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Theoretical prediction of the structural, electronic, mobility, and dynamic properties of $Mo_3N_2T_2$ (T = H, O and OH) with Li adsorption feature

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ABSTRACT

Two-dimensional (2D) MXenes are attracting increasing interest as electrode materials for lithium ion batteries (LIBs), because lithium ions can diffuse in a 2D lattice surface. The electronic structure, electron and ion motion dynamics, and structural stability upon lithiation and delithiation on the bare, H-, O-, and OH-terminated Mo_3N_2 MXene were intensively investigated using the DFT method. The theoretical results revealed that Mo_3N_2 and $Mo_3N_2O_2$ have excellent absorption and stability for lithium-ion storage. There is no band gap at the traditional Fermi level (0/eV) at any configuration, which means it has excellent electronic conductivity. The extended orbital could enhance the exchange interaction between Mo 4*d* and N 2*p* for terminated atoms, leading to an asymmetric charge distribution in Mo—N and Mo—T (T = H, O and OH) bonds. The adsorption of Li ions on $Mo_3N_2O_2$ layers indicates that the O-terminated moiety can obviously improve the diffusion of Li ions. The stability was studied by ab initio molecular dynamics (AIMD) simulation at a series of temperatures. The lithium ions have a gradual evolution of thermal motions with increasing temperature. These results suggest that Mo_3N_2 and $Mo_3N_2O_2$ can be a promising electrode material for lithium-ion batteries in terms of $Mo_3N_2O_2$ specific capacity, diffusion dynamics, and structural stability.

1. Introduction

Lithium ion batteries are increasingly popular, and [1,2] two-dimensional (2D) MXene materials have gradually become one of the most promising potential energy storage devices. Many electrode materials around MXene-layered nanostructured materials have been studied, and MXene-layered materials have excellent environmental safety, low cost, and availability [3,4]. They are compatible with future versions of rechargeable batteries, and they have high specific capacity, higher safety, and higher volume energy storage performance than other common cathode materials [5,6]. MXenes are widely used in electronic devices, catalysts, and for energy storage or energy conversion materials. In addition, the electrochemical performance of lithium ion batteries is competitive with that of other electrode materials. The structure can be considered to be a monolayer with the general formula $M_{n+1}X_n$ with M = Sc, V, Hf, Nb, Zr, Ta, Cr, and Mo; here, X is C or N, and n is set to 1, 2, or 3. MXene usually has some surface-terminated functional groups, such as H, F, O, or OH. These terminated MXene species should be defined in the general formula: $M_{n+1}X_nT_x$. So far, the MXenes have been synthesized by experimental methods as follows: Ti_3C_2, Ti_2C, $(Ti_{0.5}Nb_{0.5})_2C$, Ta_4C_3, $(V_{0.5}Cr_{0.5})_3C_2$, Ti_3CN, V_2C, and Nb_2C [7,8]. These MXenes have attracted great attention and display excellent electrochemical properties.

One of these composite electrodes (Mo_3N_2) has been extensively theoretically studied [9,10]. It has a layered structure of bare Mo_3N_2 and H-, O-, and OH-functionalized MXene nanosheets. However, there are still challenges in using it for lithium ion battery applications. These new materials are difficult to synthesize and suffer from thermodynamic instability during frequent charging and discharging [11].

A recent work has reported the electronic properties and lithium ion motion using first principles calculations. It shows that Mo_3N_2 MXene monolayers have high performance stability and storage capacity. Layered Mo_3N_2 and its terminated derivatives improve Li^+ ion mobility. The high electronic conductivity and lithium ion diffusion coefficient offers advantages [12]. Recently, there have been many efforts to replace the terminated group on the layer surface in Mo_3N_2. These have been theoretically investigated during the past few years to shed light on the synthesis of other terminated MXenes and to explain their

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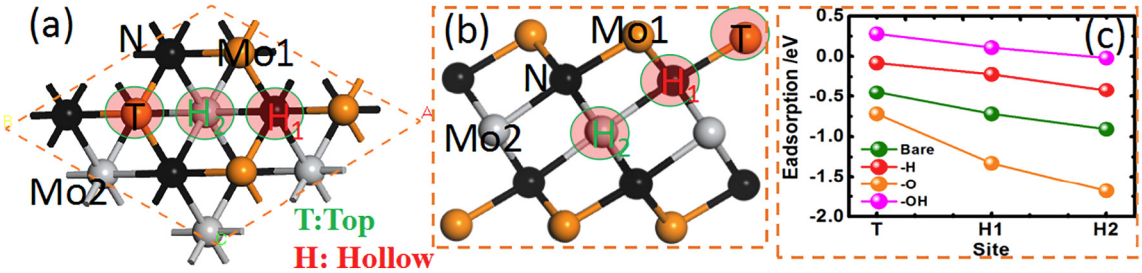

Fig. 1. Schematic diagram shows the crystal structure of a 2D Mo_3N_2 supercell (2 × 2 × 1) monolayer with (a) top view, (b) side view and (c) adsorption energy (*E*av) of Li on different site of single-layer on H, O and OH-Terminated Mo_3N_2.

physical and chemical properties. To further understand MXene features that influence the electrochemical properties when they are used as electrode materials, it is essential to investigate their electronic structure, capacity, stability, and dynamic properties. We have applied density functional theory (DFT) calculations combined with ab initio molecular dynamics (AIMD) simulations [13,14]. In addition, the evolution of complex structure, thermal stability, and lithium ion transport mobility properties of these systems at different temperatures should be considered. Molecular dynamics (MD) simulations are better than first-principles calculations because they explain the effect of structural disorder of $Mo_3N_2T_2$ (T = bare, H, O, and OH) and lithium ion transport properties. This was done via the CI-NEB method with the bond valence force fields. All of the calculations indicated that O-terminated Mo_3N_2 increases the adsorption energy of Li ions due to charge transfer and bonding, and the basic structure of the Mo_3N_2 monolayer is not influenced by Li adsorption concentration. The adsorption energy of Li ions is subject to the adsorption concentrations. We further show that Li ions tend to adsorb on both sides of the Mo_3N_2 layer rather than only on one side in 2D materials. The stability of lithiated structures was investigated by ab initio molecular dynamics. The calculated energy barriers of one Li ion diffusion on the MXene surface are quite minor. These results suggest that the Mo_3N_2 and $Mo_3N_2O_2$ layers are rather stable and can explain the experimentally observed high cycling rate [15].

2. Theoretical method

All the calculations were performed using the Perdew Burke Ernzerh (PBE) method with Generalized Gradient Approximation (GGA) exchange correlation potential as implemented in the (VASP) package [16]. The plane wave cutoff energy was 500 eV were modeled by 2 × 2 × 1 unit cells, All the calculations were carried on supercell with (2 × 2 × 1) and a vacuum spacing of 20 Å was built. For electronic structure calculations with a 7 × 7 × 1 Monkhorst-Pack k-point mesh were used for the supercell of Mo_3N_2, which until the forces converge is 1.0 e^{-6} eV/cell.

It is well known that Mo is related to strong-correlation effect and cannot be accurately described by using only the GGA function. Thus, the GGA + *U* method was used, as proposed by Dudarev [17]. The on-site Coulomb interaction parameter *U* and the exchange parameter *J* are combined into a spherically averaged, single effective interaction parameter *U-J* (U_{eff}), which does not depend on their individual values. The U_{eff} for the Mo is applied with the recommended values provide by Yang Yu et al. [18]. The electronic structures and optical properties were calculated using the hybrid density functional HSE06 (Heyd-Scuseria-Ernzerhof) [19] hybrid function, which replaced the slowly decaying long-ranged part of the Fock exchange by the corresponding density functional counterpart.

While the adsorption energy (E_{ad}) of the adsorbed ion on the surface of $Mo_3N_2T_2$ (T = Bare, H, O and OH) mono-layers are defined as follows:

$$Ea = (E_{MXLi_n} - nE_{Li} - E_{MX})/n \quad (1)$$

where E_{MXLin} is the total energy when n Li ions adsorbed on the MXene surface and E_{Li} is the energy per atom of lithium in a bulk bcc crystal. To obtain all the potential diffusion pathways and the energy barriers, we have performed the nudged elastic band (NEB) [20] calculations to search the transition state with eight images between initial and final states [21]. In order to examine the stability of during lithiated $Mo_3N_2T_2Li_2$ (T = Bare, H, O and OH) mono-layer surface. Molecular dynamic simulation is also performed in our work. The temperature is maintained at various temperatures of 300, 600, 900 and 1200 K with a time step of 0.2 fs lasted for 100 ps. All the work were performed in a NVT ensemble with a (2 × 2 × 1) supercell, the temperature was controlled by using the Nose–Berendsen method [22].

3. Results and discussion

3.1. Structure and adsorption for lithium

To analyze the structural properties and stability of all lithiated structures, we defined different positions of T (top of Mo), H_1 (hollow 1 of N), and H_2 (hollow 2 of middle layer Mo) as shown in Fig. 1. The different positions mean that Li ions are adsorbed on nonequivalent locations of both sides for T-Mo_3N_2 (T = Bare, H, O, and OH). There are three possible adsorption site modes for H, O, and OH. According to our work, the most stable configuration was the terminated groups located on the top of the Mo atoms in the middle layer H_2 (Hollow 2).

We next systematically investigated all of the possible structures of T-terminated Mo_3N_2 MXene with the locations of T atoms and Li ions as variables [23,24]. As shown in Fig. 1(c), the H_2 model for bare Mo_3N_2 and H_2 models for terminated Mo_3N_2 MXene possess the lowest *E*a among the lithiated structures, indicating that these are the two most stable phases. Negative adsorption energy of Li ions means that Li adsorption is spontaneous. It is the most energetically stable phase when fully lithiated.

The Li atoms prefer to be adsorbed on both sides of the $Mo_3N_2T_2$ monolayer at the same lithium-ion concentration, which is consistent with other 2D materials, such as Ti_3C_2 [25]. The optimized structures for $Mo_3N_2T_2$ (T = bare, H, O, and OH) are shown in Fig. 2(a–d). Oxygen atoms in $Mo_3N_2O_2Li_2$ (Fig. 2c) move away from the $Mo_3N_2O_2$ surfaces with Li adsorbed and are finally sandwiched with a Li—O bond length of 0.54 Å in Fig. 2(b). The Li—H and Li—Mo bond length is 0.74 and 6.63 Å, respectively. The formation of Li—O bonds protects the adsorbed material, but the structural features of $Mo_3N_2Li_2$ and $Mo_3N_2H_2Li_2$ result in the formation of Li dendrites.

3.2. Electronic properties

The crystal structure of $Mo_3N_2T_2Li_2$ (T = Bare, H, O, and OH) of a primitive cell is demonstrated in Fig. 1(a–d), and the overall configuration of the mono-layer (2 × 2 × 1) supercell is shown in Fig. S1. Meanwhile, Figs. 3 and 4 display the band structures and densities of state (DOS) of $Mo_3N_2T_2Li_2$ (T = Bare, H, O, and OH). The electronic band structures and total DOSs were computed to further explore the