Structural, Electronic and Electrochemical Properties of Vanadium Disulphide Material for Energy Conversion and Storage in Li/Na-ion Battery

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Authors' contributions

This work was carried out in collaboration among all authors. Author GIM designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors HBW and MM managed the analyses of the study. Author GIM managed the literature searches. All authors read and approved the final manuscript.

Article Information

Review Article

ABSTRACT

We review work on rechargeable metal-ion batteries. Rechargeable metal-ion batteries play a crucial role in modern transport, communication and electronic industries with lithium ion batteries being the most common on the market. Despite the successful application, of lithium-ion batteries; their energy density, volumetric and gravimetric capacities, life span and charge /discharge rate have raised a lot of concern. Current research is being focused on the anode materials currently in use and also substituting Lithium/Sodium ion batteries. This review, we look into the structural, electronic and electrochemical properties of a newly synthesized Vanadium disulphide as promising near future anode for both sodium and lithium ion batteries

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1. INTRODUCTION

With the growing development of social economy, there is an increase in the energy shortage and increase on environmental pollution [1,2]. In order to solve these, problems, the use of clean energy is now on the forefront [3]. For proper implementation and application of clean energy several measures including storage and conversion of the energy needs to be taken into account [4,5]. The fact that rechargeable batteries couple the functions of storage and conversions, they are most applicable in the field of electrochemical energy storage. Lithium ion batteries (LiBs) have gained popularity ever since they were discovered in 1990's [6]. However, there is concern over sustainability and cost of LiBs to be used in large-scale grid application.

Current research focuses on other promising areas of batteries to complement LIBs [7,8]. Sodium and potassium elements are in the same group with lithium, thus the chemical properties are more likely to be similar and this forms the basis of current research field. Sodium being the most abundant and second lightest metal in comparison to lithium, has shown successful research work in application in large scale energy storage devices [9]. However, the application of SIBs has been hindered by the large ionic size of Na when compared to Li. The ionic size varies in the series of K>Na>Li. The increase in the ion renders them with low mobility in solid state, leading to sluggish movement in the host materials. Such condition is further exacerbated under the ionic interaction of host materials with negative charges, which becomes the reason why they tend to degrade faster and hold less energy than LIBs.

However, basing on the fact that sodium and potassium elements are more abundant in the Earth's crust than lithium, then they are likely to replace lithium in the near future. This coupled with the unique potential and various advantages like good cycle life, high energy density, and low self-discharge features of both SIBs and KIBs, it is convincing that further technical development of electrode materials might be able to narrow down the performance gap [10].

The limitation of lithium ion batteries is majorly contributed by the electrode materials used [11,12]. LiBs commonly employ carbon-based electrode materials which are disadvantaged by low specific and volumetric capacity, energy density and poor cyclic performance [13].

The commercial carbon based anode currently in use have low specific capacity of 372mAh/g when used in LiBs and 337mAh/g for SIBs [14] hence need for further research on super performing electrode materials [15].

Among the many researches on materials are 2D transitional metal chalcogenides (TMDs). 2D materials aid to have large surface area thus can accommodate maximum number of the metal ions per unit cell. TMDs exploitation was successful after the exfoliation of graphite to graphene. TMDs with general formula of MX_2 (M =V, Mo, W, Co and X= S, Se, Te) have received much attention due to the attractive physical and chemical properties and thus highly applicable in catalysis [16], energy storage [17], and light harvesting [18].

Just like any other TMDs, VS_2 can be prepared through different methods which includes mechanical explosion chemical vapor deposition and liquid exfoliation [19]. For instance [20] synthesized VS_2 sheets through a chemical vapor deposition methods using VCl_3 and S as the precursors, with potential applications as anode for both sodium and Lithium batteries. Additionally, theoretical research work on 2D VS_2 reports that, the material has a high specific capacity of 446mAh/g, good cyclic behavior, high ion diffusion and better electrochemical performance in SIBs than LIBs [21]. In this review therefore properties of VS2 in relation to energy storage and conversion is discussed.

2. CRYSTAL STRUCTURE

Monolayer VS_2 belongs to the group of compounds referred to as the transitional metal dichalcogenides (TMDs). Most TMDs are composed of blends of X-M-X sandwich layers of M= transition metal and X= chalcogenide atom [22]. VS_2 poses similar sandwich structure with each layers forming an S-V-S structure. Atoms within each slab are connected by ionic interactions contributing to the adjacent neighbours' layers which are bound together by weak forces of attraction. This force makes it possible to exfoliate the bulk VS_2 into different monolayer sheets. The interlayer spacing is approximately 0.64nm [21] which is higher than that of graphene (0.33nm) and thus high intercalation / de-intercalation space compared to graphene [23].

According to the S-V-S stacking forms, VS_2 crystalizes into two structures; the 2H- VS_2 (S-atoms are in the trigonal prismatic coordination around the V-atom) and the 1T-VS_2 (S-atoms are in the octahedral coordination around the V-atom) [24] as illustrated in Fig. 1.

At 0K, the 2H-VS_2 is said to be stable with a biaxial strain range of -7% < ∈< 4.5% whereas 1T-VS_2 is predicted to be more stable with strain range of ∈ < -7%and ∈ >4.3%. This temperature dependency stability determines the application of VS_2 in electrochemical applications. For instance for better performance in Li/Na batteries, 1T-VS_2 monolayer and 2H-VS_2 bulk systems have been predicted to have good electrochemical characteristics.

3. ELECTRONIC BAND STRUCTURE

The electronic band structure of a compound intrinsically determines the electrochemical performance of an electrode material. Under the electronic structure we consider the conduction band minimum, band gap and the valence band maximum. The bands are obtained by considering electron affinity and the ionization potential energies.

The theoretical density functional theory (DFT) calculations done employing the generalized gradient approximation (GGA) methods reveals that density of states (DOS) at the fermi level in monolayer and bulk VS_2 is contributed by both V-3d and S-3p states showing that the monolayer and bulk systems are metallic with zero band gap [21] Fig. 2.

However Luo, et al., reports that, when GGA methods combined with the Hubbard parameter U (GGA+U), is used ($U_{eff} = 1.0eV$) an indirect band gab is achieved in 2H-VS_2. Additional, as illustrated in Fig. 3; *Min*, et al., 2015 reports a semiconducting properties in 2H-VS_2, with PBE (band gap of 0.721eV). Furthermore, by applying GGA+*U* with the Hubbard term set at $U_{eff} = 3.0eV$ a band gap of 0.721eV is obtained. The band gab increases to 1.128eV when a more correlated function state-of- the-art hybrid functional (HSE06) is used though the calculations are expensive.

HSE06 methods also indicates that 1T-VS_2 is a semiconductor with a band gap of 1.128 eV. At this point 2H-VS_2 is confirmed to be a semiconductor but the challenge is now the exact band gap.

These differences shows that the DFT calculations results highly depend on the method used. The different methods of DFT (PBE, LDA, GGA+U, HSEO6 and GW) may result in different results. In some compounds, DFT calculations based on LDA or GGA may not be reliable [26]. For instance, computing the band gap from the khan-sham valence and conduction band eigenvalues usually underestimates the band gap of most semiconductor, strongly correlated compounds and even insulators. Where by during the band structure calculation in these compounds, a metallic state at ground state is predicted .This underestimation is usually related to discontinuity in the exact exchange correlation potential at the fermi level [27]. Majorly the error in the band gap calculations based on LDA or GGA arises from electrostatic electron-electron contribution to the Hamiltonian usually referred to as the Hartree energy.

Hartree energy not only includes the correct coulomb repulsion but also a coulomb repulsion between an electron and its own charge density. This scenario termed as self-interaction is partially cancelled by GGA and LDA exchange methods hence the significant underestimation of the band gap [28].

Perder and Zunger, proposed the use of Self-interaction correction methods in order to overcome the challenge posed by LDA, and GGA. In these methods (DFT+U and GW) each particle interacts only with the density of the other particle hence no self-interaction [29]. The semiconducting property of 2H-VS_2 cannot be achieved by use of GGA methods alone thus, incorporating the Hubbard-U term reduces the band gap underestimated by GGA/LDA methods. The U-term introduces a repulsion between the localized electrons on a given atom thus could give a precise result as compared to GGA/LDA results. However the self-interaction problem is not totally fixed by DFT+U methods.

The band gap of the 2H-VS_2 given by GW methods could be looked at as the exact one. GW method is free from Non-analytic behavior of V_{xc} upon addition/removal of an electron. It is therefore considered to give reliable values for the band gaps of semiconductors and insulators [30]. However due to high computational expenses involved a single iteration which is known as the G_0W_0 method has been used in these studies [24].
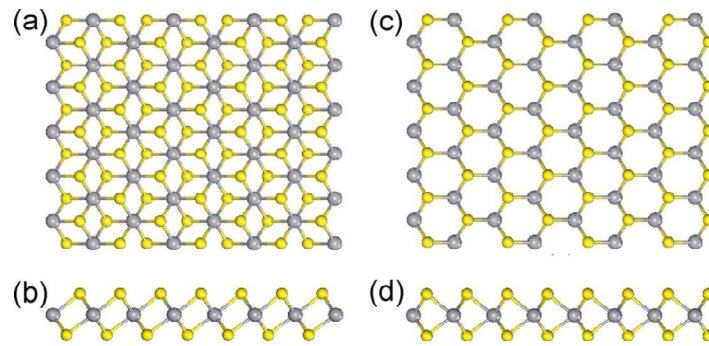
Fig. 1. Monolayer (a) side view and (c) top view geometry of 1T-VS$_2$; (b) side view and (d) top view geometry of 2H-VS$_2$. Where V-atoms and S-atoms are represented by gray and are yellow balls respectively [25]
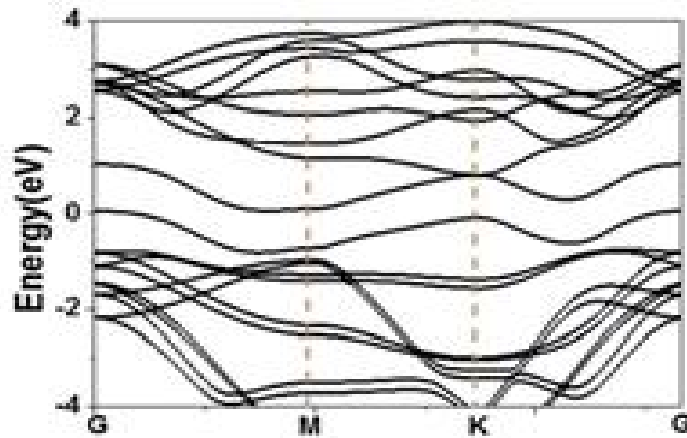

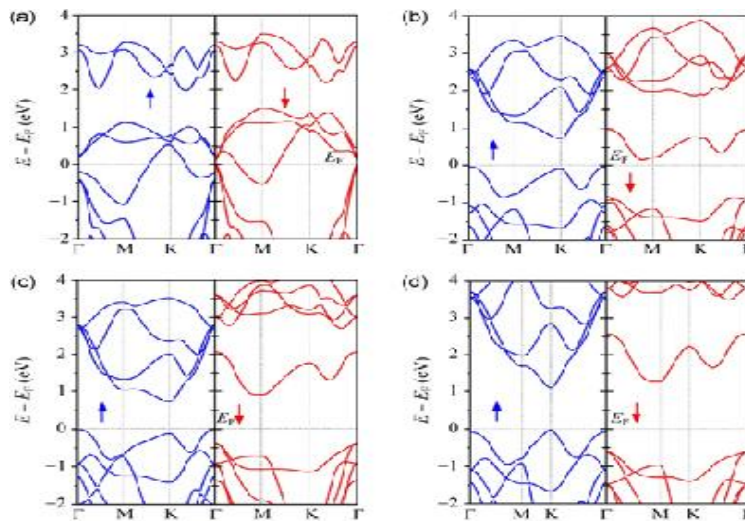**Fig. 2. Band structure of monolayer H-VS2 indicating a metallic state [21]**

Fig. 3. (color online) band structure of (a) 1T-VS$_2$ indicates a metallic state using and (b) 2H-VS2 a semimetal PBE method. The semi conductivity in 2H-VS2 is also seen in (C) and (d) by employing the GGA+U and HSE06 methods respectively [25]
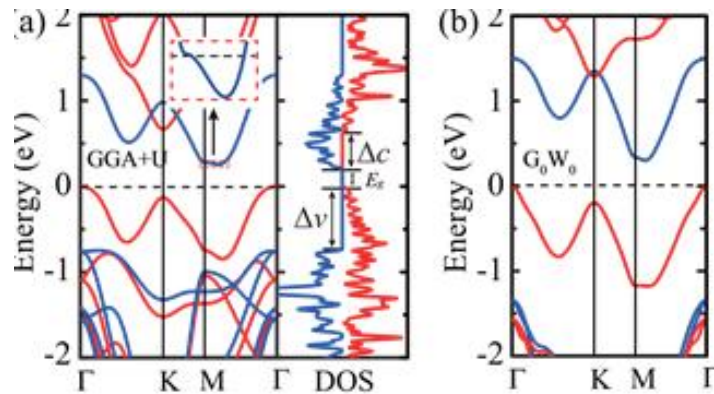
Fig. 4. Band structure using GGA+U and G_oW_o methods [24]

3.1 Adsorption and Diffusion of Li-ions on VS_2 Monolayer

Just like any other TMDs, VS_2 can be obtained by the top-down exfoliation procedures and this makes the process of surface adsorption possible [31,32]. The honeycomb structure of VS_2 has three possible sites for adsorption. The H-site (above the center of hexagonal), V-site (above the Vanadium atom) and S-site (just above the Sulphur atom) as illustrated in the Fig. 5.

All the three sites are not locally stable for adsorption. For instance the, Li-atoms adsorbed at S-site, move to V-site after full relaxation [33].Furthermore adsorption energy is calculated as per the equation (Jiag, Zhou, Cabrera, & Chen)

$$E_{ads} = E_{VS_2+Li} - E_{VS_2} - E_{Li} \qquad 1.0$$

A favorable site for adsorption must be able to result in a more negative adsorption energy [33]. According to Yu, et al*., V-site is the most favorable site with more negative energy value as well as more positive charge transfer value. The theoretical capacity depends on the number of lithium ion adsorbed on the host electrode. VS_2 can accommodate lithium atoms in the stoichiometry of Li_xVS_2 with (x=1, 2). Beyond this range of x, the adsorption energy tends to the positive (endothermic reaction) Therefore to maintain the required exothermic state, the maximum li atoms adsorbed per unit cell of VS_2 is restricted to two.

The adsorption energy of Na^+ is higher (more positive) than that of Li^+. 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 between NA^+-Na^+ bond sets in. The ions have to overcome the extra electrostatic barrier to reach the stable side of VS_2 which leads to an increase in adsorption energy.
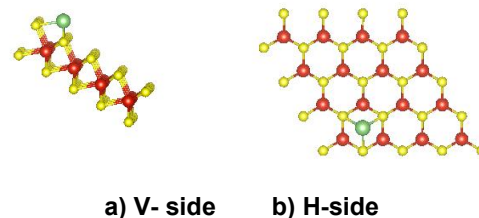

a) V- side   b) H-side

Fig. 5. Monolayer adsorption sides [34]

As an electrode material VS_2 has high lithium/sodium storage capacity of 0.93ev, in comparison to graphene and Molybdenum disulphide, MoS_2 (Li_2MoS_2=0.26ev, LiC_6=0.11) [35,36].

3.2 Diffusion and Open Circuit Voltage of Monolayer VS_2

The performance of an electrode material is determined by diffusion rate. Diffusion rate depends on the time taken by the Li/Na atoms to move from one adsorption site to next (for example move from one V-site, the next V-site) as shown in the Fig. 6. The atoms have to overcome barrier energy during this motion. The three possible diffusion path illustrated in Fig. 6 elow includes V-H-V, V-S-V, and V-V [37].
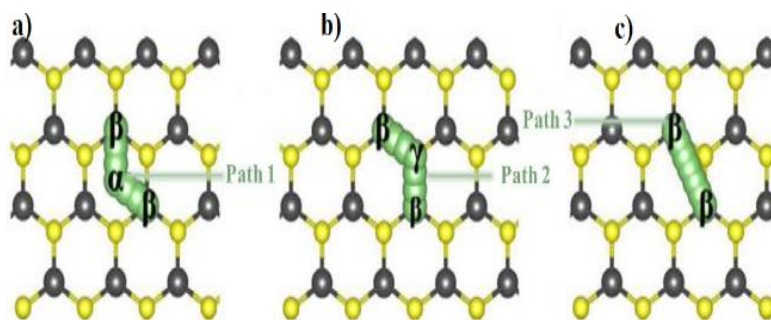
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Fig. 6. (color online) (β =V, γ =S and α =H)

3.3 Diffusion Path (a) V-H-V, (b) V-S-V and (c) V-V) for Li$^+$/Na$^+$ Ions on Monolayer 2H-VS$_2$ [38]

Out of these, V-H-S path has the minimum diffusion barrier. The equilibrium potential with respect to the atom/ion adsorption is estimated by the calculating difference in energies as per the equation [39].

$$V_{A^+/A} = \frac{[E(VS_2) + xE(A^+/A) - E(A_xVS_2)]}{xF} \qquad 2$$

Where A^+/A represents the atom and its cation (Na and Li), F is the faradays constant and x the amount of adsorbed ions.

Both Na/Li ions experience low diffusion barrier with VS$_2$ as compared to MoS$_2$ and graphene. However diffusion kinetics for Li ions are greater than that of Na. This low diffusion barrier coupled with low working voltage makes sodium the most

appropriate atom to replace Lithium in the near future [40].

V-site is also a preferred adsorption site for 1T-VS2 with V-H-V, being the preferred diffusion path. *Salavati and Rabczuk,* 2020 reported that following the diffusion path of V-H-V as in Fig. 7, the diffusion energy barrier is 0.22eV for Li and 0.1eV for Na. The ions thus have a high facile surface migration due to low diffusion energy barriers [41]. Additionally the open circuit voltage for 1T-VS$_2$ with Li and Na are in the range of 1.556V to 0.46V and 1.5V to 0.37V respectively [39]. The values are lower compared to that of MoS$_2$ and Graphene [42,43].

VS$_2$ also has strong cation binding of -2.58ev in comparison to other TMDs (MoS$_2$=-1.35eV and WS$_2$ =-1,56eV) [44]. These makes VS$_2$ a promising anode that can withstand fast charging/discharging rate.
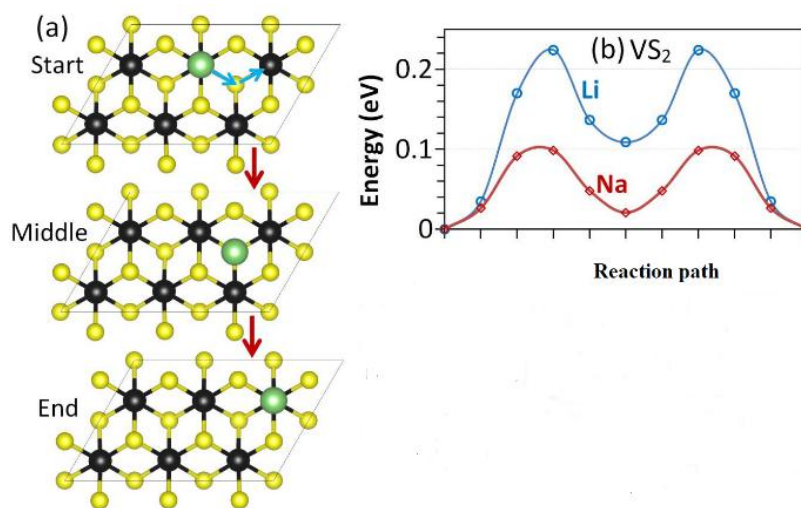

Fig. 7. (a) diffusion path along the V (start) –H (middle) –V (end) route for Li/Na ions and (b) the diffusion barrier energy profile [38]

4. CONCLUSION

Despite the successful application of lithium-ion batteries; their energy density, volumetric and gravimetric capacities, life span and charge/discharge rates have raised a lot of concern. Nevertheless, some global trends will continue to attract and spur the research on rechargeable metal ion for applications in modern transport, communication, electronic industries and for energy related applications for decades to come. Among this there is growing network in communication due to exploding population which will boost the demand of safe and affordable energy to fulfill its needs and aspirations. In this review therefore we have reviewed properties of monolayer VS_2 as an electrode material for both sodium /lithium ion batteries.

VS_2 crystalizes into two phases which are temperature dependence and this determines its applicability.

$H-VS_2$ is a semiconductor with a band gab of 0.732eV, while $T-VS_2$ is metallic at ground state. The semiconducting in $H-VS_2$ can only be realized when strongly correlated DFT methods are used in calculations.

VS_2 has three adsorption sites with the V-site being the preferred for both sodium and lithium in both the two phases. The diffusion path in the two crystals is the V-H-V path where a minimum diffusion barrier energy is experienced.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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