Tetragonal and trigonal Mo$_2$B$_2$ monolayers: two new low-dimensional materials for Li-ion and Na-ion batteries†

Tao Bo, Peng-Fei Liu, Junrong Zhang, Fangwei Wang and Bao-Tian Wang

In this study, we report two new Mo$_2$B$_2$ monolayers and investigate their stabilities, electronic structures, lattice dynamics, and properties as anode materials for energy storage by using the crystal structure prediction technique and first-principles method. The calculated phonon spectra and electrical structures indicate that our predicted tetragonal and trigonal Mo$_2$B$_2$ (tet- and tri-Mo$_2$B$_2$) monolayers possess excellent electronic conductivity and great stability. The adsorption energies of Li/Na on them are negative enough to ensure stability and safety under operating conditions. Besides, tet-Mo$_2$B$_2$ possesses a theoretical specific capacity of ~251 mAh g$^{-1}$ for both Li- and Na-ion batteries (LIBs and NIBs), while tri-Mo$_2$B$_2$ possesses ~251 and ~188 mA h g$^{-1}$ for LIBs and NIBs, respectively. The diffusion energy barriers of Li/Na over tet- (0.029/0.010 eV) and tri- (0.023/0.013 eV) Mo$_2$B$_2$ are very small, indicating their excellent charge/discharge capability. In addition, the low electrode potential of Li/Na-intercalated tet- and tri-Mo$_2$B$_2$ is beneficial to their performance as anode materials. This work is of great importance for widening the families of both anode materials for LIBs/NIBs and two-dimensional transition metal borides.

1. Introduction

Rechargeable LIBs, one of the most successful and efficient energy storage technologies, have been widely used in portable electronic devices and electric vehicles.\(^1\) LIBs have many advantages such as high power density, superior energy efficiency, long cycle life, and portability.\(^2,3\) However, the storage of lithium sources on Earth is rather limited, and the amount of Li in the earth’s crust is only 20 mg kg$^{-1}$.\(^4\) With the reduction of lithium resources, next-generation storage technology will rely on other metal-ion battery devices that are composed of earth-abundant materials. A potential candidate to replace LIBs is the rechargeable NIBs, which have attracted increasing attention because of the abundance of Na on Earth (28 400 mg kg$^{-1}$)\(^7\) and their low cost. The challenge associated with applying LIBs and NIBs is obtaining a large storage capacity and high charging/discharging rates, which is highly dependent on the performance of their electrode materials.\(^9,10\) The widely used commercial anode material for LIBs, graphite, possesses several advantages such as high coulombic efficiency, relatively good cycling stability, and low cost.\(^1,11\) However, its performance is limited due to poor rate capability arising from the low diffusivity of Li atoms within it.\(^1\) Moreover, graphite cannot function well in NIBs, primarily due to the weak Na–C interaction.\(^13\) Therefore, the search for a high-performance anode material is urgently needed for the development of both LIBs and NIBs.

In recent years, owing to their superior mechanical properties, high surface area, and high electron mobility, two-dimensional (2D) materials including pristine/defected/doped graphene, phosphorene, borophene, silicon, MXenes, and transition metal dichalcogenides (TMDs) have attracted wide attention as promising choices as anode materials for LIBs and NIBs.\(^21,22\) It is generally known that MXenes\(^24\) are attracting increasing interest due to their excellent properties for various applications. So far, many MXenes including Ti$_3$C$_2$, Ti$_2$C$_2$, Nb$_2$C, V$_2$C, Ti$_2$C$_3$, Ti$_2$CN, and Mo$_2$C have been synthesized\(^25\) and most of them have been explored as anode materials.\(^26,27\) Besides, 2D TMDs, such as VS$_2$ and MoS$_2$, have also attracted wide attention and have been applied to a broad range of applications in catalysis, hydrogen...
storage, and electrode materials.\textsuperscript{21,22,28} Recently, the successful
synthesis of borophene has aroused the research enthusiasm of
boron-related 2D materials.\textsuperscript{29} Scientists began to think about
whether transition metals and boron can form novel 2D materials
similar to MXenes.\textsuperscript{30,31} For example, Guo et al.\textsuperscript{30} investigated the
possibility of exfoliating a family of layered orthorhombic transition
metal borides into 2D materials including Mo\textsubscript{2}B\textsubscript{2}, Cr\textsubscript{2}B\textsubscript{2},
Fe\textsubscript{2}B\textsubscript{2}, and W\textsubscript{2}B\textsubscript{2} and studied the properties of Mo\textsubscript{2}B\textsubscript{2} and Fe\textsubscript{2}B\textsubscript{2} as
anode materials for LIBs. Jiang et al.\textsuperscript{31} reported an orthorhombic 2D
Mo\textsubscript{2}B\textsubscript{2} material by using \textit{ab initio} high-throughput calculations.
In our recent work, we reported a family of hexagonal 2D
transition metal borides including Ti\textsubscript{2}B\textsubscript{2}, Mo\textsubscript{2}B\textsubscript{2} and so on and
explored Ti\textsubscript{2}B\textsubscript{2} as an anode material for LIBs and NIBs.\textsuperscript{32}

As mentioned above, two kinds of structures were reported
for 2D Mo\textsubscript{2}B\textsubscript{2}: orthorhombic and hexagonal phases. Owing to the
diversity of three-dimensional structures of molybdenum borides,\textsuperscript{33,34} a question arises naturally: Are there any other
structures more stable than the reported ones? Through structural
prediction by using the CALYPSO code,\textsuperscript{35} in this work, we
obtain two new 2D structures of tetragonal and trigonal Mo\textsubscript{2}B\textsubscript{2}
tetra- and tri-Mo\textsubscript{2}B\textsubscript{2}) with lower energies than the orthorhombic
and hexagonal ones. Then, we use the first-principles method
to investigate the stabilities, electronic structures, lattice dynamics,
and the properties of our obtained tetra- and tri-Mo\textsubscript{2}B\textsubscript{2} monolayers
as anode materials for LIBs and NIBs. The targeted research
interests include: (1) geometrical structures, electrical structures
and phonon spectra of tetra- and tri-Mo\textsubscript{2}B\textsubscript{2}, (2) the adsorption sites and
ergases of Li/Na on tetra- and tri-Mo\textsubscript{2}B\textsubscript{2}, (3) the theoretical
specific capacities and voltage profiles of tetra- and tri-Mo\textsubscript{2}B\textsubscript{2} for
LIBs and NIBs, and (4) the diffusion barriers of Li/Na on tetra- and
tri-Mo\textsubscript{2}B\textsubscript{2} monolayers.

2. Computational method

The particle-swarm optimization (PSO) scheme, as implemented
in the CALYPSO code,\textsuperscript{35–37} is employed to search for the lowest-energy structures of 2D Mo\textsubscript{2}B\textsubscript{2}. In our PSO calculations, both
planar and buckled structures including one, two, and three
layers are all considered. The population size and the number of
generations are set to be 30. Simulating cells containing 1, 2, and
4 formula units are considered for 2D Mo\textsubscript{2}B\textsubscript{2}. After all the
structure search calculations are completed, thousands of new
structures of 2D Mo\textsubscript{2}B\textsubscript{2} are generated. The CALYPSO code can
rank these new structures in order of enthalpy from low to high.
Then we select more than ten different structures with the lowest
energies for more accurate optimization and phonon spectrum
calculation. After optimization, the accurate total energies of
these structures are obtained and the structure with the lowest
total energy is the global minimum structure.

The energy calculations and structure optimizations are
carried out by using the density functional theory (DFT) method,
within the Perdew–Burke–Ernzerhof form of the generalized gradien
approximation (PBE-GGA)\textsuperscript{38} as implemented in the Vienna
Ab initio Simulation Package (VASP).\textsuperscript{39} The projector augmented
wave (PAW) method\textsuperscript{40} is used to treat the electron–ion interaction.

Spin-polarization is included in all the studied systems. The cutoff
energy is set as 600 eV and the atomic positions are fully relaxed
until the maximum force on each atom is less than 0.005 eV Å\textsuperscript{-1}.
The optB86b-vdW exchange functional\textsuperscript{41} is used for the van der
Waals (vdW) correction since it can properly treat the long-range
dispersive interactions. A $2 \times 2$ supercell of Mo\textsubscript{2}B\textsubscript{2} monolayers is
employed to model the adsorption and diffusion of Li and Na, and
the Brillouin zone (BZ) integration is performed using a $5 \times 5 \times 1$
k-point grid. A vacuum separation is set to more than 20 Å to
prevent any interaction between two neighboring monolayers.

Phonon dispersion calculations are based on density-functional
perturbation theory (DFT)\textsuperscript{42} as done in the Phonopy code.\textsuperscript{43} The
Born–Oppenheimer \textit{ab initio} molecular dynamics (AIMD) simulations
in the NVT ensemble are employed at different temperatures
up to 2400 K to investigate the thermal stability of the Mo\textsubscript{2}B\textsubscript{2}
monolayers. The AIMD simulations are performed using a $3 \times 3$
supercell and last for 10 ps with time steps of 1.0 fs. The climbing
image nudged elastic band (CI-NEB) method\textsuperscript{44} is employed to
investigate the diffusion pathway and energy barriers for transport
of Li and Na over the Mo\textsubscript{2}B\textsubscript{2} monolayers. Eight images including
the initial and the final positions are used for the CI-NEB
calculations.

The cohesive energy is defined as:

\[ E_{\text{coh}} = \frac{(2E_{\text{Mo}} + 2E_{\text{B}} - E_{\text{Mo}\textsubscript{2}B\textsubscript{2}})}{4} \]  

(1)

where $E_{\text{Mo}}$, $E_{\text{B}}$, and $E_{\text{Mo}\textsubscript{2}B\textsubscript{2}}$ are the total energy of a Mo atom, a
B atom and a unit cell of the Mo\textsubscript{2}B\textsubscript{2} monolayer, respectively.

The adsorption energy of Li/Na on the monolayer is defined as:

\[ E_{\text{ad}} = (E_{\text{M}\textsubscript{Mo}\textsubscript{2}B\textsubscript{2}} - E_{\text{Mo}\textsubscript{2}B\textsubscript{2}} - nE_{\text{M}})/n \]  

(2)

where $E_{\text{M}\textsubscript{Mo}\textsubscript{2}B\textsubscript{2}}$ and $E_{\text{Mo}\textsubscript{2}B\textsubscript{2}}$ are the total energies of Mo\textsubscript{2}B\textsubscript{2} with
and without Li/Na adatoms, respectively, $E_{\text{M}}$ represents the
total energy per atom for the bulk Li/Na metal, and $n$ denotes the
number of adsorbed Li/Na atoms. The average adsorption
ergy of Li/Na on the second layer is defined as:

\[ E_{\text{ave}} = (E_{\text{M}\textsubscript{Mo}\textsubscript{2}B\textsubscript{2} - E_{\text{Mo}\textsubscript{2}B\textsubscript{2} - nE_{\text{M}}}}/n \]  

(3)

where $E_{\text{M}\textsubscript{Mo}\textsubscript{2}B\textsubscript{2}}$ and $E_{\text{Mo}\textsubscript{2}B\textsubscript{2}}$ are the total energies of 2D
Mo\textsubscript{2}B\textsubscript{2} with $m$ and $(m-1)$ adsorbed Li/Na layers, $n$ denotes the
number of adsorbed Li/Na atoms in each layer, $E_{\text{M}}$ stands for
the total energy per atom for the bulk Li/Na. The theoretical
capacity can be obtained from:

\[ C_A = czF/M_{\text{Mo}\textsubscript{2}B\textsubscript{2}} \]  

(4)

where $c$ is the number of adsorbed Li/Na atoms, $z$ is the valence
number of Li/Na, $F$ is the Faraday constant (26 801 mA h mol$^{-1}$),
and $M_{\text{Mo}\textsubscript{2}B\textsubscript{2}}$ is the molar weight of Mo\textsubscript{2}B\textsubscript{2}. The enthalpies of
formation for all $M_{\text{Mo}\textsubscript{2}B\textsubscript{2}}$ ($M = \text{Li}, \text{Na}$) compounds with respect
to Mo\textsubscript{2}B\textsubscript{2} and Li/Na metal as the reference states are calculated
using the following equation:

\[ \Delta H = (E_{\text{M}\textsubscript{Mo}\textsubscript{2}B\textsubscript{2} - E_{\text{Mo}\textsubscript{2}B\textsubscript{2} - xE_{\text{M}}}}/(x + 1) \]  

(5)

where $E_{\text{M}\textsubscript{Mo}\textsubscript{2}B\textsubscript{2}}$ is the energy of the $M_{\text{Mo}\textsubscript{2}B\textsubscript{2}}$ compound per
Mo\textsubscript{2}B\textsubscript{2} formula unit, $E_{\text{Mo}\textsubscript{2}B\textsubscript{2}}$ is the energy of Mo\textsubscript{2}B\textsubscript{2} per Mo\textsubscript{2}B\textsubscript{2}
formula unit, and $E_{\text{M}}$ is the energy per atom for the Li/Na
bulk metal. For every concentration $x$ of the $M_{\text{Mo}\textsubscript{2}B\textsubscript{2}}$
compound, the electrode potential $V$ with respect to M/M$^+$ is calculated as:\textsuperscript{45}

$$V = -\frac{E(x_2) - E(x_1) - (x_2 - x_1)E(M)}{e(x_2 - x_1)} \quad (M = \text{Li, Na}) \quad (6)$$

where $E(x_2)$ and $E(x_1)$ are the total energies of $\text{M}_x\text{Mo}_2\text{B}_2$ at two adjacent concentrations $x_2$ and $x_1$, and $E(M)$ is the total energy per atom for the bulk Li/Na.

### 3. Results and discussion

#### 3.1 Geometrical structures of tetr- and tri-Mo$_2$B$_2$

We successfully obtained several low-energy 2D Mo$_2$B$_2$ structures through a thorough structural search by using the CALYPSO code. The obtained tetragonal Mo$_2$B$_2$ monolayer (see Fig. 1a) is the global minimum structure, which is energetically (by 0.093 eV per atom) more stable than the obtained trigonal Mo$_2$B$_2$ monolayer (see Fig. 1b) which possesses the second lowest energy. The other metastable structures are shown in Fig. S1 in the ESI.\textsuperscript{1} We find that the structure of the tetr-Mo$_2$B$_2$ monolayer (see Fig. 1a) is similar to that of 2D TiC reported by Fan \textit{et al}.\textsuperscript{46} which is subjected to the tetragonal $P4/nmm$ space group. The optimized lattice parameters are $a = b = 3.07$ Å, which are close to those of TiC (2.99 Å).\textsuperscript{46} In this tetr-Mo$_2$B$_2$ monolayer, each Mo (B) atom is surrounded by the nearest four B (Mo) atoms in the $xy$ plane and the nearest one B (Mo) atom in the $z$ direction to form a tetragonal lattice. The calculated bond length of Mo–B in tetr-Mo$_2$B$_2$ is 2.19 Å in the $xy$ plane and 2.25 Å in the $z$ direction. The minimum value of line charge density along Mo–B bonds is about 0.07–0.08 e per a.u.$^3$, which is prominently higher than that of the Na-Cl bond in the typical ionic crystal NaCl (0.007 e per a.u.$^3$)\textsuperscript{47} but is smaller than that of the Si covalent bond (0.104 e per a.u.$^3$).\textsuperscript{47} This indicates that Mo and B atoms are bonded with covalent and ionic mixed features. The obtained tetr-Mo$_2$B$_2$ (see Fig. 1b) is subjected to the trigonal $P$3$m$1 space group, which consists of a distorted boron honeycomb sheet sandwiched between two hexagonal planes of Mo atoms with the calculated lattice parameters of $a = b = 2.85$ Å. The minimum value of line charge density for B–B bonds (0.116 e per a.u.$^3$) is higher than that of the Si covalent bond (0.104 e per a.u.$^3$)\textsuperscript{47} indicating that the B layers are strongly bonded by B–B bonds. Besides, the minimum value for Mo–B bonds is about 0.08 e per a.u.$^3$, which is similar to that for Mo–B bonds in tetr-Mo$_2$B$_2$, indicating covalent and ionic mixed features in the Mo–B bonds. The optimized bond lengths of B–B and B–Mo are 1.76 and 2.27 Å, respectively. We also obtain an orthorhombic 2D Mo$_2$B$_2$ monolayer (see Fig. S1b, ESI\textsuperscript{1}), which has been reported by Guo \textit{et al}.\textsuperscript{30} The energy of this orthorhombic 2D Mo$_2$B$_2$ is higher by 0.205 (0.113) eV per atom than that of our obtained tetr-Mo$_2$B$_2$ (tri-Mo$_2$B$_2$), indicating that our obtained tetr- and tri-Mo$_2$B$_2$ monolayers are more stable in energy.

#### 3.2 Electrical structures and phonon spectra of tetr-Mo$_2$B$_2$ and tri-Mo$_2$B$_2$

The electronic properties of anode materials have an important influence on the cycle characteristics of LIBs.\textsuperscript{48,49} Therefore, we calculated the electronic band structures and PDOS of the tetr- (see Fig. 2a) and tri-Mo$_2$B$_2$ (see Fig. 2c) monolayers. The nonzero DOS at the Fermi energy indicates that tetr- and tri-Mo$_2$B$_2$ possess metallic properties. The metallicity of tetr-Mo$_2$B$_2$ mainly originates from Mo 4p orbital contribution, while the metallicity of tri-Mo$_2$B$_2$ mainly originates from Mo 4p and 4d orbital contribution. The contribution of B-2p is negligible. The outstanding electronic conductivity indicates that these Mo$_2$B$_2$ monolayers have potential application prospects for LIBs and NIBs.

The stability of anode materials is very important due to hundreds of charge–discharge cycles in practical applications. Cohesive energy is a well-accepted parameter that can be used to evaluate whether a predicted 2D material is easy to synthesize experimentally.\textsuperscript{6,50} According to eqn (1), the calculated cohesive energies of the tetr- and tri-Mo$_2$B$_2$ monolayers are 6.49 and 6.40 eV per atom, respectively, which are higher than those of Cu$_2$Si (3.46 eV per atom),\textsuperscript{51} Al$_2$C$_2$ (4.58 eV per atom),\textsuperscript{52} Be$_2$C (4.86 eV per atom),\textsuperscript{53} and h-BeN$_2$ (4.98 eV per atom)\textsuperscript{54} monolayers. The relatively large cohesive energies suggest that these Mo$_2$B$_2$ monolayers are likely to be synthesized under certain experimental conditions. To obtain the dynamic stability of the tetr- and tri-Mo$_2$B$_2$ monolayers, we calculate their phonon dispersion curves. There are no imaginary frequencies within the entire BZ, indicating that both tetr- (see Fig. 2b) and tri-Mo$_2$B$_2$ (see Fig. 2d) monolayers are dynamically stable. Furthermore, the highest frequencies of the tetr- and tri-Mo$_2$B$_2$ monolayers are 22 THz (733 cm$^{-1}$) and 25 THz (833 cm$^{-1}$), respectively, which are higher than those of tetragonal TiN (668 cm$^{-1}$),\textsuperscript{46} silicene (580 cm$^{-1}$),\textsuperscript{55} Cu$_2$Si (420 cm$^{-1}$),\textsuperscript{56} arsenene (225 cm$^{-1}$),\textsuperscript{57} antimonene (325 cm$^{-1}$),\textsuperscript{56} and MoS$_2$ (473 cm$^{-1}$),\textsuperscript{57} indicating strong abilities of these two 2D Mo$_2$B$_2$ structures. For both tetr- and tri-Mo$_2$B$_2$ monolayers, the main contribution to the phonon modes at high-frequency is entirely from the B atoms while at low-frequency the contribution is entirely from Mo atoms. In order to understand the thermal stability, AIMD simulations were carried out for these Mo$_2$B$_2$ monolayers at temperatures of 300, 900, 1500, and 2100 K, respectively. Fig. S2 and S3 (ESI\textsuperscript{1}) show the variation of total energy with time for the tetr- and tri-Mo$_2$B$_2$ monolayers.
tri-Mo$_2$B$_2$ monolayers at different temperatures, respectively. The average value of the total energy of the tetr- and tri-Mo$_2$B$_2$ monolayers remains almost constant during the whole simulation at 300, 900, and 1500 K. After simulating for 10 ps at 1500 K, the original geometries of the tetr- and tri-Mo$_2$B$_2$ monolayers remain intact with only slight in-plane and out-of-plane deformations (see Fig. S4 and S5, ESI†). These results confirm that the tetr- and tri-Mo$_2$B$_2$ monolayers are thermally stable even at a high temperature of 1500 K. The radial distribution function (RDF) of the tetr- (see Fig. S6, ESI†) and tri-Mo$_2$B$_2$ (see Fig. S7, ESI†) monolayers is also calculated at 300, 900, 1500, and 2100 K, respectively. At 300, 900, and 1500 K, for both tetr- and tri-Mo$_2$B$_2$ monolayers, the RDF has many peaks between 1 and 8 Å, indicating that these two materials are in long range order. The above results indicate that the geometric configurations of these Mo$_2$B$_2$ monolayers are expected to be highly stable.

3.3 Adsorption sites of Li and Na on tetr- and tri-Mo$_2$B$_2$

If a material is to be used as an anode in LIBs/NIBs, it must have a strong ability to adsorb the Li/Na adatoms. In order to obtain stable adsorption structures of Li/Na on the surfaces of the tetr- and tri-Mo$_2$B$_2$ monolayers, we carried out a lot of simulations starting with different initial states (as shown in Fig. S8 and S9, ESI†). It can be seen that for different initial states, the Li ions will eventually be optimized on the high symmetry adsorption sites. According to the above results and the symmetry of the structures, three and four high symmetry adsorption sites will be discussed for the tetr- (see Fig. 3a) and tri-Mo$_2$B$_2$ (see Fig. 3b) monolayers, respectively. For tetr-Mo$_2$B$_2$, sites S1 and S3 are on top of Mo and B atoms, respectively, while site S2 is above the center of two B atoms. According to eqn (2), the adsorption energies of Li/Na (see Fig. 3c) are $-0.450/-0.704$, $-0.777/-0.837$, and $-0.748/-0.826$ eV on the S1, S2, and S3 sites, respectively. The calculated results show that the most stable adsorption site for Li/Na is above the center of two B atoms (S2 site). The adsorption energy of Li on S2 ($-0.777$ eV) is comparable to that on the orthorhombic 2D Mo$_2$B$_2$ monolayer ($-0.81$ eV) reported by Guo et al.$^{30}$ Obviously, this adsorption energy ($-0.777$ eV) is much lower than that on tetr-TiC ($-0.16$ eV) and tetr-TiN ($+0.31$ eV),$^{46}$ indicating more stable adsorption of Li on tetr-Mo$_2$B$_2$ than on tetr-TiC or tetr-TiN which has a uniform structure. For tri-Mo$_2$B$_2$, sites S1 and S4 are on top of B and Mo atoms, respectively, while sites S2 and S3 are above the center of three Mo atoms and two Mo atoms, respectively. The adsorption energies of Li/Na (see Fig. 3d) are $-0.540/-0.671$, $-0.542/-0.677$, $-0.519/-0.664$, and $-0.316/-0.537$ eV on S1, S2, S3, and S4 sites, respectively. We find that the adsorption of Li/Na on S2 is the most stable, and the adsorption energies are comparable to those on the well-known Mo$_2$C$_{26}$ ($-0.58/-0.77$ eV for Li/Na) which is made up of two sheets of Mo atoms and an intermediate sheet of C atoms. Besides, the adsorption energies on S4 are the largest, which are larger by 0.127–0.226 eV than those on S1, S2, and S3. This indicates that it is not possible for Li/Na to appear on top of Mo atoms. The similarity of the adsorption energies on S1, S2, and S3 suggests that the Li/Na atoms easily transfer along the S1–S3–S2 direction. For both tetr- and tri-Mo$_2$B$_2$, the adsorption of Na is more stable.
than that of Li for all the adsorption sites. In general, negative adsorption energies for all the adsorption sites mentioned above indicate that Li and Na atoms prefer adsorption over tetr- and tri-Mo$_2$B$_2$ rather than cluster formation, which is important for the safe operation of LIBs and NIBs.

### 3.4 Theoretical specific capacity

As we know, the storage capacity is a key factor in evaluating the performance of an electrode material, and promising electrode materials require large storage capacity. In order to obtain the storage capacities of tetr- and tri-Mo$_2$B$_2$, we calculate the Li/Na adsorption at higher concentrations on the surfaces of tetr- and tri-Mo$_2$B$_2$. We present in Fig. 4 the most stable adsorption structures and the corresponding adsorption energies for Li adsorption on the surface of tetr-Mo$_2$B$_2$. As discussed above, the S2 site is the most stable adsorption site for the adsorption of a single Li atom which corresponds to Li$_{0.25}$Mo$_2$B$_2$ and possesses an energy of $-0.777$ eV. For the adsorption of two Li atoms, corresponding to Li$_{0.5}$Mo$_2$B$_2$, Li atoms adsorbed on the S2 sites of both sides are the most stable. The average adsorption energy is $-0.772$ eV, which is almost the same as that of Li$_{0.25}$Mo$_2$B$_2$. For the adsorption of three Li atoms, corresponding to Li$_{0.75}$Mo$_2$B$_2$, two Li atoms adsorbed on the S3 sites of one side and the third Li atom adsorbed on the S2 site of the other side are the most stable. We find that when two Li atoms adsorb on one side of tetr-Mo$_2$B$_2$, they prefer to adsorb on S3 sites rather than on S2 sites, which is different from the adsorption of one Li atom. The average adsorption energy ($-0.716$ eV) is about $0.06$ eV higher than those of Li$_{0.25}$Mo$_2$B$_2$ and Li$_{0.5}$Mo$_2$B$_2$, which results from the repulsion between Li atoms. For the adsorption of four Li atoms, corresponding to Li$_{1.0}$Mo$_2$B$_2$, unlike the above three configurations, the most stable adsorption structure is that in which all Li atoms adsorb on S3 sites at the same side. The average adsorption energy is $-0.785$ eV, which is lower than those of the above three configurations. The same phenomenon occurred in tetr-TiN.$^{46}$ In that work, the authors found that compared with the adsorption of a single Li atom, more electrons are transferred from the adsorbed Li to the substrate for the adsorption of four Li atoms, resulting in the decrease in average adsorption energy of Li. For the adsorption of five, six, and seven Li atoms, corresponding to Li$_{1.25}$Mo$_2$B$_2$, Li$_{1.5}$Mo$_2$B$_2$, and Li$_{1.75}$Mo$_2$B$_2$, respectively, the average adsorption energies are $-0.799$, $-0.784$, and $-0.785$ eV, respectively, which are comparable to that of Li$_{1.0}$Mo$_2$B$_2$. However, the average adsorption energy for the adsorption of eight Li atoms is $-0.835$ eV, which is the lowest among all the configurations mentioned above. The average adsorption energy gradually decreases as the Li concentration increases from Li$_{0.25}$Mo$_2$B$_2$, via Li$_{1.0}$Mo$_2$B$_2$, to Li$_{2.8}$Mo$_2$B$_2$. This trend is also seen in the orthorhombic 2D Mo$_2$B$_2$ monolayer.$^{30}$
The adsorption energies of Li on the orthorhombic 2D Mo\(_2\)B\(_2\) monolayer are \(-0.81\), \(-0.98\), and \(-1.01\) eV for Li\(_{0.25}\)Mo\(_2\)B\(_2\), Li\(_{1.0}\)Mo\(_2\)B\(_2\), and Li\(_{1.0}\)Mo\(_2\)B\(_2\), respectively.\(^{30}\)

For Na adsorption on tetra-Mo\(_2\)B\(_2\), we calculate the adsorption of one to eight Na atoms and present in Fig. S10 (ESI\(^\dagger\)) the most stable adsorption structures and the corresponding adsorption energies. For the adsorption of one, two, and three Na atoms, corresponding to Na\(_{0.25}\)Mo\(_2\)B\(_2\), Na\(_{0.5}\)Mo\(_2\)B\(_2\), and Na\(_{0.75}\)Mo\(_2\)B\(_2\), respectively, the most stable structures are the same as those for Li adsorption. However, for the adsorption of four Na atoms (Na\(_{1.0}\)Mo\(_2\)B\(_2\)), the most stable adsorption structure is that in which two Na atoms adsorb on the S3 sites of one side and the other two Na atoms adsorb on the S3 sites of the other side, which is different from the adsorption structure of four Li atoms. The average adsorption energies are \(-0.837\), \(-0.822\), \(-0.733\), and \(-0.702\) eV for Na\(_{0.25}\)Mo\(_2\)B\(_2\), Na\(_{0.5}\)Mo\(_2\)B\(_2\), Na\(_{0.75}\)Mo\(_2\)B\(_2\), and Na\(_{1.0}\)Mo\(_2\)B\(_2\), respectively. It can be seen that the average adsorption energy increases with the increase of Na concentration, which is because of the large exchange interaction between the Na atoms. With the increase of Na concentration, the adsorption energy continues to increase. Though the adsorption energy for Na\(_{2.0}\)Mo\(_2\)B\(_2\) (\(-0.515\) eV) is about 0.3 eV higher than that of Na\(_{0.25}\)Mo\(_2\)B\(_2\), the large negative value is enough to stabilize the adsorption of eight Na atoms. Thus, the first layer can accommodate at most eight Li/Na atoms on both sides of the tetra-Mo\(_2\)B\(_2\) surface.

The most stable adsorption structures for Li and Na adsorption on the tri-Mo\(_2\)B\(_2\) surface are presented in Fig. S11 and S12 (ESI\(^\dagger\)), respectively. For Li adsorption, the average adsorption energy remains almost unchanged as the Li concentration increases from Li\(_{0.25}\)Mo\(_2\)B\(_2\) to Li\(_{1.0}\)Mo\(_2\)B\(_2\) but keeps increasing as the Li concentration increases from Li\(_{1.75}\)Mo\(_2\)B\(_2\) to Li\(_{2.0}\)Mo\(_2\)B\(_2\). For Na adsorption, the average adsorption energy increases rapidly from Na\(_{0.3}\)Mo\(_2\)B\(_2\) to Na\(_{1.5}\)Mo\(_2\)B\(_2\). The smaller lattice constant of tri-Mo\(_2\)B\(_2\) (2.85 Å) than that of tetra-Mo\(_2\)B\(_2\) (3.07 Å) enables a larger exchange interaction between the adatoms. We find that the first layer can accommodate at most eight Li atoms (see Fig. S11, ESI\(^\dagger\)) or six Na atoms (see Fig. S12, ESI\(^\dagger\)) on both sides of the tri-Mo\(_2\)B\(_2\) surface.

It is well known that temperature rise can influence the simulations. In order to evaluate the thermal stability for Li/Na adsorption on the tetra- and tri-Mo\(_2\)B\(_2\) surfaces, we carry out AIMD simulations at a temperature of 300 K for the tetra- and tri-Mo\(_2\)B\(_2\) monolayers adsorbed with one layer of Li/Na. The variation of total energies with time is presented in Fig. S13 (ESI\(^\dagger\)), while the final structures after 3 ps simulations are presented in Fig. S14 (ESI\(^\dagger\)). We find that the total energies remain almost constant during the whole simulation. Besides, the final structures after 3 ps simulations remain intact and Li/Na ions are still adsorbed on the tetra- and tri-Mo\(_2\)B\(_2\) monolayers. These results confirm that Li/Na can adsorb on the tetra- and tri-Mo\(_2\)B\(_2\) monolayers stably at an ambient temperature of 300 K.

The adsorption of two layers of Li/Na on tetra- and tri-Mo\(_2\)B\(_2\) is also investigated. According to eqn (3) that has been applied to many materials,\(^{26,54,59}\) the adsorption energies of Li/Na in the second layer are close to zero or a very small positive value, which indicates that the adsorption of two layers of Li/Na is not stable on tetra- and tri-Mo\(_2\)B\(_2\) monolayers. Furthermore, in practical applications, a much larger spacing is needed between the Mo\(_2\)B\(_2\) monolayers to accommodate multilayer adsorption. Thus, the maximum capability of Li storage is Li\(_{2.0}\)Mo\(_2\)B\(_2\) for both tetra- and tri-Mo\(_2\)B\(_2\) monolayers, while the maximum capability of Na storage is Na\(_{2.0}\)Mo\(_2\)B\(_2\) and Na\(_{4.0}\)Mo\(_2\)B\(_2\) for tetra- and tri-Mo\(_2\)B\(_2\) monolayers, respectively. The capability of Na storage for our tetra- and tri-Mo\(_2\)B\(_2\) is much larger than that of the well-known hexagonal Mo\(_2\)C monolayer (NaMo\(_2\)C).\(^{36}\) According to these results and eqn (4), the theoretical specific capacities of tetra-Mo\(_2\)B\(_2\) as an electrode are \(-251\) mA h g\(^{-1}\) for LIBs and NIBs, while the theoretical specific capacities of tri-Mo\(_2\)B\(_2\) are \(-251\) and \(-188\) mA h g\(^{-1}\) for LIBs and NIBs, respectively.

### 3.5 Voltage profile

During the operation of the LIBs and NIBs, the Li/Na ion concentration and the corresponding electrode potential vary with the current direction.\(^{60}\) The voltage profiles are of great...
significance for deep understanding of the performance of an electrode material. Thus, according to eqn [5], we calculate the enthalpies of formation for Li/Na-Mo2B2 at each Li/Na concentration to investigate the stability of all the intermediate phases. Then, according to the stable intermediate phases and eqn [6], we investigate the concentration-dependent profile of the electrode potential for Li/Na-intercalated tetra- and tri-Mo2B2. We present in Fig. 5a and b the enthalpies of formation for Li0.5Mo2B2 and Na0.5Mo2B2 with respect to tetra-Mo2B2 and Li/Na bulk metal and the convex hull for the enthalpies of formation. Structures located on the hull are thermodynamically stable relative to dissociation into other configurations. The detailed reasons are given in Section S4 of the ESI.† As shown in Fig. 5a, the calculated convex hull of Li0.5Mo2B2 displays only one stable intermediate phase, Li2.0Mo2B2. Thus, the calculation of the electrode potential vs. Li/Li+ only needs to consider one phase located on the hull. We present in Fig. 5c the voltage profile for Li insertion. It presents only one plateau at 0.835 V vs. Li/Li+. On the other hand, Na insertion winds up with the Na0.5Mo2B2 (x = 0.25, 0.5, 1.0, and 2.0) compounds lying on the convex hull (see Fig. 5b). Therefore, the calculation of the electrode potential vs. Na/Na+ should contain stable Na contents, Na0.5Mo2B2 (x = 0.25, 0.5, 1.0, and 2.0). As shown in Fig. 5d, the electrode potential for Na insertion varies in the range of 0.328–0.837 V with a decreasing trend with increasing capacity. Four main plateaus exist in the whole process of Na insertion. The initial plateau displays a voltage of 0.837 V vs. Li/Li+. The second and third plateaus show voltages of 0.807 V (Na0.25Mo2B2 → Na0.5Mo2B2) and 0.582 V (Na0.5Mo2B2 → Na1.0Mo2B2), respectively. The fourth plateau goes to 0.328 V vs. Na/Na+ which corresponds to Na1.0Mo2B2 → Na2.0Mo2B2. The average electrode potential of Na-intercalated tetr-Mo2B2 is 0.515 V, which is smaller than that of MoS2 (0.75 V).21

For tri-Mo2B2, we present in Fig. 6a and b the enthalpies of formation for Li0.5Mo2B2 and Na2.0Mo2B2 as well as the convex hull and in Fig. 6c and d the voltage profiles for Li and Na insertion. As shown in Fig. 6a, the Li0.5Mo2B2 (x = 0.5, 0.75, 1.0, 1.5, 2.0) compounds lie on the convex hull for Li insertion. Thus, there are five main plateaus in the Li insertion process from Mo2B2 to Li2.0Mo2B2 (see Fig. 6c), which correspond to Mo2B2 → Li0.5Mo2B2, Li1.5Mo2B2 → Li1.0Mo2B2, Li0.75Mo2B2 → Li1.5Mo2B2, Li1.0Mo2B2 → Li1.5Mo2B2, and Li1.5Mo2B2 → Li2.0Mo2B2, respectively. The voltages of these five plateaus are 0.562, 0.513, 0.464, 0.317, and 0.259 V vs. Li/Li+, respectively, and the average value is 0.407 V. For Na insertion, as shown in Fig. 6b, the Na2.0Mo2B2 (x = 0.5, 0.75, 1.0, 1.5) compounds lie on the convex hull, which indicates that there are four plateaus in the voltage profile. As shown in Fig. 6d, these four plateaus have voltages of 0.697, 0.379, 0.228, and 0.149 V vs. Na/Na+, respectively, and the average value is 0.383 V. The average potential of Na-intercalated tri-Mo2B2 (0.383 V) is similar to that of Li-intercalated tri-Mo2B2 (0.407 V). Interestingly, they are both smaller than that of MoS2 (0.75 V vs. Na/Na+).21 Since ideally a good anode material should have a low electrode potential,21 our calculated plateaus for tetra- and tri-Mo2B2 suggest that these two Mo2B2 monolayers show good performance as anode materials for LIBs and NIBs.

3.6 Diffusion barriers of Li/Na on tetra- and tri-Mo2B2 monolayers

The fast charge/discharge capability is a key factor in evaluating the performance of an electrode material. Because the rate capability of LIBs and NIBs is closely linked with Li/Na diffusion properties,
we need to investigate the diffusion paths and the corresponding energy barriers for Li/Na on tetr- and tri-Mo$_2$B$_2$. Fig. 7 illustrates three possible pathways (A-B, A-C, and A-D) between the neighboring lowest-energy adsorption sites (S2 sites) and the corresponding diffusion energy barriers for Li/Na diffusion on tetr-Mo$_2$B$_2$. The A–B (see Fig. 7a) and A–C (see Fig. 7b) pathways are both from one S2 site to another S2 site by passing over a boron atom on the surface. The energy barriers for Li diffusion along A–B and A–C pathways are 0.031 and 0.029 eV, respectively, while those for Na diffusion are 0.013 and 0.010 eV, respectively. We find that the energy barriers for Li/Na diffusion along the A–C pathway are a little smaller than those along the A–B pathway. However, the A–D pathway (see Fig. 7c) starting from one S2 site to another S2 site by passing over one surface Mo atom possesses very high energy barrier for Li/Na diffusion. The values are 0.350 and 0.159 eV for Li and Na diffusion, respectively, which are about ten times larger than those for A–B and A–C pathways. In general, the A–C pathway is the most suitable path for Li/Na diffusion on tetr-Mo$_2$B$_2$ owing to the lowest energy barriers.

![Fig. 6](https://example.com/fig6.png)

**Fig. 6** Enthalpies of formation for (a) Li$_n$Mo$_2$B$_2$ and (b) Na$_n$Mo$_2$B$_2$ systems with respect to 2D tri-Mo$_2$B$_2$ and Li/Na bulk metal. Data points located on the convex hull (solid squares) represent stable adsorption against any type of decomposition. The metastable phases are indicated by open squares. The abscissa represents the percentage of Li/Na in Li/Na$_n$(Mo$_2$B$_2$). Electrode potential of (c) Li-intercalated tri-Mo$_2$B$_2$ against Li/Li$^+$ and (d) Na-intercalated tri-Mo$_2$B$_2$ against Na/Na$^+$.

![Fig. 7](https://example.com/fig7.png)

**Fig. 7** (a–c) Top views of three pathways for Li/Na diffusion on the tetr-Mo$_2$B$_2$ monolayer. The Mo, B, and Li/Na atoms are denoted in violet, green, and blue, respectively. (d) Diffusion energy barriers of Li and Na on tetr-Mo$_2$B$_2$. 

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for Li/Na. Thus, according to the characteristics of the A–C pathway, the Li/Na atom can diffuse along a straight line in the B–B direction.

We present in Fig. 8 the most favorable pathway and corresponding energy barriers for Li/Na diffusion on the surface of tri-Mo$_2$B$_2$. Since the most stable adsorption site for Li/Na is the S$_2$ site, we consider one possible pathway starting from one S$_2$ site to another S$_2$ site. As shown in Fig. 8a, the optimized pathway is from A to B and can be viewed as S$_2$–S$_3$–S$_1$–S$_3$–S$_2$. The energy barriers for Li and Na diffusion are 0.023 and 0.013 eV, respectively. We find that the diffusion energy barrier for Li on tri-Mo$_2$B$_2$ (0.023 eV) is smaller than that on tetr-Mo$_2$B$_2$ (0.029 eV), while that for Na on tri-Mo$_2$B$_2$ (0.013 eV) is larger than that on tetr-Mo$_2$B$_2$ (0.010 eV). In any case, the energy barriers for Li/Na diffusion on tetr- and tri-Mo$_2$B$_2$ are all very low, which would be beneficial to increase the charge/discharge rate of LIBs and NIBs.

3.7 Comparison with other anode materials

To have a more comprehensive view of the properties of tetr- and tri-Mo$_2$B$_2$ as anode materials, we compare their theoretical specific capacities and diffusion barriers with those of other previously reported 2D anode materials. For Li storage as shown in Table 1, the theoretical specific capacities of tetr- and tri-Mo$_2$B$_2$ are 251 and 188 mA h g$^{-1}$, respectively, which are lower than those of graphite, orth-Mo$_2$B$_2$, silicene, 1T-Ti$_3$C$_2$, Mo$_2$C, and VS$_2$. Their Na conductivities are much faster than those of 1T-Ti$_3$C$_2$, B$_2$H$_2$, and Ca$_2$N. It is noteworthy that the diffusion energy barriers of Na on tetr- (0.010 eV) and tri-Mo$_2$B$_2$ (0.013 eV) are much lower than those on any other materials in Table 2, indicating a very high rate capability. The above evidence demonstrates that both tetr- and tri-Mo$_2$B$_2$ are promising candidates for anode materials in LIBs and NIBs.

4. Conclusions

The search for high-performance anode materials is urgently needed for the development of both LIBs and NIBs. In this study, we firstly reported two new 2D Mo$_2$B$_2$ structures with lower energies than that of previously reported ori-Mo$_2$B$_2$ by using crystal structure prediction techniques. Then, the geometric structures, phonon spectra, dynamical properties, and electrical properties of our obtained tetr- and tri-Mo$_2$B$_2$ monolayers have been studied. The results confirm that both tetr- and...
tri-Mo$_2$B$_2$ possess excellent electronic conductivity and great stability. Then, we investigated the adsorption and diffusion of Li and Na over tetr- and tri-Mo$_2$B$_2$ and evaluated their suitability as anode materials for LIBs and NIBs. The adsorption energies of Li/Na on tetr- and tri-Mo$_2$B$_2$ are $-0.777/-0.837$ and $-0.542/-0.677$ eV, respectively, which are negative enough to ensure stability and safety under operating conditions. Besides, the calculated theoretical specific capacities of tetr-Mo$_2$B$_2$ as an electrode are $\sim 251$ mA h g$^{-1}$ for LIBs and NIBs, while the theoretical specific capacities of tri-Mo$_2$B$_2$ are $\sim 251$ and $\sim 188$ mA h g$^{-1}$ for LIBs and NIBs, respectively. The capability of Na storage for our tetra- and tri-Mo$_2$B$_2$ is much larger than those of the well-known Mo$_2$C ($\sim 132$ mA h g$^{-1}$) and Mo$_2$S$_2$ ($\sim 146$ mA h g$^{-1}$). The calculated low electrode potential of tetra- and tri-Mo$_2$B$_2$ suggests that these two monolayers show very high Li/Na diffusion rates. The diffusion energy barriers of Li/Na over tetra- (0.029/0.010 eV) and tri-Mo$_2$B$_2$ (0.023/0.013 eV) are very small, which indicates that these two monolayers possess excellent charge/discharge capability for Li/Na. Overall, both tetra- and tri-Mo$_2$B$_2$ monolayers are excellent candidates as anode materials for LIBs and NIBs. Our work also opens up an avenue to explore new 2D transition metal borides with excellent properties.

**Conflicts of interest**

The authors declare no competing financial interest.

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