

Original Research Article

ADSORPTION ENERGIES OF LITHIUM AND SODIUM IONS ON VANADIUM DISULPHIDE: A DFT STUDY.

ABSTRACT

Various energy sources are utilized at present with a challenge of energy storage in many cases. The existing rechargeable storage batteries which include sodium-ion and lithium-ion batteries have some limitations in their gravimetric capacities. Ab initio methods based on density functional theory (DFT) was used to investigate the adsorption of lithium ions and sodium ions on layered Vanadium disulphide. Metallic VS₂ monolayer has a higher theoretical gravimetric capacity of 466mAh/g. This study showed that Sodium adsorbs on monolayer VS₂ with lower adsorption energy of -2.00eV compared to Lithium (1.47eV) and it is more stable.

Keywords: [Li-ion/Na-ion battery, Adsorption energy.]

1. INTRODUCTION

Layered metal Chalcogenides have attracted great scientific interest for both sodium and lithium ion batteries in the attempt to meet the raising energy demand. The current Lithium batteries have a challenge of storage capacity⁽¹⁾. An alternative being researched to replace lithium is sodium. Sodium ion batteries are currently attracting attention since sodium is more abundant compared to lithium⁽²⁾. Production cost is significantly low. However the availability of more stable non-aqueous electrolytes⁽³⁾ makes sodium-based batteries safer in prolonged use. One main drawback of using sodium is its larger ionic volume and weight compared to lithium, which could lower the battery's gravimetric energy density and thus limiting its adoption in the mobile applications segment.

To meet this challenge, better performance electrode materials must be developed. Finding battery electrode materials that can accommodate sodium/lithium in high capacity and with reasonable binding stability is therefore one way of solving high energy demand. The desired material should possess reasonably high Na/Li intake capacity and excellent exothermic reactions between the reactants, as well as good structural stability. Research on innovating new materials is therefore on the fore front⁽⁴⁾. The main research focus in ion batteries is to develop electrode materials that can provide a high gravimetric capacity, cyclic stability and high-rate capability⁽⁵⁾. Intercalated anode materials in both lithium and sodium ion batteries started in 1990s with electrochemical insertion of Mg²⁺ into various metal oxides and sulfide of different transitional metals⁽⁶⁾ were studied. This opened ways and interest for different scholars to research on intercalations behavior of polyvalent ions in various electrode materials with reference to sodium and lithium batteries.

Recently the use of 2D material is on the fore front in most researches. Graphene has been on extensive studies with a gravimetric capacity of 372mAh/g⁽⁷⁾. Despite its positive merits such as ultrahigh surface area, good conductivity, ultrafast intrinsic carrier mobility and mechanically stability⁽⁸⁾ graphene has a low gravimetric capacity. However the fact that the cations can be absorbed on both sites of the layers graphene, it was adopted as an anode material in most cases. The application of graphene is limited by the presence of edge effects as well as its defects⁽⁹⁾.

LTMDs nanomaterial such BN, MoS₂ WS have also been studied with more emphasis being done on MoS₂. Theoretically Li ions can be adsorbed on the surface of MoS₂ with low diffusion barriers⁽¹⁰⁾ however the electrochemical performance is limited by its semiconducting behavior in 2D state⁽⁴⁾. As a semiconductor it has poor electron transport efficiency⁽¹¹⁾.

Furthermore, Molybdenum is a heavy metal and highly electronegative that leads to strong covalent bonds with Sulphur within its structures.

Recently new LTMD (Vanadium disulphide) have been realized. VS_2 Nano sheets can be obtained experimentally through exfoliation using ammonia⁽¹²⁾. Each layer is made up of hexagonal close-packed sheets of Vanadium atom surrounded of the Chalcogenides of Sulphur atoms. Interlayer bonds are covalent while the intralayer is stacked by Van der Waals forces. The interlayer spacing is roughly 6.15 Å which are very large making the compound to undergo rapid change in volume during expansion upon lithium storage. It also mitigates the strain endured in the intercalated or reversible reaction leading to enhanced cycling stability. Compared to MoS_2 , VS_2 monolayer is metallic with spin-polarized ground state⁽¹³⁾. In addition, metallic VS_2 could facilitate good performance in Li-ion battery as an anode. In this research we performed a systematic DFT computation to explore the possibilities of using VS_2 monolayer as anode material for both LiBs and NaBs.

2. COMPUTATIONAL DETAILS

First-principle calculations were performed within the density functional theory (DFT) framework as implemented in Quantum Espresso (QE) package⁽¹⁴⁾ using generalized gradient approximation (GGA)⁽¹⁵⁾ with Perdew-Burk-Ernzerhof (PBE) exchange correlations functional. The plane-wave cutoff was taken at 40.0Ry for all the total energy calculation with Monkhorst pack⁽¹⁷⁾ Kpoint grid of 3 3 1. A vacuum of 20Å was used in the out of plane (z) direction. The structures were optimized by Fletcher Gold forb Shanno⁽¹⁷⁾ and visualized by XCRYSDEN⁽¹⁸⁾. A 4x4x1 supercell was employed in this calculation. Electronic convergence was set at 10^{-6} eV while atomic positions were optimized until the final forces were below 1.0×10^{-4} eV/Å. Adsorption configurations were expressed in stoichiometry of X_nVS_2 where n is the number of Na/Li atom concentration per VS_2 formula unit. The Na/Li atoms were randomly placed on the H-monolayer VS_2 followed by structure optimization for all concentrations. The adsorption sites with lowest energy were then used in the succeeding analyses.

3. RESULTS AND DISCUSSION

Similar to other TMDs, VS_2 monolayer exhibits a 2D hexagonal lattice which is periodically along the x and y directions. Each V atom of the monolayer VS_2 is surrounded by three neighboring atom of S atoms while each S atom is surrounded with three V atoms (figure1). There are two phases of VS_2 , (trigonal T-phase and hexagonal H- phase) and both are sensitive to temperature changes. H-phase is stable at room temperature⁽¹⁹⁾ and therefore our investigations were based on the H-phase monolayer.

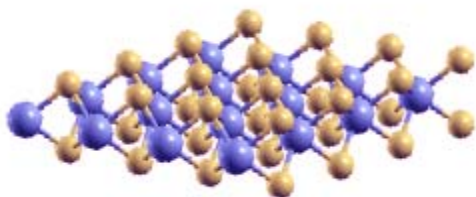


Figure 1 H-phase monolayer Vanadium disulphide.

After optimization the monolayer H-phase VS_2 , the lattice parameters were calculated to be $a=b=12.69$ Å and the bond length as 2.36 Å. During this calculation, the active sites for adsorption were first optimized. From calculations there are three possible sites for Li adsorption on VS_2 monolayer. The available adsorption sites are V-site (on top of vanadium atom), S-site (just above the sulphur atom) and the H-site (At the center of each hexagonal V-S-V-S-V-S-V shape). The S-site⁽¹⁸⁾ (just above the S atom) is not local minimum for adsorption since the Lithium atom moves to the V-site after relaxation

An exothermic reaction between the cations and VS_2 that yields negative adsorption energy indicates more favorable site for adsorption. V-site has the lowest potential energy with indicates that it is the more favorable site for cation adsorption. Figure two shows side view of the V-site adsorption.

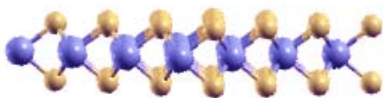
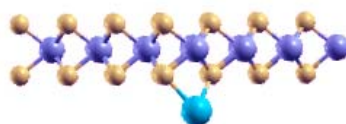


Figure 2 side view V-site adsorption of VS₂. Large ball represents the vanadium atom and yellow small ball represents the sulphur atoms. The V-S Covalent Bond is all through.

We therefore optimized the possibility of adsorbing both lithium and sodium atoms on the V-site VS₂. Our calculation shows that in each case two atoms can be stably be adsorbed on the monolayer VS₂ as shows in figure 3 below.



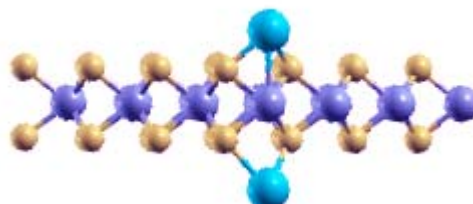
a) Single Lithium ion



b) single sodium ion.



c) Double lithium ions



d) double sodium ions

Figure 3: Schematic illustration of the (a) single lithium ion, (b) double lithium ions adsorption (c) single sodium ion adsorption and (d) double sodium ions adsorption on V-site of VS₂. The purple balls represents lithium ion while the green ball represents the sodium ions.

To determine the storage capacities of the sodium and lithium ions on the surface of VS₂, the adsorption energy was calculated by the following equation:

$$E_{ads} = \frac{E_{VS_2+X} - E_{VS_2} - nE_X}{n} \quad 1.0$$

Where: E_{ads} is the adsorption energy, $E_{(VS_2+X)}$ is the total energy of VS₂ and sodium or lithium ions, E_{VS_2} is the energy of pure VS₂ and E_X is the chemical potential of either sodium or Lithium i.e. the cohesive energy per atom of bulk metal. The capacity of the battery is also determined by the reversible reaction between the host electrode and the Li-ions which is given by the following equation



The ΔE value is a negative value indicating the reaction is exothermic. A favorable reversible reaction is the one with the more negative reaction energy

From equation (1.0) different values of the energy were achieved when X is substituted by either Na/Li. The resultant adsorption energies were maintained at negative values all through in order to maintain the state of the reaction that is exothermic state

Table 1: Tabulated results of adsorption energies, Li-V and Li-S bond length for the possible insertion sites of Li-ion on monolayer VS₂

Lithium/Sodium ion		Active sites	Adsorption energy (eV)		Bond length(Å)	
			Li ⁺	Na ⁺	Li-S	Na-S
	Calculated	V	-1.47	-2.00	2.38	2.77
	Other DFT.	V	-2.13 ⁽²⁰⁾	-2.17 ⁽²¹⁾	2.42	2.72

The V-site is the most favored site with more negative adsorption energy for adsorption of both sodium and lithium ions. This indicates a more favorable reaction occurring between VS₂ and lithium ions/ sodium ions.

From the results the adsorptions energies at lower concentration of the cations is almost the same. The increase in adsorption energy Na is attributed to larger atomic radius of sodium ion compared to lithium ion. Therefore as the number of the ions is varied from one to two, a larger electrostatic repulsion is between Na⁺-Na⁺ bond is set in. thus the ions have to overcome the extra electrostatic barrier to reach the stable side of VS₂ which leads to an increase in adsorption energy⁽²²⁾. Our results differ slightly with other DFT computations which may be attributed to convergence and plane wave basis set by different DFT code. The Na-S bound is larger because of the large volume of sodium ion which leads to lattice distortions that come across as a result of stress filed induced by the excess volume in the grain boundaries. Despite this, the adsorption of Sodium is more stable than Lithium.

VS₂ monolayer can provide a negative binding energy even when double ions are used. However, increasing the number of ions, the energy values tend to be positive this may introduce an endothermic reaction (positive binding energy values) that is not favorable for intercalation. The theoretical capacity of a cell is therefore calculated as per the following equation⁽²³⁾

$$Q_{the} = \frac{nF}{3600 \times Mw} \quad 3.0$$

Where: n is the number of charge carries, F is the Faraday constant and Mw is the molecular weight of the active material used in the electrode. With VS₂ as the active material we set n to be one and applying equation 3.0 the theoretical capacity was calculated as 233mAh/g.

As a comparison to other TMDs for instance MoS₂, which can also store lithium/Sodium ions to XMoS₂, the capacity is 157.5mah/g³. This is lower than that of VS₂; this is due to high molecular weight of MoS₂. In both cases the gravimetric capacity increases with the increase in the number of charge carries. From this we can conclude that VS₂ monolayer as a host electrode material boosts the capacity of Li-ion/Na-ion battery.

4. CONCLUSION

In conclusion we have investigated the possibility of using VS₂ monolayer as an anode material for both Li-ion and Na-ion battery by DFT methods. The adsorption energy of Lithium and sodium storage was calculated, where sodium provides a more negative adsorption energy value than Lithium. Therefore the adsorption of Sodium is more stable than Lithium. However, Lithium ions can be adsorbed to VS₂ surface with less electrostatic repulsion.

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