New family of layered N-based cathode materials for sodium-ion batteries

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The cathode materials of sodium-ion batteries (SIBs) have received considerable attention not only because of their abundant natural reserves and chemical properties similar to those of lithium-ion batteries but also their great potential in energy storage and conversion technologies. However, their low capacity and high diffusion barrier remain unsolved problems. In this work, we systematically studied the theoretical capacity and sodium ion diffusion barrier in a new family of layered transition metal compounds, named MX₂ (M = Ti, V, Cr, Mn, and Fe; X = C, N, and O), as the cathode materials of SIBs. The results indicate that all 2H-phase MX₂ materials possess a high theoretical capacity of over 300 mA h g⁻¹. Moreover, it is found that the 2H-phase CrN₂ exhibits a desirable sodium ion diffusion barrier, indicating high mobility of sodium ions. In addition, the layered CrN₂ has a remarkable voltage window (3.1–3.8 V) and outstanding electrochemical performance arising from the charge transfer between Na and N atoms, which is induced by the large electronegativity of nitrogen. Our research provides a promising candidate for application in SIB cathode materials in the future.

1. Introduction

Sodium-ion batteries (SIBs) have increasingly received attention not only because of their similar intercalation properties to lithium-ion batteries but also the wide distribution and low cost of sodium. Sodium-ion batteries exhibit remarkable electrochemical performance, including good cycle stability and high rate performance, which endow them with great application potential in the field of electric vehicles and large-scale energy storage. Cathode materials, as an important component of the sodium-ion battery, play a key role in improving battery performance and bringing down battery costs.

High-performance cathode material for SIBs calls for not only a high theoretical capacity but also good cycle stability and high-rate performance. Following the success of cathode materials of lithium-ion batteries, various cathode materials for SIBs have been reported, such as layered transition metal oxides, polyanionic compounds, Prussian blue analogs and organic materials. It is found that layered metal oxides, such as NaMO₂ (M = Co, Mn, Fe), have high theoretical capacity. However, the multi-phase transition is easily induced in layered metal oxide during the charge and discharge processes, which badly hinders the diffusion of sodium ions. On the contrary, polyanionic compounds, like NaMPO₄ (M = Mn, Fe, Co, Ni), have excellent cycle stability and high rate performance due to their fast sodium ion diffusion rates. The heavy polyanions lead to a limited specific capacity. Experimentally, the electrochemical performance of the electrode material has been improved by ion doping and morphology control, while their intrinsically low specific capacity and sodium ion diffusion properties have not been enhanced.

Recently, transition metal dichalcogenides (TMDs), such as MX₂ (M = Mo, W, Nb, Ta; X = S, Se), have attracted considerable attention due to their high theoretical capacity and graphite-like layered structure, which facilitates the intercalation and de-intercalation of sodium ions in the interlayer of TMDs. However, the phase transition and poor conductivity of TMDs impede their practical applications. Therefore, it is desirable to design a high-performance cathode material featuring high theoretical capacity, long cycle life and high rate performance. Some two-dimensional materials, such as monolayer ScO₂ (ref. 22), BP₂ (ref. 23) and V₂O₅, have a large specific surface area and an unrestricted sodium diffusion path, which make their excellent sodium storage capacity and diffusion properties. However, their generally poor conductive properties hinder the transmission of electrons. Furthermore, it is difficult for single-layer materials to achieve practical
applications in sodium-ion batteries. Recently, transition metal nitrides have been fabricated experimentally, and they have also received increasing attention theoretically. It is shown that N-based compounds have ultra-high hardness and good electrical conductivity, especially N-based TMDs-like layered transition metal compounds with a large interlayer spacing, which is conducive to the diffusion of large sodium ions. Two-dimensional transition metal N-based materials \((\text{N-based TMDs-like bulk materials})\) hold a great potential to become excellent cathode materials of SIBs.

Thanks to their excellent electrochemical performance, including suitable sodium ion diffusion rate, extraordinary theoretical capacity, stable structural framework, and high electronic conductivity, layered N-based TMDs-like bulk materials hold a great potential to become excellent cathode materials of SIBs. In this work, we have systematically studied the theoretical capacity and sodium ion diffusion barrier in layered bulk transition metal compounds named MX\(_2\) \((\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{and Fe}; \text{X} = \text{C}, \text{N}, \text{and} \text{O})\). Our results indicated that most of them possess high theoretical capacity and low sodium ion diffusion barrier. 2H-Phase bulk CrN\(_2\) in particular shows the lowest sodium ion diffusion barrier, revealing the high Na intercalation concentration in layered CrN\(_2\). Besides, the formation energy and phonon spectrum of materials. The formation energy \(E_{\text{form}}\) and phonon spectrum of materials. The formation energy \(E_{\text{form}}\) is defined as the formula (1):

\[
E_{\text{form}} = (E_{\text{NaMX}_2} - \mu_{\text{Na}} - \mu_{\text{M}} - 2\mu_{\text{X}})/4
\]

where the \(E_{\text{NaMX}_2}\) represents the total energy of a NaMX\(_2\) unit cell, and the \(\mu_{\text{Na}}, \mu_{\text{M}}\) and \(\mu_{\text{X}}\) are the chemical potential of Na, M and X atoms, respectively.

To study the diffusion properties of sodium ions in MX\(_2\), a 3 \times 3 \times 1 supercell consisting of 18 M atoms and 36 X atoms is used, and a 6 \times 6 \times 6 \text{K-point grid} is adopted. The diffusion performance of sodium in MX\(_2\) is calculated through the climbing image nudge elastic band (CI-NEB) method. \(\text{Specifically, a series of intermediate images are inserted between the optimized initial structure and the final structure, and then each image finds the lowest potential energy configuration along the reaction path. The energy and force convergence criteria of diffusion calculation are set to be } 10^{-8} \text{ eV and } 0.02 \text{ eV Å}^{-1} \text{ respectively to improve the calculation efficiency. This method can accurately locate the diffusion path of the lowest energy and the diffusion barrier.}

The theoretical capacity of C is calculated according to formula (2):

\[
C = \frac{nF_{\text{Faraday}}}{3.6M}
\]

where \(n\) is the valence electron number of sodium (here \(n = 1\)), \(F\) is the Faraday constant \((96485 \text{ C mol}^{-1})\), and \(M\) is the relative molecular mass of the MX\(_2\) molecular formula unit.

The equation for deriving voltage \(V\) is expressed as:

\[
V = -(E_{\text{Na}_{x_1}CrN}_2 - E_{\text{Na}_{x_1}x_1CrN}_2 - (x_2 - x_1)E_{\text{Na}})/(x_2 - x_1)e
\]

where \(E_{\text{Na}_{x_1}CrN}_2\) and \(E_{\text{Na}_{x_1}x_1CrN}_2\) represent the total energy of \(\text{Na}_{x_1}CrN_2\) and \(\text{Na}_{x_2}CrN_2\) respectively, \(E_{\text{Na}}\) represents the energy of a single sodium atom in metal sodium, and \(e\) is the electric quantity carried by every single electron \((1.6 \times 10^{-19} \text{ C})\).

3. Results and discussion

3.1. Screening of materials

There is a sandwich-like X-M-X structure similar to TMDs in MX\(_2\), in which each M atom is coordinated with six X atoms to form a triangular prism or octahedral coordination configuration, and each X atom is coordinated with three M atoms. Due to the difference in the coordination configuration of M and the stacking period along the c-axis, the materials have different configurations, among which 1T-phase and 2H-phase are the most common structural configurations in this type of material. In the 2H-phase, each M atom and six X atoms form a triangular prism, and the MX\(_2\) layer is stacked in AB order (as is shown in Fig. 1a). In the 1T-phase, each M atom is surrounded by six X atoms to form an octahedral coordination configuration, and the MX\(_2\) layer is stacked in AA order (as is shown in Fig. 1b). Therefore, a 1 \times 1 \times 2 supercell of 1T-phase
and $1 \times 1 \times 1$ unit-cell of 2H-phase were calculated, both of which have 2 MX$_2$ layers containing 2 M atoms and 4 X atoms.

To study the structural properties of different phases, we have fully optimized all 1T- and 2H-phase MX$_2$, and the fully optimized structures of these MX$_2$ are shown in Fig. S1,† and the lattice parameters of all MX$_2$ are shown in Table S1.† The cell parameters of 2H-phase VN$_2$ we calculated are in agreement with those of theoretically reported H-phase VN$_2$ monolayer, as is shown in Table S2.† The results indicate that almost all 2H-phase MX$_2$ maintained layered structures well, but most of 1T phase structures tend to collapse or slope, 1T-MC$_2$ in particular. Fig. 1c gives the interlayer spacing of all 1T- and 2H-phase MX$_2$. It is shown that most of MX$_2$ has an interlayer spacing from 1.4 Å to 2.7 Å. However, 1T-phase TiC$_2$, VC$_2$, MnC$_2$, FeC$_2$, and 2H-phase TiC$_2$, VC$_2$ have no interlayer spacing because they have formed compounds. From the comparison of interlayer spacing between 1T- and 2H-phase MX$_2$, it is obvious that most 2H-phase MX$_2$ have larger interlayer spacing than 1T-phase. Larger interlayer spacing is beneficial to intercalation and diffusion for Na. Therefore, 2H-phase MX$_2$ is fitter to serve as electrode materials.

![Fig. 1](image1.png)  
**Fig. 1** The top and side views of 2H-phase (a) and 1T-phase (b) MX$_2$ structure respectively (brown balls represent M atoms (M = Ti, V, Cr, Mn and Fe), and blue balls represent X atoms (X = C, N and O)). (c) The interlayer spacing of all 1T- and 2H-phase MX$_2$.

![Fig. 2](image2.png)  
**Fig. 2** The formation energy of all 2H-phase NaMX$_2$ systems (M = Ti, V, Cr, Mn and Fe; X = C, N and O).
To ascertain the energy stability of the NaMX₂ structure, we have computed the formation energy of all 2H-phase NaMX₂ systems (as is shown in Fig. 2). The results show that the corresponding nitrides and oxides have a negative formation energy while carbides have a positive formation energy, which indicates the NaMN₂ and NaMO₂ systems enjoy better stability than NaMC₂. Better stability is beneficial to the preparation of materials. Therefore, N and O are the selected anions for its compounds whose formation energy is lower than C. Negative formation energy suggests that better cycling stability can be expected for N- and O-based compounds when they are used as the electrode materials for SIBs.

Theoretical capacity, as we know, is an important factor in the applications of electrode materials, so we have calculated the theoretical capacity of different MX₂ (M = Ti, V, Cr, Mn and Fe; X = N and O) materials, and the results are shown in Fig. 3. Benefiting from the lighter relative atomic masses of 3d transition metals and 2p non-metallic elements, all MX₂ (M = Ti, V, Cr, Mn and Fe; X = N and O) materials possess a higher theoretical capacity (305–353 mA h g⁻¹). Among them, CrN₂ has a theoretical capacity of 335 mA h g⁻¹, which is much larger than traditional oxide materials⁴⁶ and polyanionic compound materials⁴⁷ and is nearly twice that of MoS₂ (167 mA h g⁻¹).⁴⁸ Ion diffusion is a key issue in the application of electrode materials for sodium-ion batteries. The rapid sodium diffusion determines the high-rate performance of the battery, ensuring the battery a high charge and discharge rate.⁴⁹,⁵⁰ Therefore, we have studied the migration properties of 2H-phase MX₂ (M = Ti, V, Cr, Mn and Fe; X = N and O) materials. It is found that the most stable intercalation site of sodium is an octahedral gap (O₁ or O₂), as is shown in Fig. 3a and b. And according to the previous reporting on the migration of TMDs materials,⁵¹ the migration path of sodium is between two adjacent octahedral interstitial sites through tetrahedral interstitial sites (O₁–T–O₂), as is shown in Fig. 4a and b. The diffusion barrier of all Na in MX₂ (M = Ti, V, Cr, Mn and Fe; X = N and O) are shown in Fig. 4c. And the diffusion energy profile along the diffusion path is shown in Fig. 5a and S2.† It is shown that all of the materials have a lower barrier. In particular, the diffusion barrier of sodium ions in CrN₂ is the lowest, about 0.49 eV. Thus, CrN₂ as an electrode material of sodium-ion battery boasts satisfactory rate performance.

3.2. Properties of CrN₂ as an electrode material

Due to the lowest diffusion barrier of CrN₂ (0.49 eV), lower than CrC₂ (0.7 eV) and CrO₂ (0.52 eV), it was chosen as the best electrode material for SIBs (as is shown in Fig. 5a). To better understand the dynamic stability of CrN₂ materials, we have calculated the phonon spectrum. There is no virtual frequency in the phonon spectrum (as is shown in Fig. 5b), which indicates CrN₂ is dynamically stable. Thus, CrN₂ possesses not only thermal stability (see Fig. 2) but also dynamical stability, which indicates a good cycling stability when it is used as electrode material for SIBs.

As intercalation energy is a crucial parameter for measuring the level of difficulty in inserting sodium ions into the materials, we have calculated the intercalation energy of sodium inserting CrN₂ at different sodium concentrations. It suggests that CrN₂ has a large negative intercalation energy indicating the feasibility of inserting Na into it (see Fig. S3†). The most stable configurations of NaₓCrN₂ (x ranges from 0 to 1) at different sodium concentrations are shown in Fig. S4 in the ESI.† Fig. 6a shows the calculated intercalation energy at different concentrations. It suggests that the intercalation energy initially decreases at the concentration from 0.00 to 0.33 as the effective interaction of the sodium ions is attractive, and then increases at the concentration from 0.33 to 1.00 when the
effective interaction of the sodium ions becomes repulsive. When sodium reaches the maximum concentration of 1, its intercalation energy achieves the maximum value of $-3.4 \text{ eV}$. Overall, negative intercalation energy is conducive to sodium ion intercalated. And volume expansion rate of sodium in the process of embedding CrN$_2$ is less than 10%, which is beneficial to the cyclic stability of the material.

As voltage is also a critical parameter for electrode materials, we have calculated the voltage of CrN$_2$ under different sodium concentrations. The calculated voltage is a function of sodium concentration in CrN$_2$ (see Fig. 6b). It shows CrN$_2$ boasts a high voltage window of about 3.1–3.8 V. Such a high voltage makes it ideal for cathode materials. When $x_1 = 0$ and $x_2 = 1$, the computed voltage (3.4 V) is the open-circuit voltage. Combining

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**Fig. 4** The top view (a) and side view (b) of diffusion paths (O1–T–O2) of sodium ion in MnX$_2$ and the most stable adsorption sites (O1 or O2) of sodium ions in 2H-phase MnX$_2$ (light brown balls represent sodium, red balls represent M atoms (M = Ti, V, Cr, Mn and Fe), and blue balls represent X atoms (X = N and O)). (c) The diffusion barrier of sodium ions in 2H-phase MX$_2$ materials.

**Fig. 5** (a) Energy profile of Na diffusion along the diffusion path in 2H-phase CrX$_2$ (X = C, N, O). (b) Phonon spectrum of 2H-phase CrN$_2$. 
the open-circuit voltage and theoretical capacity, the CrN$_2$ has a high energy density of 1139 W h kg$^{-1}$, which is much higher than that of traditional cathode materials, like transition metal oxides (less than 800 W h kg$^{-1}$), polyanionic compounds (no more than 500 W h kg$^{-1}$) and Prussian blue analogs (about 500 W h kg$^{-1}$). To reveal the mechanism of sodium ion intercalation, we have examined the charge transfer after sodium ion intercalated. The differential charge density is shown in Fig. S5 in the ESI.$^\dagger$ The yellow electron-rich regions on the nitrogen atom and the cyan electron-deficient regions around the sodium atom indicate that the charge has been transferred from the sodium atom.

Fig. 6  (a) Intercalation energy ($E_{\text{inter}}$) of Na$_x$CrN$_2$ ($x=0–1$) under different sodium concentrations. (b) Voltage profile under different sodium concentrations. Insets represent the intercalation configurations for Na$_x$CrN$_2$ ($x=0.33$ and $x=0.67$), respectively (red and blue arrow point to Na$_{0.33}$CrN$_2$ and Na$_{0.67}$CrN$_2$, respectively) (for more configurations at all sodium concentrations please see Fig. S4 in the ESI.$^\dagger$).

Fig. 7  Band structure and density of states of 2H-phase CrN$_2$ (a) and 2H-phase NaCrN$_2$ (b), respectively. The Fermi level is set to zero.
atom to the CrN\textsubscript{2} substrate. Bader charge analysis calculated the number of charge transfers in great detail. The results show that the sodium atom transfer 0.73 electrons and the electrons are mainly transferred from Na to the N atom. Charge transfer means that sodium is in a cationic state, and the Na–N bond has obvious ionic characteristics. In addition, the strong sodium–nitrogen interaction further shows that sodium can be stably embedded into CrN\textsubscript{2}.

To further study the electronic structure of CrN\textsubscript{2}, we have calculated band structures and density of states, which are shown in Fig. 7. In band structure, it is shown that the CrN\textsubscript{2} material exhibits metallic features both before and after sodium-ion intercalation, which endows it with a fast charge and discharge rate. According to the density of states near the Fermi level, the CrN\textsubscript{2} exhibits ferromagnetism before sodium-ion intercalation in TDOS, which is mainly contributed by the Cr-d orbital electrons in PDOS. The fully sodiated state of CrN\textsubscript{2} presents non-magnetic, and the density of N-p orbital states near the Fermi level is significantly enhanced, and the hybridization of Cr-d orbital and N-p orbital is enhanced, improving the cycle stability of the CrN\textsubscript{2} material. In addition, the electrical double-layered structure induced by strong charge transfer between sodium and nitrogen enables the sodium-ion diffusion barrier to be reduced greatly.

4. Conclusions

In this paper, we systematically studied the theoretical capacity and ion diffusion barrier in a new type of layered bulk transition meta compounds, named MX\textsubscript{2} (M = Ti, V, Cr, Mn, Fe; X = C, N, O). Our results show that most of these layered MX\textsubscript{2} materials possess a high theoretical capacity of over 300 mA h g\textsuperscript{-1}. In particular, 2H-phase layered bulk CrN\textsubscript{2} possesses a proper theoretical capacity (335 mA h g\textsuperscript{-1}) and a desirable sodium ion diffusion barrier (0.49 eV). In addition, the layered CrN\textsubscript{2} has both good thermal and dynamical stability. Importantly, the results of charge transfer and electronic properties lead to the high voltage platform from 3.1 to 3.8 V and extraordinary electrochemical performance of layered CrN\textsubscript{2}. Moreover, CrN\textsubscript{2} boasts a high energy density of 1139 W h kg\textsuperscript{-1} thanks to its high open-circuit voltage (3.4 V) combined with high theoretical capacity. Our predicted 2H-phase layered transition-metal nitrides enjoy great potential to be ideal candidates for SIBs cathode materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by the National Natural Science Foundation of China [No. 11772285, 11774298, 11604278]. Research Foundation of Xiangtan University (21DQZ39) and Education Department of Hunan Province (21C0093).

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