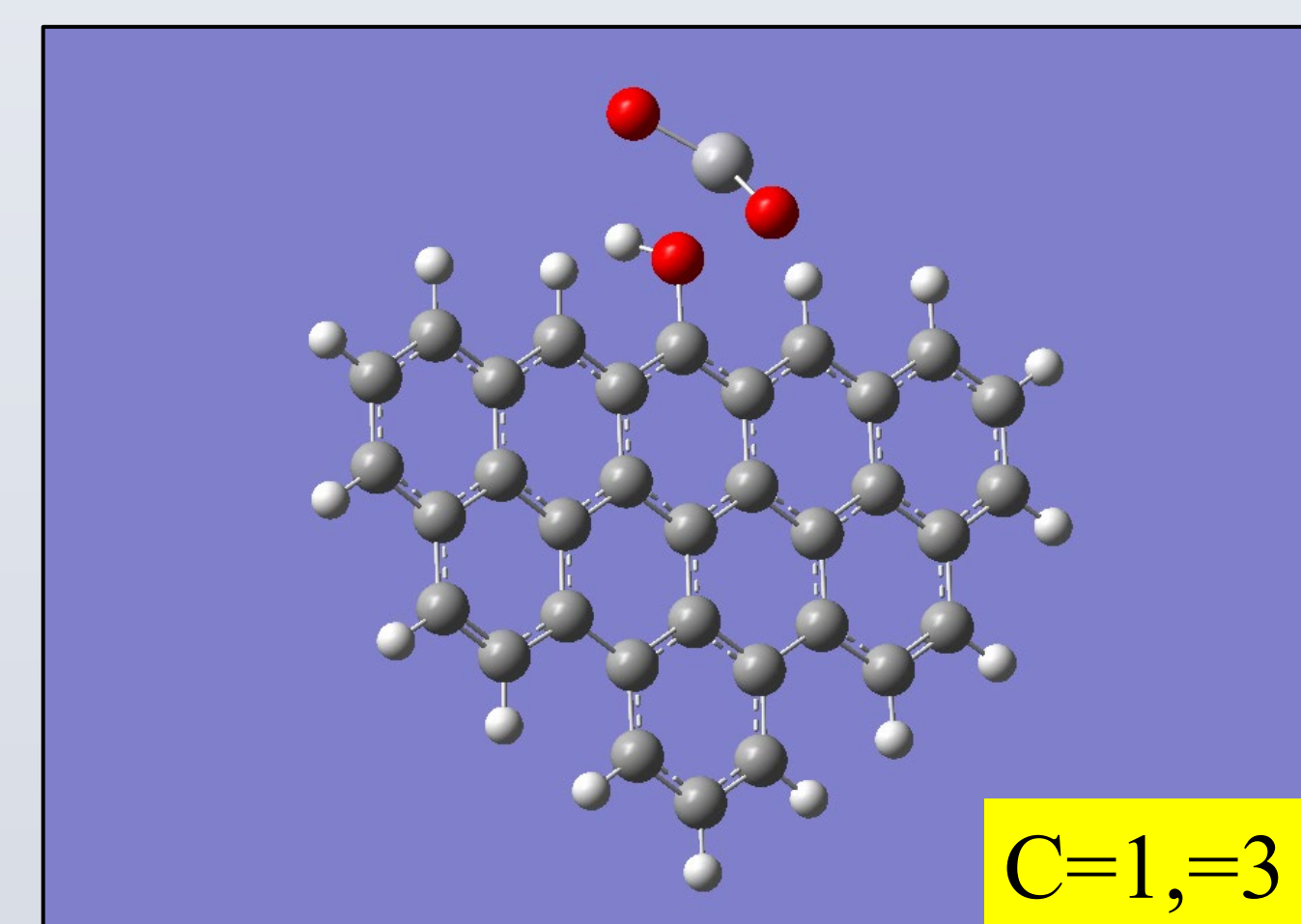
Results

C=1,=3

Figure 3. VO_2^+ interaction with hydroxyl active site.

VO_2^+ did not adsorb to the –OH active site, in contrast to what has been suggested in the literature (Figure 3). The distance between the O atom from the –OH group and the V atom from VO_2^+ is 0.211 nm. Gaussian lacks a visual bond between O and V suggesting the interaction is unlikely.

The edge carbon active site successfully adsorbed VO_2^+ as either V-down or O-down. While both are possible, the distance between the edge C and V in the V-down approach is 0.207 nm (rather large and unfavorable), while the O-down approach distance between the edge carbon and oxygen is 0.127 nm. A transition state has been identified with imaginary frequency of i242 cm^{-1} showing a rotation from V-down to the favorable O-down adsorption.

ΔG = +24 kcal/mol   ΔG = -58 kcal/mol

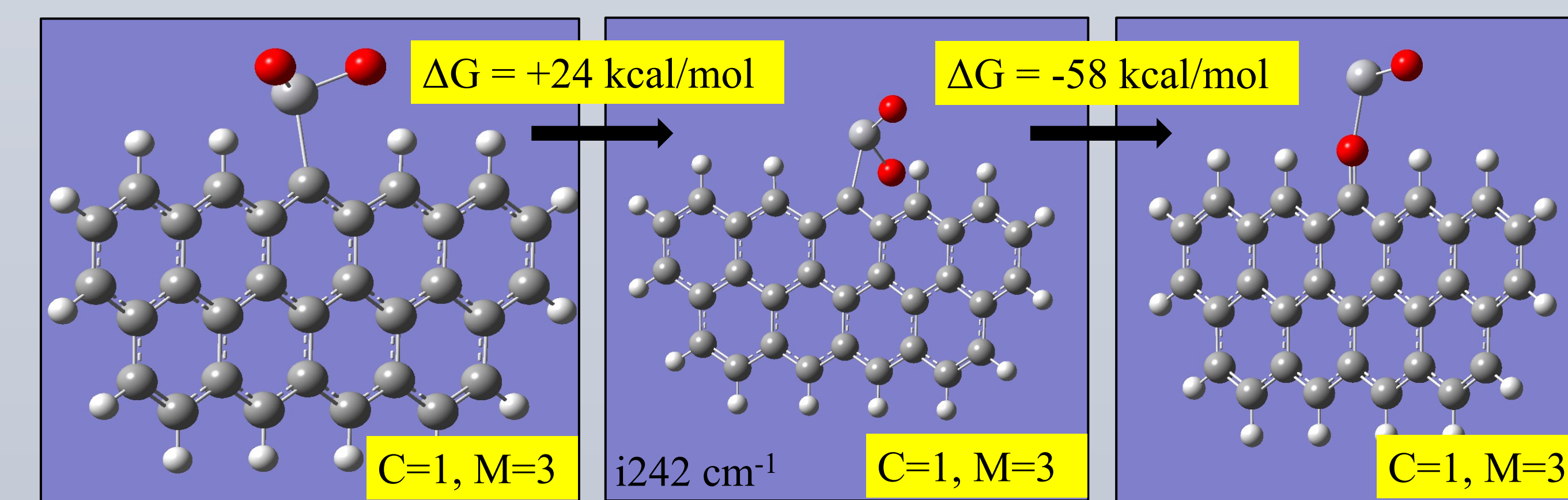C=1, M=3   i242 cm^{-1} C=1, M=3   C=1, M=3

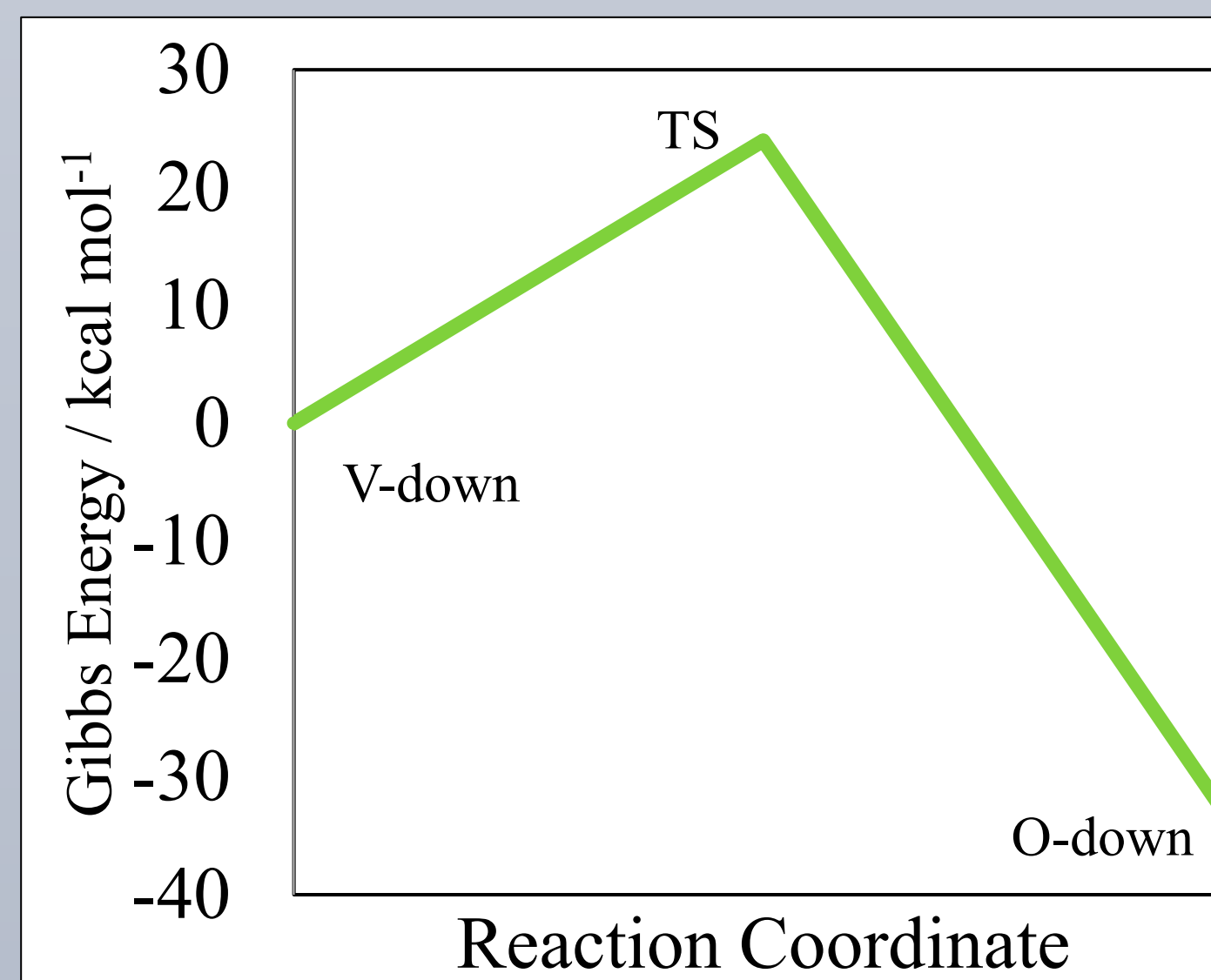Figure 4. Thermodynamics and kinetics of vanadium down and oxygen down adsorption to edge carbon.

Figure 5. Reaction Coordinate transitioning from V-down to O-down.

O-down allows for the most favorable adsorption step for VO_2^+ to interact with the edge carbon active site (Figure 3). For continuation of the edge site reaction mechanism, it also appears to be like the oxygen transfer step of CO_2 adsorption [4].

Conclusion

DFT allowed a theoretical look into the popular hydroxyl active site and its role in VO_2^+ adsorption. The interaction between VO_2^+ and –OH appears unlikely, the edge carbon active site allows for both vanadium down adsorption and oxygen down adsorption. The oxygen down approach is favorable by 34 kcal/mol. Furthermore, this step is remarkably analogous to the adsorption of CO_2 in the (much more extensively investigated) process of oxidation and gasification of graphene-based materials. Oxygen transfer at the carbon electrode may prove to be a key missing link toward a much-improved understanding of the vanadium redox flow battery. By identifying the true active sites and VO_2^+ interaction with them, the enhanced reaction kinetics at the positive electrode containing graphene-based materials can become a more realistic goal.

Future Work

☐ Pursue the remaining reaction mechanism steps for O-down adsorption to the edge carbon active site.

Figure 6 . Representative graphene cluster with –COOH adjacent to edge carbon active site.

☐ Explore the influence of adjacent oxygen functional groups to the edge carbon active site on VO_2^+ adsorption (Figure 6).
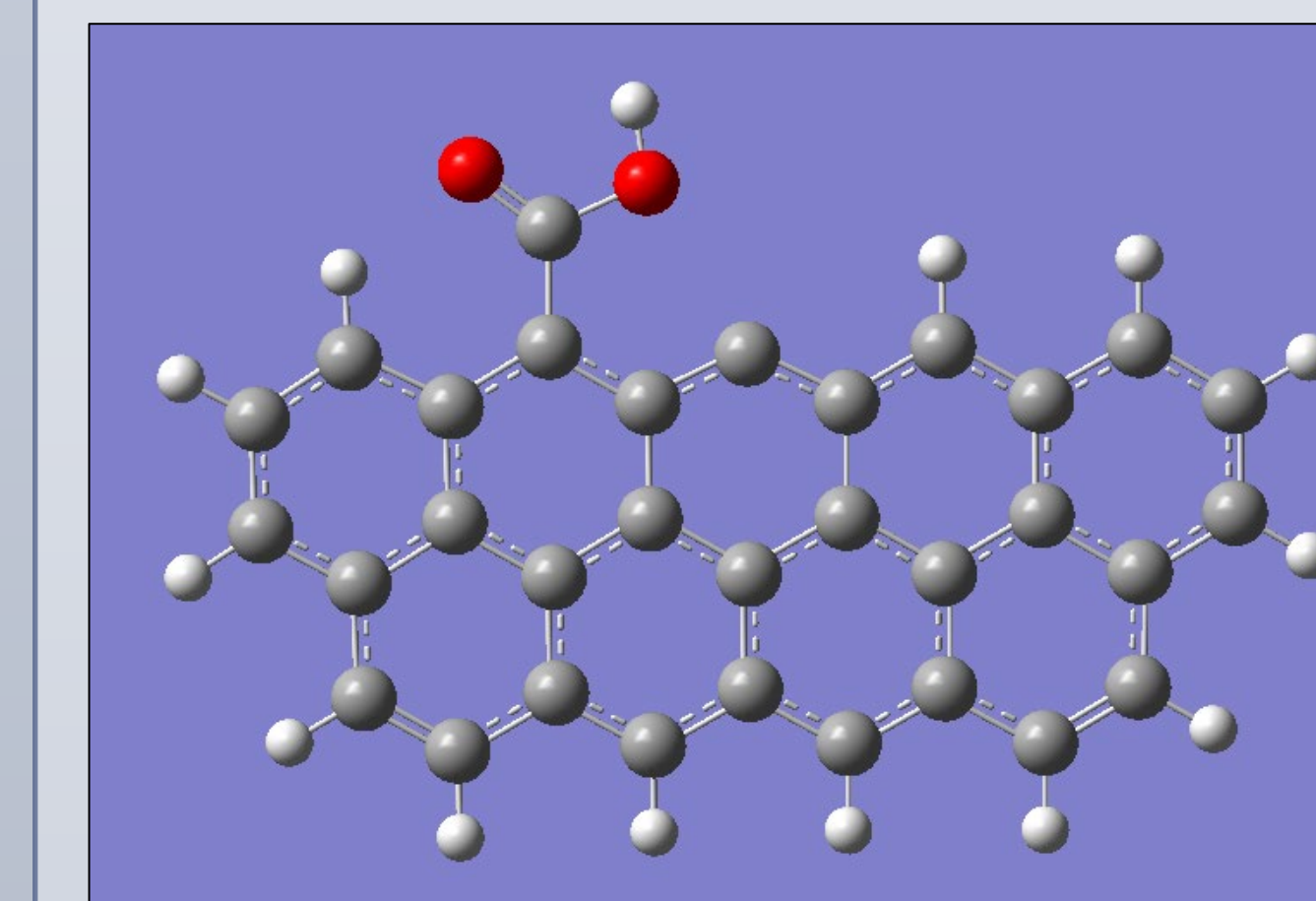
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