Flatten the Li-ion Activation in Perfectly Lattice-Matched MXene and 1T-MoS\textsubscript{2} Heterostructures via Chemical Functionalization

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The complexity of the ionic and electronic dynamics in MXene based hybrids, which are normally involved for device integration, triggers both challenges and opportunities for its application. Herein, as a prototype of metallic hybrids of MXene, heterostructures consisting of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} (T = None, O and F atoms) and metallic MoS\textsubscript{2} (IT phase) are investigated for lithium-ion battery (LIB) applications. It is found that different surface atomic groups in MXene significantly alter the affinity, redox reaction and kinetics of Li atoms in the interface of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} and 1T-MoS\textsubscript{2}. Through examining the three possible pathways of Li by first-principles calculations and ab-initio molecular dynamics, the diffusion curve becomes significantly flattened from the naked to O- and F-terminated Ti\textsubscript{3}C\textsubscript{2} MXene with activation barriers reducing dramatically from 0.80 to 0.22 and 0.29 eV, respectively, and accordingly promoted diffusion coefficients. The functionalization with O or F eliminates the steric hindrance of Li intercalation by breaking the strong interaction between two layers and provides additional adsorption sites for Li diffusion in the meantime. The work suggests that surface functional groups play a significant role in Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2}/1T-MoS\textsubscript{2} modification and similar strategy via chemical modification of metallic hybrids provides hints for designing high performance anode material for LIBs.

1. Introduction

The energy demand grows faster than ever in the modern world. With the decrease of exhaustible energy on the earth, people turn to pay more attention to renewable energy such as rechargeable batteries, wind power, and solar heat. Among these kinds of green energy, rechargeable batteries or secondary batteries have been prominent due to their portability and a variety of usage scenarios. Therefore, a deep and comprehensive study is required in promoting the performance of these batteries such as lithium-ion batteries (LIBs) that are the most successful systems and widely used right now.[1] Exploring new anode material that has good performance in lithium diffusion and storage has been one of the primary targets.[2–6]

MXene, first discovered in 2011, is a class of 2D carbides and nitrides.[7] MXenes can be expressed in a general formula M\textsubscript{1−x}X\textsubscript{n}T\textsubscript{x} (where M is the early transition metal, X is carbon or nitrogen, and n is 1–3, and T is surface termination). Normally, MXenes are produced by selectively etching from the parent compounds MAX, where A is an A-group element, such as Al or Si. Since been discovered, MXenes are proved to have great potential and application in energy storage and catalysis because of their highly active surfaces, good conductivity, abundant functional groups, and facile synthesis.[8–11] For instance, Ti\textsubscript{3}C\textsubscript{2} has been proved to have good performance as anode materials for LIB with 123.6 mAh g\textsuperscript{-1} at 1 C rate.[12] Theoretical study identified a low barrier (0.068–0.070 eV) of Li diffusing above the surface.[13,14] Notably, the multiple possibilities of the surface terminations like F, OH, and O enable a unique tunability of the electronic structures that lack in most of other 2D materials.[15–17] However, different from other atomically thin 2D materials like graphene, the MXene has a thicker layer and the Li atoms that cannot be accommodated within the dense backbone layer consisting of the short M-X bond that is tightly bonded.[14,18–20] Therefore, the Li atoms can only be adsorbed above and across the surface that leads to a relatively small capacity. One effective measure to remedy this is to combine MXene with other materials or molecules for composite anode material.[21–24]

MoS\textsubscript{2}, a typical material of layered transitionmetal dichalcogenide, has been widely applied in LIBs due to its high theoretical capacity (670 mAh g\textsuperscript{-1}) and attracted great attention owing to its unique crystal structure. A strong lattice and orbital coupling together with a wealth of polymorphs (semiconducting 2H phase and metallic IT, IT’ phases) also ensure MoS\textsubscript{2} for various applications.[25–33] Different from the semiconducting 2H-MoS\textsubscript{2}, the IT phase is less prone to capacity fading.[31,32,36] MXene/2H-MoS\textsubscript{2} hybrid has been examined as the anode material of LIBs. Kun Ma et al. prepared layered MoS\textsubscript{2} into 2D Ti\textsubscript{3}C\textsubscript{2} with the subsequent CTAB...
intercalation, showed a Li⁺ storage capacity of 340 mAh g⁻¹ even at 20 A g⁻¹ beyond 1000 cycles.[57] Guanyuan Du et al. also synthesized MoS₂/Ti₃C₂T₂ (T = O, F, OH) composite by a simple hydrothermal method, exhibited a reversible capacity of 614.4 mAh g⁻¹ at 100mA g⁻¹ after 70 cycles.[38] Zongli Hu et al. reported a core-shell structure MoS₂/Ti₃C₂ with low Ti₃C₂ content (8.87 wt%), delivered a capacity of 706.0 mAh g⁻¹ after 1390 cycles at 5 A g⁻¹.[39] While previous studies[32–39] demonstrate the encouraging charging–discharging performance of MXene/2H-MoS₂ hybrid, there is less study on the synergy between MXene and 1T-MoS₂. In addition, we speculate the homogeneous metallic nature across MXene and 1T-MoS₂ would allow a fast response of lithium atoms to the external electric field due to the absence of the screening built-in potential unavoidable in MXene/2H-MoS₂ and other similar metallic–semiconducting interfaces. These all motivate us to examine the MXene/1T-MoS₂ composite that could take advantage of the facile surface decoration of MXene and the ultrathin metallic nature of 1T-MoS₂ for LIBs.

In this work, we construct a MXene/1T-MoS₂ heterostructure based on the most popular form of MXene with the Ti₃C₂ type. We find that the Ti₃C₂ and 1T-MoS₂ have a good lattice registration with a small lattice mismatch. The electronic property and the kinetics of LIB of the hetero-layer have been examined by using density functional theory (DFT). We are particularly interested in the different surface structures of MXene on the energetics and kinetics of Li species. By considering the various surface terminations of MXene, representing as Ti₃C₂T₂ (T = None, O, and F atoms), the role of functional groups in the binding and activating the Li atoms is examined. Interestingly, we find that different surface terminations of MXene would lead to strikingly different Li absorptions and barriers in the Ti₃C₂T₂/1T-MoS₂ heterostructure, and properly surface stoichiometric and functionalization would be critical in applications.

2. Results and Discussions

2.1. Structural Properties and Stability

First, we start with measuring the structural properties of Ti₃C₂/1T-MoS₂ as well as its functionalized derivatives (Ti₃C₂O₂/1T-MoS₂ and Ti₃C₂F₂/1T-MoS₂). The hexagonal Ti₃C₂T₂ layer is built from the Ti₃AlC₂ phase by striping Al atoms. Two carbon atomic layers interleave into three titanium atomic layers forming a Ti₃C₂ octahedral. In functionalized structures, fluorine or oxygen atoms coordinate with surface Ti atoms respectively. Notably, there is a small lattice mismatch of around 0.038% between Ti₃C₂ and 1T-MoS₂ with relaxed lattice constants of 6.162 and 6.399 Å. This allows the homogeneous and functionalization would be critical in applications.

To find out electrons’ redistribution after functionalization, we also analyze the charge transfer between the 1T-MoS₂ and Ti₃C₂T₂. Figure 3 shows the isosurfaces of differential charge density (DCD) ∆ρ(z) and its line-profile curves ∆ρ(x) along z-direction by integrating the in-plane DCD among x-y plane. The total amount of transferred electrons along z-direction ∆τ(z) is calculated by the integration of the line-profile curves ∆ρ(x) from bottom expressed as ∆τ(x) = ∫∆ρ(z')dz'.[48] Regarding the original Ti₃C₂/1T-MoS₂, the Ti₃C₂ layer delivers a relatively strong charge transfer of 0.40 electron to MoS₂ for the supercell,
amount to 0.10 e per S atom. The charge redistribution occurs in the whole IT-MoS₂ sheet, signifying a strong interaction between unpassivated Ti₃C₂ and IT-MoS₂. The lobes in the DCD isosurface appear at the mid-gap of the interface suggesting a purely ionic interaction between Ti₃C₂ and IT-MoS₂, largely associated with the interfacial Ti-S interactions. Comparing with the

Figure 1. Schematic diagram of optimized Ti₃C₂T₂/IT-MoS₂ structures. a) Top and side views of Ti₃C₂/IT-MoS₂, the interlayer distance $h_1 = 2.38 \, \text{Å}$. b),c) are two shifted forms of Ti₃C₂O₂/IT-MoS₂, the interlayer distance $h_2 = 2.95 \, \text{Å}$, $h_3 = 2.65 \, \text{Å}$. Panels (d-f) show three possible aligned structures of Ti₃C₂F₂/IT-MoS₂, the interlayer distance $h_4$, $h_5$, and $h_6$ are 3.10, 2.78, and 2.72 Å, respectively.
Ti₃C₂/1T-MoS₂, O functionalized MXene has a different process as shown in Figure 3b. The trend of charge transfer is opposite with 0.034 electron transferring from 1T-MoS₂ to Ti₃C₂O₂ (−0.017 e per S atom). This implies that the O atoms, each coordinating with two Ti atoms, still are not fully compensated for its 2p₄ sub-shell, which triggers more electrons transferred from 1T-MoS₂. Another reason for this strong charge transfer is due to the much smaller work function of 1T-MoS₂ than that of the Ti₃C₂O₂ as shown above. For the F functionalized Ti₃C₂F₂/1T-MoS₂, the trend of electron transfer is the same as the original Ti₃C₂ case: 0.053 e (0.013 e per S atom) is transferred from Ti₃C₂F₂ to MoS₂. Comparing the F- and O-functionalized heterostructure with the pristine MXene case, the much smaller interfacial charge transfer indicates that the Ti₃C₂ layer, especially surface Ti atoms are stabilized by functional groups O or F atoms. The insertion of O, F atoms also weakens the bond between S and Ti atoms, which is crucial for the interlayer adsorption and diffusion of alkaline atoms like lithium and sodium. For both decorations, significant amount of electrons are accumulated within the interface between Ti₃C₂O₂/Ti₃C₂F₂ and IT-MoS₂, reflecting van der Waals plus the slightly covalent nature of the interfacial bonding of S and O/F atoms that is different from the purely ionic interfacial bonding of the Ti₃C₂/1T-MoS₂.

2.3. Lithium Adsorption and Diffusion

Next, we explore the energetics and kinetics of Li in the interlayer of Ti₃C₂T₂/1T-MoS₂. First, the interaction between Li atoms and the heterostructure is investigated by comparing the binding energies (Eₘ) for different MXene being involved. The adsorption sites are shown in Figure 4a. Eₘ is calculated according to the equation showing below:

\[
E_b = E_{\text{total}} - E_{\text{Ti}_3\text{C}_2\text{T}_2/\text{MoS}_2} - E_{\text{Li}}
\]

where \(E_{\text{total}}\) and \(E_{\text{Li}}\) are the total energies of Li-Ti₃C₂T₂/IT-MoS₂ and isolated Li atom, respectively. Originally, Ti₃C₂/1T-MoS₂ exhibits a quite small \(E_b\) (negative) with −0.24 eV, while O, F functionalized types deliver a significantly promoted binding of −3.14 and −2.36 eV, respectively. This difference reveals that surface functional groups, especially O atoms enhance the performance of Li adsorption. Comparing with the adsorption energy of Li within Ti₂CO₂ with 2H-MoS₂ heterostructure (−2.30 eV),[39] functionalized Ti₃C₂O₂/1T-MoS₂ behaves better. Such a large \(E_b\) value ensures that Li would less likely to form clusters[19,20,41] during the diffusion process that will improve the safety as an anode for LIB. In addition, we also computed the adsorption ability of Li on both top and bottom surfaces of this heterostructure. For the top surface, the IT-MoS₂ layer, Ti₃C₂/IT-MoS₂ exhibits extremely high adsorption energy, while Ti₃C₂O₂/IT-MoS₂ and Ti₃C₂F₂/IT-MoS₂ are lower than the prototypes. For the bottom surface, similar results are achieved. Clearly, functional groups’ insertion would lead to the increment of the adsorption of Li. Despite this, for better guidance of experiments, we also consider the variance of surface F/O atoms. As shown in Table 1, by adjusting the ratio of F and O atoms from 1:3 to 3:1, the shift of adsorption energy is around...
0.2 eV that is relatively low that would not influence the total performance seriously.

To further understand the diffusion behavior of Li during the charging and discharging process, the diffusion energy barriers from different migration paths are calculated by the climbing-image nudged elastic band (CI-NEB) method. As shown in Figure 4b, by utilizing the symmetry of the Ti$_3$C$_2$T$_2$/1T-MoS$_2$, we design three possible pathways (denoted as P1, P2, and P3) between the two nearest neighboring adsorption sites of Li: initial state (IS) and final state (FS). Figure 4a,c displays configurations of IS and FS corresponding to the three different Ti$_3$C$_2$T$_2$/1T-MoS$_2$ heterostructures. As shown in Figure 4b, along P1 (IS→FS) path, the Li atom adopts a straightforward pathway. For P2 (IS→S2→FS) path, the Li atom is supposed to migrate from IS to a metastable state S2 (shown in Figure 4b), then from S2 to IS. The Li in S2 structure is placed directly under a Mo atom (the nearest layer to Ti$_3$C$_2$) while in the middle of three Ti atoms for Ti$_3$C$_2$ or right above surface O or F atom for Ti$_3$C$_2T_2$ case. For P3 (IS→S3→FS) route, the Li atom is supposed to diffuse from IS to S3 state (shown in Figure 4b), where the Li is right beneath an S atom and above a Ti atom (the neighboring surface layer of MXene), and next migrate to FS.

First, for both P1 and P2, for all three types of Ti$_3$C$_2$T$_2$/1T-MoS$_2$, metastable states are found and shown in Figure 4g,h, respectively. According to Figure 4g, these local energy-minimum points adopt similar structures from P1. Although the Ti$_3$C$_2$/1T-MoS$_2$ has the weakest $E_b$ comparing with others, its energy barrier for Li diffusing along P1 is the largest, around 0.80 eV. This is caused by the strong interfacial adhesion between MoS$_2$ and Ti$_3$C$_2$ layer where a narrow interlayer gap of 2.38 Å leads to huge steric hindrance and Coulomb repulsion, hence upgrading the migration barrier. For bare Ti$_3$C$_2$/1T-MoS$_2$, the saddle state of P1 corresponds to Li is located in the hollow site of four S atoms. The distance between S and Li is around 2.09 Å that leads to a strong fixation of Li. While for Ti$_3$C$_2$O$_2$/1T-MoS$_2$ and Ti$_3$C$_2$F$_2$/1T-MoS$_2$, the average distance between S-Li is 2.35 and 2.32 Å, and the bond between O-Li is 1.81 Å and F-Li is 1.79 Å. For O and F functionalized heterostructures, the addition of surface atoms not only provides adsorption sites for Li, but also weakens the chemical bonding between layered MoS$_2$ and Ti$_3$C$_2$. Therefore, the diffusion barrier is much lower than that of the original Ti$_3$C$_2$/1T-MoS$_2$ (0.80 eV), which is only 0.22 eV for Ti$_3$C$_2$O$_2$/1T-MoS$_2$ and 0.29 eV for Ti$_3$C$_2$F$_2$/1T-MoS$_2$, both are lower than Li diffusing in the single phase of Ti$_3$C$_2$F$_2$ (0.36 eV). Overall, the introduction of surface functional groups induces a much lower activation barrier of Li in the interlayer of Ti$_3$C$_2$T$_2$/1T-MoS$_2$.

For P2 pathway (Figure 4h), the diffusion barrier is slightly higher than P1 for all three heterostructures. The barriers are 0.82, 0.23 and 0.34 eV for Ti$_3$C$_2$/1T-MoS$_2$, Ti$_3$C$_2$O$_2$/1T-MoS$_2$ and Ti$_3$C$_2$F$_2$/1T-MoS$_2$, respectively. This difference can be explained by the more rigorous pathway that results in higher diffusion energy. For diffusion along P3 pathway (Figure 4i), the bare Ti$_3$C$_2$/1T-MoS$_2$, due to the intact cohesion with a short bonding length of 2.38 Å between S and Ti atoms, the spatial repulsion in S3 is so large that is energetically unreasonable and will lead to structural collapse. Therefore, only Ti$_3$C$_2$O$_2$/1T-MoS$_2$ and Ti$_3$C$_2$F$_2$/1T-MoS$_2$ are allowed for diffusion along P3 pathway. However, both structures show a higher diffusion energy barrier than P1 and P2, with 0.44 and
0.56 eV for Ti₃C₂O₂/1T-MoS₂ and Ti₃C₂F₂/1T-MoS₂ respectively. These increasing barriers are caused by the increased spatial hindrance and van der Waals reaction between S and Ti at S3. The local energy-minimum point for Li diffusion on Ti₃C₂O₂/1T-MoS₂ is identified to be right beneath the S atom and in the middle of three O atoms, in which the Li atom is located around 2.20 Å between oxygen atoms and 2.30 Å from the S atom. The corresponding energy barrier is 0.44 eV. For Ti₃C₂F₂/1T-MoS₂, the barrier site also appears when Li is in the hollow site of three F atoms and right beneath the S atom. Li-ion is oriented 2.26 Å from the S atom, and the average distance of Li-F is 2.01 Å. Despite diffusion behavior in the interlayer, Li migration on the top and bottom surfaces along the direct path is also computed as shown in Figure 4j,k. For the

Figure 4. Schematic diagram of CI-NEB, a) side view of initial positions, b) top view of three possible paths P1, P2, P3 of Ti₃C₂Tₓ/1T-MoS₂, c) side view of final positions. Diffusion barrier through d) P1, e) P2, and f) P3. Optimized structures of energy minimum points in g) P1, h) P2, and i) P3 with an order of Ti₃C₂/1T-MoS₂ (left panel), Ti₃C₂O₂/1T-MoS₂ (middle panel), and Ti₃C₂F₂/1T-MoS₂ (right panel). Note for P3 only Ti₃C₂O₂/1T-MoS₂ and Ti₃C₂F₂/1T-MoS₂ are considered. Diffusion barrier through j) top surface and k) bottom surface.
top layer, MoS$_2$, all of them exhibit the highest diffusion barrier (0.17–0.37 eV) and the functionalization increases the diffusion barrier by around 0.17 eV. As expected, Li diffusion on the bottom layer (Ti$_3$C$_2$T$_2$) is inhibited by the functionalization atoms, especially O (0.39 eV). Comparing Li diffusion ability at different surfaces, the interlayer with a moderate diffusion barrier is relatively ideal one for electrochemical reactions of LIBs.

From the above discussion, by comparing the calculated diffusion energy barrier along three possible pathways P1, P2, and P3, P1 is obviously most energetically favorable for all three kinds of heterostructures. The diffusion barrier among them follows the sequence of Ti$_3$C$_2$O$_2$/1T-MoS$_2$ < Ti$_3$C$_2$F$_2$/1T-MoS$_2$ < Ti$_3$C$_2$/1T-MoS$_2$, which means the interlayer functionalization with O and F will prompt the diffusion of Li between the interlayer of Ti$_3$C$_2$T$_2$ and 1T-MoS$_2$.

**2.4. Ab Initio Molecular Dynamics**

We further performed ab initio molecular dynamics (AIMD) to investigate the dynamic behavior of the Li atom migrating across the interlayer between MXene and IT-MoS$_2$ (Figure 5). We are particularly interested in the effect of the surface-functionalized groups on the intercalation behaviors of Li atom. To this end, here we analyze the mean square displacements (MSDs) from which the diffusion coefficient ($D$) that dominates the charge and discharge rate is also computed that is shown below

$$ D = \frac{\text{MSD}(t) - x(t) - x(t_0) + y(t) - y(t_0) + z(t) - z(t_0)}{2d\Delta t} $$

(2)

where $x_i$, $y_i$, and $z_i$ are coordinates of lithium atom $i$, $d$ is the dimension of the structure, and $\Delta t$ is the time relative to the initial moment. For Ti$_3$C$_2$T$_2$/IT-MoS$_2$, $d$ is taken as 2, and $\Delta t$ is taken between 1 and 12 ps to eliminate the nonlinear snippet.\(^{[42]}\)

First of all, we examine the AIMD at 300 K. The initial position of the Li atom is placed at the adsorption site with energetical preference. As can be seen in Figure 5a, Ti$_3$C$_2$F$_2$/IT-MoS$_2$ exhibits a much higher value of MSD. The corresponding trajectory (Figure 5g) also identifies the highly "active" nature of the Li atom between F-decorated MXene and IT-MoS$_2$. According to our previous results, the Ti$_3$C$_2$/IT-MoS$_2$ has the lowest $E_b$ (0.24 eV) that means an easier migration of Li. Nevertheless, the relatively narrow gap separating the MoS$_2$ and Ti$_3$C$_2$ shifts to a spatial hindrance and restricts the migration of Li. This is reasonable and consistent with the large activation barrier (0.80 eV) from our CI-NEB calculation. For Ti$_3$C$_2$O$_2$/IT-MoS$_2$, the Li also has a relatively limited diffusion rate that on the other hand could be due to the largest $E_b$ (-3.14 eV) with Li albeit with a moderate diffusion barrier (0.22 eV). In contrast, Ti$_3$C$_2$F$_2$/IT-MoS$_2$ is most suitable for Li diffusion owing to the co-existence of a moderate $E_b$ (-2.36 eV) and a small barrier (0.29 eV). The derived $D$ of Ti$_3$C$_2$/IT-MoS$_2$, Ti$_3$C$_2$O$_2$/IT-MoS$_2$, and Ti$_3$C$_2$F$_2$/IT-MoS$_2$ are $1.20 \times 10^{-6}$, $2.75 \times 10^{-6}$, and $1.70 \times 10^{-4} \text{ cm}^2 \text{s}^{-1}$, respectively. Comparing with the diffusion coefficient of Li in graphite: C$_6$Li ($1.46 \times 10^{-11} \text{ cm}^2 \text{s}^{-1}$),\(^{[43,44]}\) the Ti$_3$C$_2$T$_2$/IT-MoS$_2$ exhibits an inherent much higher activity.

To further exploring the role of functional group in Li diffusion, the variation of bond distance of Li-S, Li-F, and Li-O are calculated as shown in Figure 5b,d,f, respectively. The probability density is given by the atomic distance distribution with a bin size of 0.02 Å. Bare Ti$_3$C$_2$/IT-MoS$_2$ exhibits a strong binding between Li and S atoms with an average 1.57 Å bond length, which leads to a distortion of the nearby S atom as can be seen in Figure 5c. In contrast, Ti$_3$C$_2$O$_2$/IT-MoS$_2$ and Ti$_3$C$_2$F$_2$/IT-MoS$_2$ show a stable MoS$_2$ layer during AIMD with 2.72 and 2.57 Å Li-S bond due to the wider interlayer gap and the stronger adsorption ability of F, O atoms. Comparing the Li-T (O, F atom) distance between Ti$_3$C$_2$O$_2$/IT-MoS$_2$ (2.00 Å) and Ti$_3$C$_2$F$_2$/IT-MoS$_2$ (2.14 Å), with a smaller average bond length and centralized distribution of probability density, O atoms exhibit a stronger fixation capacity than F atoms, leading to a sluggish Li diffusion behavior. The wide distribution of Li-F and Li-S bond length in Ti$_3$C$_2$F$_2$/IT-MoS$_2$ also identifies the active diffusion behavior of Li as shown in Figure 5f,g.

As discussed above, it is evident that functional groups of MXene afelect the thermal activity of intercalated species, and according to our results, the F functionalization is most favorable for the fast diffusion of the Li atom.

**2.5. Theoretical Li Storage Capacity and Open-Circuit Voltage**

In this part, we investigate the performance of Ti$_3$C$_2$T$_2$/IT-MoS$_2$ as anode materials for LIBs through the calculation of theoretical Li storage capacity and open-circuit voltage (OCV) with different loads of Li. As shown in Figure 6a,b, the max capacity of Li atoms is found by filling all energetically favorable sites: A, B, C, and D. For bare Ti$_3$C$_2$/IT-MoS$_2$, only one site is eligible for Li adsorption. The theoretical capacity can be calculated through the following equation:\(^{[41]}\)

$$ C = \frac{nxF}{M} $$

(3)
where $x$ is the number of absorbed atoms, $n$ is the valence number of Li, $F$ is the Faraday constant (26,801 mAh g$^{-1}$), and $M$ is the atomic mass of Ti$_3$C$_2$/1T-MoS$_2$ (327.7, 359.7, and 365.7 g mol$^{-1}$ for Ti$_3$C$_2$/1T-MoS$_2$, Ti$_3$C$_2$O$_2$/1T-MoS$_2$, and Ti$_3$C$_2$F$_2$/1T-MoS$_2$, respectively). Based on a full load of Li atoms at energetically favorable sites and the radius of Li as 0.76 Å, the max theoretical
capacity of Ti$_3$C$_2$/IT-MoS$_2$, Ti$_3$C$_2$O$_2$/IT-MoS$_2$, and Ti$_3$C$_2$F$_2$/IT-MoS$_2$ are 81.78, 298.04, and 293.15 mAh g$^{-1}$, respectively. Compared with the reported single Ti$_3$C$_2$F$_2$ (130.0 mAh g$^{-1}$), the Ti$_3$C$_2$F$_2$/IT-MoS$_2$ has a noticeable improvement, which is comparable to graphite. While it is still lower than pure IT-MoS$_2$ (670.0 mAh g$^{-1}$) as anode materials for LIBs.

The OCV is another critical metric for the anode material of LIBs. The OCV can be computed by the following equation:[45,46]

$$V = -\frac{\Delta G}{nF} = -\frac{\Delta E}{nF}$$

where $\Delta G = \Delta E + PAV - T\Delta S$ is the difference in Gibbs energy. Here, $PAV$ can be neglected (10$^{-5}$ eV) and $T$ is set to 0 K. $\Delta G$ could be mainly dominated by the variation in the total energy $\Delta E$. The OCV obtained from $\Delta E$ can be calculated as

$$V = \frac{E_{C1} - [E_{C0} + (C_{1} - C_{0})E_{el}]}{(C_{1} - C_{0})e^{-}}$$

where $E_{C1}$ and $E_{C0}$ are total energies of two heterostructures with Li concentrations $C_1$ and $C_2$ ($C_1 > C_2$). As shown in Figure 6b, with the increment of adsorbed Li atoms, the corresponding OCV gradually reduced to 2.30 V. For Ti$_3$C$_2$O$_2$/IT-MoS$_2$, similar to Ti$_3$C$_2$F$_2$/IT-MoS$_2$, the OCV can be computed by the following equation:

$$V = \frac{E_{C1} - [E_{C0} + (C_{1} - C_{0})E_{el}]}{(C_{1} - C_{0})e^{-}}$$

where $E_{C1}$ and $E_{C0}$ are total energies of two heterostructures with Li concentrations $C_1$ and $C_2$ ($C_1 > C_2$). As shown in Figure 6b, with the increment of adsorbed Li atoms, the corresponding OCV gradually reduced to 2.30 V. For Ti$_3$C$_2$O$_2$/IT-MoS$_2$, the initial OCV is 3.14 V, after insertion of more Li, the corresponding OCV gradually reduced to 2.30 V. For Ti$_3$C$_2$F$_2$/IT-MoS$_2$, similar to Ti$_3$C$_2$O$_2$/IT-MoS$_2$, the OCV of pure Li atoms is 0.24 V. The OCV of Ti$_3$C$_2$/IT-MoS$_2$, the OCV is 2.30 V. For the Ti$_3$C$_2$/IT-MoS$_2$, the initial OCV is 3.14 V, after insertion of more Li, the corresponding OCV gradually reduced to 2.30 V. For Ti$_3$C$_2$/IT-MoS$_2$, with the uptake of more Li atoms, the corresponding OCV gradually decreases from 2.36 to 0.88 V. Regarding practical application, when the operating voltage of the anode is lower than 1 V versus pure Li, the Fermi energy of the anode will be lower than the lowest unoccupied molecular orbital (LUMO) of the organic electrolyte, resulting in the decomposition of solid electrolyte interphase (SEI) and electrolyte.[47] Therefore, a higher OCV associated with decorating functional groups F and O atoms will increase the performance of MXene/MoS$_2$ as anode materials for LIB. In addition, a higher OCV is also beneficial for avoiding Li plating and a high rate capability.[45]

3. Conclusions

In summary, via first-principles calculations, we explored the interfacial electronic properties of heterostructures consisting of MXene and IT-MoS$_2$ that have a small lattice mismatch allowing homogeneous and epitaxial integration. We found that the surface functional groups in MXene can dramatically alter the interfacial electronic affinity, that the –O and –F terminated surface will significantly increase the work function of MXene and thus reducing the leakage of the electrons. By adjusting surface functional groups (-O, -F), the total performance of Ti$_3$C$_2$/IT-MoS$_2$ is greatly promoted. The insertion of F, O atoms leads to a smaller charge transfer and weakening of S-Ti bonds, which is necessary for the uptake (i.e., stronger adsorption) and activation (i.e., more mobile) of Li atoms. Our AIMD results also confirm the fast kinetics of Li atoms in residual-contained MXene heterostructure. In particular, we reveal that O atoms exhibit stronger fixation capacity than F atoms, leading to a sluggish Li diffusion behavior. The high diffusivity and great capacity suggest that MXene derivatives and hybrids are highly promising for LIB applications.

4. Experimental Section

First-principles calculations were carried out by the plane wave code Vienna ab initio simulation package (VASP)[48] with projector augmented wave (PAW) method. Exchange-correlation energy was performed under the generalized gradient approximation (GGA) with the form of PerdewBurkeErnzerhof (PBE).[49] DFTD3 functional with Grimme[50] correction was employed to describe the weak van der Waals (vdW) interaction between 1T-MoS$_2$ and MXenes. An energy cutoff of 450 eV and energy convergence of 10$^{-4}$ eV were used in all calculations. All of the structures were optimized until the forces exerted on each atom were <0.005 eV Å$^{-1}$. A 2 $\times$ 2 $\times$ 1 supercell was adopted and the Brillouin zone Kpoint mesh was set as $4 \times 4 \times 1$ for structural optimization, then a $12 \times 12 \times 1$ Kpoint mesh was applied for electronic structural computations. The thickness of the vacuum region was set to $>15$ Å to avoid interference of periodic images. The diffusion barriers are calculated through the climbing-image nudged elastic band (CI-NEB).[51] The ab initio molecular dynamics simulations in the NVT ensemble were employed based on the Nosé-Hoover thermostat[52] with a time step of 1 fs.

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