Comparative studies on two dimensional VCl2 and VBr2 as anodes of Li ion batteries

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Abstract. Lithium-ion battery, one of the most commonly used portable power supply devices, still has many drawbacks, such as low rate of charging and discharging, poor safety and low energy density. Through using the appropriate two-dimensional (2D) anode materials, the performance of lithium-ion batteries (LIBs) can be greatly improved. In this study, through first principles calculation, we compare two 2D materials as anode materials, VCl2 and VBr2, and we find that: (1) VCl2 cannot stably adsorb lithium, because lithium breaks down the original crystal structure of VCl2; (2) VBr2 not only adsorbs lithium stably, but also has good properties of voltage, conductivity and diffusion barrier. Given these advantages, VBr2 is predicted to be promising for being applied as an anode material of LIBs. It is hopeful that this study has a guiding significance for the research and development of two-dimensional materials as battery anode materials.

1. Introduction
With the rapid development of the society, lithium-ion batteries (LIBs) have been widely employed for electrochemical energy storage in many applications, such as electrical vehicles (EVs) and portable electronic devices. However, because of the low energy density and charge-discharge rate, both lithium-ion batteries and sodium-ion batteries (NIBs) cannot satisfy customers’ needs currently [1]. Meanwhile, safety problems due to electrolyte and dendrite are frequently reported in recent years [2-3]. Therefore, the demand for new generation of metal-based batteries is growing. In recent years, rechargeable batteries based on two dimensional materials as promising anode materials, which have high surface area, have started to attract researchers’ attention because of their excellent gravimetric and volumetric capacities [4-10].

For instance, Larson et al. [11] used density functional theory (DFT) calculations to investigate the structural and electrochemical properties of lithium intercalated graphene/MoS2 heterostructures as the anode Li ion batteries (LIBs). Aierken et al. [12] compared the performances of two layer MXene and MXene/graphene heterostructure as the anodes of LIBs. They found that M2CX2/graphene heterostructures exhibit lower molecular mass, inducing high storage capacity, and in addition, the presence of graphene guarantees the good electrical conductivity that is necessary for battery anode applications. Demiroglu et al. [13] further investigated the feasibility of M2CX2/graphene heterostructure anodes for sodium, potassium, and calcium ion batteries. They concluded that Ti2CO2/graphene and also V2CO2/graphene anodes are with great promise for Na ion batteries. Recently, more 2D materials are found and their properties for batteries are needed to be explored.

In the present study, we systematically investigated and compared the properties of VCl2 and VBr2 used as the anode of the battery. Our results show VBr2 has a good stability when adsorbing Li ions.
and the good conductivity, moderate voltage and low diffusion barrier, which identify monolayer VBr₂ as promising anode materials for LIBs.

2. Methods

We perform all the calculations under the framework Density Functional Theory (DFT), as implemented in CASTEP [1] module of Materials Studio code. Exchange correlation interactions are considered using the generalized gradient approximation (GGA) within the frequently-used Perdew-Burke Ernzerhof (PBE) formulation [2]. The single electron wavefunctions are expanded to plane waves with an energy cutoff of 270 eV. In the structure optimizations, a $2 \times 2 \times 1$ k-point mesh of the Monkhorst-Pack scheme in Brillouin-zone are used for a quick calculation with the convergence criterion of 0.05 eV/Å and $2 \times 10^{-5}$ eV for ionic and electronic relaxations. To minimize the $z$ direction periodic interaction, a 15 Å vacuum space is used. Then, the van der Waals (vdW) interactions are taken into account by the DFT-D3 method [3]. A $3 \times 3 \times 1$ k-point mesh is adopted for the electronic band structure, binding energy and charge transfer calculations.

3. Results and discussions

3.1 Stability of loading with lithium atoms

First of all, we analyse the stability of VCl₂ and VBr₂ when loaded with lithium respectively, which is the basis for the battery anode to work properly. Figure 1 shows the structures of VCl₂ and VBr₂ before and after adsorption of lithium atoms. We find that, in Fig. 1(a), the loading of Li destroys the original structure of VCl₂, however, in Fig. 1(b), the same problem does not exist in VBr₂. The reason for this phenomenon may be the tremendous ability of chlorine to grab electrons and the relatively weak ability of bromine. As the lithium ion approaches, the chloride ion leaves its original position and combines with the lithium ion to form lithium chloride (LiCl), destroying the original structure of VCl₂. In short, a process similar to the substitution reaction occurs in VCl₂, which demonstrates VCl₂ is not competent to be the anode material of LIBs. Bromine has a larger atomic radius, its electron trapping ability is lower than that of chlorine, so the structure of VBr₂ is not broken when loaded with Li. Therefore, in the following study, we only analyse the properties of VBr₂ as anode materials.

![Figure 1. Structures of VCl₂ and VBr₂ with and without Li loading, where front view and top view of (a) the $1 \times 1 \times 1$ VCl₂ a with two Li ions, and (b) the $1 \times 1 \times 1$ VBr₂ a with two Li ions are displayed.](image)

3.2 Electrochemical properties

The binding energies of Li loaded system are defined as,

$$ E_b = \frac{E_{VBr₂, NLi} - E_{VBr₂} - N \cdot E_{Li}}{N} $$. (1)
where $E_{\text{VBr}_2\text{Li}}$, $E_{\text{VBr}_2}$ and $E_{\text{Li}}$ are the free energies of the VBr$_2$ monolayer with Li, without Li, and Li atom in the most stable bulk crystal, respectively, and $N$ is the total number of Li atoms on the surface. Then, according to the binding energy, the open-circuit voltage of the heterostructure anode can be calculated by the following equation,

$$V_x = \frac{E_{\text{VBr}_2\text{Li}}N_1-E_{\text{VBr}_2\text{Ni}}(N_1-N_2)\text{Li}}{(N_1-N_2)e}$$  \hspace{1cm} (2)

where $V_x$ is the voltage at $x$ concentration, $N_1, N_2=4\times x_1, x_2$, are the number of Li on the VBr$_2$ surface, and $x_1>x>x_2$ is the concentration.

As a next step, the effect of lithium ion concentration on the surface of VBr$_2$ is investigated, where we define the ratio of the number of lithium ions and the two times of the number of VBr$_2$ formula units as the value of concentration. Our calculations show that, as more and more lithium ions are adsorbed (from 0 to 1), the lithium valence drops from 0.7 to 0.3. We can see that because the number of bromines is limited, the more lithium on the surface of VBr$_2$, the weaker the attraction between bromine and the outer electrons of lithium. Therefore, the valence of lithium decreases with lithium concentrations. Figure 2(b) shows that as the number of Li ions increases, the average $E_b$ increases accordingly. The decline of binding energy is due to two factors: one is the weaker attraction between VBr$_2$ and Li ions, and the other one is the increased Li-Li repulsive forces. The reasons above can also explain the reduced valence of Li as Li concentrates. In Fig.2 (c), we can see, with the increase of lithium ions concentration, the calculated voltage decreases gradually. However, the voltage is always positive, suggesting that VBr$_2$ is a promising candidate for the electrode material in battery, because the positive voltage shows there is no phase transition during the increasing concentration of Li.
3.3 Electrical conductivity

Figure 3 displays the density of electronic states of VBr$_2$ with different Li concentrations, where (a)-(e) are with concentration of 0, 0.25, 0.5, 0.75 and 1. The dotted line indicates the Fermi level. Generally, the density of electronic states near the Fermi energy determines the electrical conductivity of the material. When VBr$_2$ does not adsorb Li, the DOS of $\sim$29 electron/eV means that VBr$_2$ is a conductor, as shown in Fig. 3(a). By observing the following figures, we found that the density of states at Fermi energy have the values of $\sim$29 electron/eV, regardless of whether Li ions are adsorbed, indicating a high electrical conductivity of VBr$_2$, which is beneficial to the performance of the battery anode material.
3.4 Charge transfer

Deformation charge density (DCD) could well explain the change of Li valence during concentration increase. In Fig. 4, we displayed DCDs of the VBr$_2$ monolayer and adsorbed Li in different concentrations, which is helpful for the analysis to the interaction mechanism between the Br atom and Li atoms. The yellow and blue areas represent the electron consumption and accumulation regions respectively. In Fig. 4(a), the area of yellow region is huge, so it demonstrates the electron of Li is consumed by Br in that area, indicating a significant charge transfer form Li to Br. We can see that, with the increasing concentration of Li, the area of yellow regions decreases, fewer electrons being consumed.

3.5 Diffusion properties

To make electrode materials efficient, anode materials require a low diffusion barrier and high mobility. Especially, during the process of charging and discharging, the mobility of a metal atom on an electrode material determines the rate of charging and discharging of a battery. Here we investigated the single kinetic of Li on VBr$_2$ single layer. Between two adjacent binding sites, we
given the lowest energy Li atom diffusion path as shown in the inset of Fig. 5. Compared to a recent study [12], we found that VBr₂ monolayer has a relatively smaller diffusion barrier than bilayer materials, which indicates monolayer structure, as an anode material, has a better diffusion property, i.e. lower internal resistance of a battery. Small diffusion barriers indicate a high rate of charging and discharging, promising to solve the most troubling problems of LIBs currently.

4. Conclusions
In a word, by using first-principles calculations, we systematically compare two dimensional VCl₂ and VBr₂ as anodes of LIBs. The calculated structure of VCl₂ is unstable when adsorbing Li ions, showing that VCl₂ is not favorable for battery applications. However, VBr₂ displays good compatibility with Li ions. Therefore, we ruled out the possibility that VCl₂ could be used as the anode material of the battery. Calculations of Li valence exhibit that Li atoms become positively charged when adsorbed on the surface of the VBr₂, which is essential for stably loading. Meanwhile, the charge transfer between Li and Br decreases as Li concentration increases. The average binding energy also approaches zero as the Li concentration increases. The calculated average voltage remains positive as Li ions concentrate from 0 to 100%. The calculated density of electronic states near the Fermi level is always considerable and increases with the increase of Li ion concentration, proving the excellent electrical conductivity of VBr₂. The figures of density of electrons figuratively illustrate the mechanism of charge transfer. Finally, low diffusion energy barriers are found, which suggests the anodes made of VBr₂ have a high charge and discharge rate. Generally speaking, these results show the two-dimensional material, VBr₂, is very promising for being used as anodes of LIBs.

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