A systematical ab-initio review of promising 2D MXene monolayers towards Li-ion battery applications

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Abstract

Two-dimensional materials have been attracting increasing interests because of their outstanding properties for Lithium-ion battery applications. In particular, a material family called MXenes ($M_{n+1}C_n$, where $n = 1, 2, 3$) have been recently attracted immense interest in this respect due to their incomparable fast-charging properties and high capacity promises. In this article, we review the state-of-the-art computational progress on Li-ion battery applications of MXene materials in accordance with our systematical DFT calculations. Structural, mechanical, dynamical, and electrical properties of 20 distinct MXenes (M: Sc, Ti, V, Cr, Nb, Mo, Hf, Ta, W, and Zr) have been discussed. The battery performances of these MXene monolayers are further investigated by Li-ion binding energies, open circuit voltage values, and Li migration energy barriers. The experimental and theoretical progress up to date demonstrates particularly the potential of non-terminated or pristine MXene materials in Li ion-storage applications. Stability analyses show most of the pristine MXenes should be achievable, however susceptible to the development progress on the experimental growth procedures. Among pristine MXenes, Ti$_2$C, V$_2$C, Sc$_2$C, and Zr$_2$C compounds excel with their high charge/discharge rate prospect due to their extremely low Li diffusion energy barriers. Considering also their higher predicted gravimetric capacities, Sc, Ti, V, and Zr containing MXenes are more promising for their utilization in energy storage applications.

1. Introduction

Today's technology is becoming increasingly mobile by the rapid development of portable devices and electric vehicles. Lithium-ion batteries (LIBs) are currently energizing the portable devices, electric vehicles, and other mobile technologies, because of their high energy densities, despite the smaller size and lightweight. Currently, the main aim of the research on LIB technology is to improve energy efficiency as the required power in mobile technologies is increasing rapidly in order to improve the overall device performances and capabilities. Despite the improvements, finding more efficient materials as electrodes in LIBs is crucial to meet the expected energy demand for mobile technologies.

In this respect, following the discovery of graphene and its extraordinary properties [1], many two-dimensional (2D) materials, such as germanene [2], silicene [3], hexagonal BN [4], black phosphorous [5], and a large family of transition metal dichalcogenides (TMDC) [6] have been discovered. Although most of the research on the applications of 2D materials have been focused on electronic devices such as p-n junctions [7, 8] and field-effect transistors [9] to benefit from their semiconductor properties possible energy storage applications, including supercapacitors [10], thermoelectric devices [11] and batteries [12] of 2D materials such as graphene and TMDCs has also been investigated. Particularly, Li-ion batteries based on 2D materials have attracted growing interest because of their fast ion diffusion property [13]. TMDCs, for...
example, have low diffusion barriers and high lithium (Li) storage capacity, but they are mainly semiconductors [14]. Graphene is thought to be another option for anode material because of its metallic properties. However, low binding capacity for Li has been found for graphene as a drawback [15, 16].

On the other hand, metallic MXenes, a recent member of 2D materials family, have been demonstrated to be good candidates as electrode materials for Li-ion Batteries and Li-ion capacitors [17–19]. Furthermore, many different types of MXene materials (see figure 1) have been synthesized by chemical exfoliation methods up to date, and even more are predicted to be stable and experimentally accessible [20]. One of the most remarkable features of MXenes is the versatility of their physical properties by tailoring its composition, thickness, and/or the surface termination. However, this leads to dozens of combinations to produce and to try for their battery performances experimentally, which needs a considerable amount of effort and resources. Thus, for further experimental progress, it is very important to assess which combinations are more promising among others beforehand. Here come the computational approaches into play to direct the research and reduce the workload on the experimental efforts. However, one of the biggest challenges here is the coherence of theoretical predictions with experimental results. Density functional theory (DFT) is the mainstream approach for inorganic and periodic systems but this approach intrinsically lacks to define weak interactions such as van der Waals. However, nowadays dispersion corrections are pretty standardized for DFT codes and improve the modelling accuracy of weakly bound systems [21].

Recent experimental and theoretical studies already showed a promising future for MXene materials towards Li-ion batteries, yet more comprehensive and comparative knowledge about which MXenet systems are more appropriate to which applications are as essential and required. In this article, we review the state-of-the-art computational progress on Li-ion battery applications of MXene materials in accordance with our systematically DFT calculations. For the sake of comparability of different systems with varying computational approaches and parameters, we will introduce our novel results as well by comparing with the literature to allow a direct comparison with exactly the same computational methodology.

2. MXene monolayers

MXene (M_{n+1}X_n) is the general name of the 2D material family of early transition metal carbides, nitrides and carbonitrides since they have been initially synthesized by selective etching of A atoms from the so-called MAX (MA_{n+1}X_n) phase materials, where M is an early transition metal, A is an element from group IIIA or IV A, and X is carbon (C) and/or nitrogen (N) [22, 23]. The crystal structure of the monolayer M\textsubscript{X} system is a hexagonal lattice, which consists of triple layers stacked in a sequence of M-X-M as can be seen in figure 1(b). Similarly, monolayer M_3\textsubscript{X} composes from quintuple layers stacked in a sequence of M-X-M-X-M. Both crystals are derived from their corresponding bulk MAX structure by removing A atoms. In both M_2C and M_3C_2 systems, the layer of C-atoms is enclosed in the layer of M-atoms forming M_6C octahedrons. To date, many different types of MXene have been synthesized with chemical exfoliation, such as Ti_3C_2T_x, Ti_2CT_x, Nb_3CT_x, Nb_3C_2T_x, V_2CT_x, (Ti_{0.5}Nb_{0.5})_2CT_x, (V_{0.5}Cr_{0.5})_2CT_x, Ta_2C_3T_x, Mo_2TiC_2T_x, and Mo_2Ti_2C_3T_x [23–26]. Here T_x represents the terminal groups (also referred to as functional groups) inherently coming from exfoliation process commonly as -O, -F, and/or -OH and usually exhibits a mixture of terminations [27, 28]. Further experimental studies by electron energy-loss spectroscopy in transmission electron microscopy [29, 30], x-ray photoelectron spectroscopy [31], neutron scattering [32] and NMR...
Table 1. Experimental Li-ion battery performances of MXene systems.

| Structure                | Cycle | Rate       | Capacity       | Ref  |
|--------------------------|-------|------------|----------------|------|
| Hf$_2$C$_7$T$_x$         | 200   | 200 mA g$^{-1}$ | 146 mAh g$^{-1}$ | [38] |
| Mo$_2$Ti$_2$C$_7$T$_x$   | 2     | 1 C        | 176 mAh g$^{-1}$ | [39] |
| Mo$_2$CT$_x$             | 10 000 | 2 mV s$^{-1}$ | 196 F g$^{-1}$  | [27] |
| Mo$_2$CT$_x$             | 10 000 | 100 mV s$^{-1}$ | 120 F g$^{-1}$  | [27] |
| Nb$_2$CT$_x$             | 100   | 1 C        | 170 mAh g$^{-1}$ | [40] |
| Nb$_2$CT$_x$             | 150   | 10 C       | 110 mAh g$^{-1}$ | [40] |
| Nb$_2$C$_7$T$_x$         | 1     | C/3        | 16 mAh cm$^{-2}$ | [41] |
| Nb$_2$C$_7$T$_x$         | 50    | C/3        | 6.7 mAh cm$^{-2}$ | [41] |
| Nb$_2$C$_7$T$_x$         | 1     | 0.1 A g$^{-1}$ | 310 mAh g$^{-1}$ | [42] |
| Nb$_2$C$_7$T$_x$         | 100   | 0.1 A g$^{-1}$ | 380 mAh g$^{-1}$ | [42] |
| Nb$_2$C$_7$T$_x$         | 1     | 1 A g$^{-1}$   | 116 mAh g$^{-1}$ | [42] |
| Nb$_2$C$_7$T$_x$         | 100   | 1 A g$^{-1}$   | 320 mAh g$^{-1}$ | [42] |
| Nb$_2$C$_7$T$_x$         | 25    | 0.2 mV s$^{-1}$ | 189 mAh g$^{-1}$ | [43] |
| (Nb$_{0.8}$Ti$_{0.2}$)$_2$C$_7$T$_x$ | 20 | 0.2 mV s$^{-1}$ | 158 mAh g$^{-1}$ | [43] |
| (Nb$_{0.8}$Zr$_{0.2}$)$_2$C$_7$T$_x$ | 20 | 0.2 mV s$^{-1}$ | 132 mAh g$^{-1}$ | [43] |
| Ti$_2$O$_2$/Ti$_2$CT$_x$ | 5000  | 100 mA g$^{-1}$ | 389 mAh g$^{-1}$ | [44] |
| Ti$_2$CT$_x$             | 5     | C/25       | 225 mAh g$^{-1}$ | [19] |
| Ti$_2$CT$_x$             | 80    | 1 C        | 110 mAh g$^{-1}$ | [19] |
| Ti$_2$CT$_x$             | 120   | 3 C        | 80 mAh g$^{-1}$  | [19] |
| Ti$_2$CT$_x$             | 200   | 10 C       | 70 mAh g$^{-1}$  | [19] |
| Ti$_2$C$_7$T$_x$         | 1     | 1 C        | 126.3 mAh g$^{-1}$ | [35] |
| Ti$_2$C$_7$T$_x$         | 100   | 3 C        | 88 mAh g$^{-1}$  | [35] |
| Ti$_2$C$_7$T$_x$         | 100   | 10 C       | 69 mAh g$^{-1}$  | [35] |
| Ti$_2$C$_7$T$_x$         | 100   | 1 C        | 410 mAh g$^{-1}$ | [18] |
| Ti$_2$C$_7$T$_x$         | 100   | 36 C       | 110 mAh g$^{-1}$ | [18] |
| Ti$_2$C$_7$T$_x$         | 100   | 1 C        | 15 mA cm$^{-2}$  | [41] |
| Ti$_2$C$_7$T$_x$         | 50    | C/3        | 59 mAh cm$^{-2}$ | [41] |
| Ti$_2$C$_7$T$_x$         | 1000  | 0.05 A g$^{-1}$ | 343 mAh g$^{-1}$ | [36] |
| Ti$_2$C$_7$T$_x$         | 1000  | 0.5 A g$^{-1}$ | 300 mAh g$^{-1}$ | [36] |
| V$_2$CT$_x$              | 1     | 370 mA g$^{-1}$ | 291 mAh g$^{-1}$ | [37] |
| V$_2$CT$_x$              | 20    | 370 mA g$^{-1}$ | 260 mAh g$^{-1}$ | [37] |
| V$_2$CT$_x$              | 150   | 1 C        | 260 mAh g$^{-1}$ | [40] |
| V$_2$CT$_x$              | 150   | 10 C       | 125 mAh g$^{-1}$ | [40] |

spectroscopy [33, 34] also confirm there is a random distribution of terminations on MXene surfaces, rather than regions terminated by a certain kind of terminal group.

Table 1 introduces electrochemical battery performances of MXene in Li-ion batteries obtained from experimental studies [18, 19, 27, 35–44]. Note that all the MXenes studied here have random surface termination groups (T$_x$) usually in an unidentified structure and composition. According to table 1, very diverse capacity values have been observed from around 70 up to 410 mAh g$^{-1}$. However, gravimetric capacities are still far from the desired high capacities, which are predicted from the theoretical works. It can be seen that more than 300 mAh g$^{-1}$ variance can be seen even for the same composition and thickness as in the case of Ti$_2$C$_7$T$_x$ [18, 35, 39]. Thus, it is clear that the effect of terminal groups causes significant changes in the intercalation behavior of MXenes and should be controlled or optimized.

In computational approaches, however, it is difficult to model MXene structure with mixed and random terminations of -O, -F, and -OH on their surfaces. Thus, most of the theoretical studies have focused on models with the uniform adsorption of one of the chemical groups on specific sites on MXene surfaces. The predicted Li-ion battery performances of several MXene systems investigated by using DFT methods are summarized in table 2 [45–69].

Xingshuai Lv et al [68] studied the battery performance of pristine Sc$_2$C and their reported value of 0.018 eV is the lowest diffusion energy barrier among all of the calculated MXene systems despite low intercalation strength and low open-circuit voltage (OCV). However, later theoretical studies report instability for Sc$_2$C MXene systems [62, 70]. Yang et al [65] investigated Li storage capability of Hf-based MXenes both for terminated (-O, -F, and -OH) and non-terminated pristine cases. According to their results, pristine Hf$_2$C$_2$ has the lowest Li diffusion energy barrier and the highest theoretical capacity with respect to terminated Hf$_2$C$_2$ structures. Among terminated cases, they report the highest intercalation strength for -O terminated case while the lowest diffusion energy barrier for -F terminated case. Zhou et al [66] performed a similar study with Mn$_2$C as a MXene electrode. They also report the highest capacity for pristine case with a
Table 2. Theoretical Li-ion battery performances of MXene systems compared to black phosphorus, graphene, graphite, MoS$_2$, and Silicene. $E_{\text{bind}}$ is the Li binding energy, $E_{\text{barrier}}$ is the diffusion energy barrier for Li atom on MXene monolayer, OCV is the predicted open-circuit voltage, and C is the gravimetric Li capacity.

| Structure         | $E_{\text{bind}}$ (eV) | $E_{\text{barrier}}$ (eV) | C (mAh g$^{-1}$) | Ref |
|-------------------|------------------------|---------------------------|-----------------|-----|
| Black Phosphorus  | −1.7                   | 0.084                     | −               | [45]|
| Graphite          | −                      | 0.3                       | −               | [46]|
| Graphene          | −1.5                   | 0.327                     | −               | [57]|
| MoS$_2$           | −1.32                  | 0.21                      | 670             | [63]|
| Silicene          | −2.08                  | 0.23                      | −               | [64]|
| Hf$_2$C$_2$       | −2.23                  | 0.027                     | 1034.7          | [65]|
| Hf$_2$C$_2$O$_2$  | −3.83                  | 0.371                     | 978.72          | [65]|
| Hf$_2$C$_2$F$_2$  | −2.08                  | 0.225                     | 80.74           | [65]|
| Hf$_2$C$_2$(OH)$_2$| −1.99                  | 0.44                      | 162.57          | [65]|
| Mn$_2$C           | −1.93                  | 0.05                      | 439             | [66]|
| Mn$_2$CO$_2$      | −4.45                  | 0.2                       | 348             | [66]|
| Mn$_2$CF$_3$      | −3.65                  | 0.22                      | 167             | [66]|
| Mo$_2$C           | −0.97                  | 0.043                     | 526             | [60]|
| Mo$_2$C           | −0.58                  | 0.035                     | 526             | [61]|
| Nb$_2$C           | −0.71                  | 0.036                     | 305             | [67]|
| Nb$_2$CO$_3$      | −2.28                  | 0.3                       | 292             | [67]|
| Nb$_2$CO$_3$F$_{0.5}$| −2.53                | 0.12                      | 29              | [67]|
| Nb$_2$CF$_2$      | −1.61                  | Unstable                  | −               | [67]|
| Nb$_2$(OH)$_3$    | 0.51                   | No absorption             | −               | [67]|
| ScC               | −0.2                   | 0.018                     | 462             | [68]|
| Sc$_2$CO$_3$      | −9.99                  | unstable                  | 362.7           | [62]|
| Sc$_2$(OH)$_3$    | 0.05                   | 0.51                      | 357.8           | [62]|
| T$_3$C            | −2.13                  | 0.02                      | −               | [69]|
| T$_3$C            | −1.16                  | −                         | 497             | [47]|
| T$_3$CO$_2$       | −                      | 0.6                       | 192             | [48]|
| T$_3$CO$_2$       | −                      | −                         | 192             | [47]|
| T$_3$CO$_2$       | −1.87                  | 0.27                      | 348.9           | [62]|
| T$_3$C(OH)$_2$    | 0.146                  | No absorption             | 344.4           | [62]|
| T$_3$CF$_2$       | −                      | −                         | 92              | [47]|
| T$_3$N            | −0.75                  | 0.0215                    | 484             | [49]|
| T$_3$NO$_2$       | −1.5                   | 0.2496                    | 378             | [49]|
| T$_3$NF$_2$       | −0.2                   | 0.2788                    | 90              | [49]|
| T$_3$N(OH)$_2$    | 0.75                   | No absorption             | −               | [49]|
| T$_3$C$_2$        | −0.50                  | 0.07                      | 320             | [50]|
| T$_3$C$_2$        | −4.4                   | 0.068                     | 447.8           | [51]|
| T$_3$C$_2$O$_2$   | −2.28                  | 0.41                      | 268.53          | [52]|
| T$_3$C$_2$O$_2$   | −                      | 0.6                       | 134             | [48]|
| T$_3$C$_2$F$_2$   | −0.95                  | 0.16                      | 130             | [50]|
| T$_3$C$_2$(OH)$_2$| −0.20                  | 0.9                       | 67              | [50]|
| T$_3$C$_2$S$_2$   | −1.94                  | 0.25                      | 462.61          | [52]|
| T$_3$C$_2$Se$_2$  | −1.11                  | 0.15                      | 329.32          | [52]|
| T$_3$C$_2$Te$_2$  | −0.07                  | −                         | −               | [52]|
| T$_3$CN           | −2.42                  | 0.024                     | 320             | [53]|
| T$_3$CNO$_2$      | −3.32                  | 0.26                      | 269             | [53]|
| T$_3$CNF$_2$      | −2.38                  | 0.24                      | −               | [53]|
| T$_3$C(NO)H$_2$   | −0.89                  | 0.22                      | −               | [53]|
| T$_3$C$_3$O$_2$   | −                      | 0.73                      | 103             | [48]|
| V$_2$C            | −0.78                  | 0.06                      | 1412.39         | [54]|
| V$_2$C            | −0.16                  | 0.045                     | 941             | [55]|
| V$_2$CO$_2$       | −1.45                  | 0.19                      | 735             | [56]|
| V$_2$CO$_2$       | −1.8                   | 0.15                      | 367.64          | [58]|
| V$_2$CO$_2$       | −                      | 0.82                      | 276             | [48]|
| V$_2$CO$_2$       | −2.79                  | 0.18                      | 335.5           | [62]|
| V$_2$CF$_2$       | −1.57                  | 0.336                     | 116             | [55]|
| V$_2$(OH)$_3$     | −0.17                  | −                         | 331.3           | [62]|
| V$_2$(OH)$_3$     | −0.27                  | 0.589                     | 181             | [55]|
| V$_2$CS$_2$       | −1.66                  | 0.22                      | 301.22          | [58]|
| V$_2$C$_2$        | −0.73                  | 0.05                      | 909.62          | [54]|


drastically lower diffusion energy barrier for Li atoms. In this study -O terminated case has slightly lower Li diffusion energy barrier and higher capacity than -F terminated case although having also higher intercalation strength. Zhu et al [67] reported the same type of investigation with Nb-based MXenes. Interestingly they found -F terminated case is unstable and they found that Nb2C(OH)2 has positive adsorption energy, i.e. it cannot adsorb Li-atoms. They also found that the highest capacity is for the pristine case with lowest diffusion energy barrier. They also studied mixed composition of terminations and found that Nb2CO3F0.5 has slightly lower diffusion energy barrier than solely -O terminated case, however its capacity is drastically low. In another study Zhu et al [59] also studied Zr-based MXene system with the inclusion of -S, -Se and -Te terminations as well. They observed that -Se and -Te unfavors Li adsorption and -S termination substantially lowers the diffusion barrier compared to -O terminated case while keeping capacity similar. Still their report shows that the pristine case has the lowest diffusion energy barrier and highest capacity.

Ti-based MXenes are probably the most studied case in MXene family as traditionally Ti3C2T x is the first produced one. Zhao et al [69] and Kurahashi et al [47] studied the Li- Ti2C system and reported low diffusion barriers for pristine Ti2C which are almost equal to Sc2C while having higher open-circuit voltage and theoretical capacity than Sc2C. Kurahashi et al [47] reports much lower capacities for -O and -F terminated MXenes than pristine Ti2C. According to the study of Wang et al [49], Ti3N has also a very low diffusion barrier similar to Ti3C. Again in this study -OH terminated Ti2N(OH)2 has positive absorption energy, and thus found not to be suitable for ion battery applications as in the case of Nb-based Mxenes. They also reported high capacity for -O terminated Ti3NO3, but with more than 10 times higher diffusion energy barriers than the pristine case. For pristine Ti3C2 higher diffusion energy barriers and lower capacities than Ti3C are reported [50, 51]. Chen et al [53] showed that replacing one carbon with N lowers the diffusion energy barrier for Ti3C2 while keeping the capacity in the same order. Ashton et al [48] studied the effect of thickness by studying V- and Ti-based MXenes and showed that in general the capacities and diffusion energy barriers are decreasing with increasing thickness. However, all in all, the values for pristine cases are still much better when compared to their terminated cases for Ti-based MXenes.

The same story is also observed for V-based MXenes in general, however, the absolute values of capacities and diffusion energy barriers of the same systems differ from each other due to the slight differences in their respective calculation parameters. Thus, it reminds the importance of the usage of the same methodology when comparing different systems with each other, especially for different chemical composition MXenes. With this in mind, we also report our DFT calculation results for pristine MXenes based on Sc, Ti, V, Cr, Nb, Mo, Hf, Ta, W, and Zr in the next section to compare their relative Li-ion battery performances and assess the best candidates among a dozen of possible MXene materials. Thus, from this point on all the data presented are from the results of our systematical calculations unless otherwise stated.

3. Pristine MXene monolayers

As the terminations significantly affect the physical and chemical properties of MXenes, lots of experimental efforts have been given to tailor the terminations in MXene materials [71]. For example, Cl was recently added to the list of terminations by synthesis from MAX phases through Lewis acidic melts and was demonstrated as an exclusive termination for MXenes [72]. Sulphur termination is also achieved by reacting sulfur with the hydroxylated surface of Ti2C nanosheets and studied for battery applications [71], and nowadays becoming hot topic [73–77].

Despite all the experimental efforts, pristine (non-terminated) MXenes are not yet synthesized. However, recent advances show partial surface termination removal by post-synthesis processes such as heating treatment [78] and vacuum annealing [79, 80]. Hart et al [80] report that the termination removal increases
the electronic conductivity of MXenes, and also notes that -O terminations are more stable and thus harder to remove. Persson et al [81] show H2 exposure at elevated temperatures is a facile route for removing O-terminations. Another study shows that -F termination can be prevented by HF-free syntheses [82].

Although the chemical exfoliation method is appropriate to study the fundamental properties of MXenes, the implementation of MXene materials in practical device applications would require more scalable synthesis methods [83]. Furthermore, termination group generation should be minimized in a controllable way to achieve fundamental MXene properties. For example, epitaxial Mo2C MXenes have already been synthesized by using chemical vapor deposition (CVD) technique [84] and by chemical conversion from MoS2 by carburization [83], and such growth processes may be pivotal to attain pristine monolayers.

In practical Li-ion battery applications, the mechanical and dynamical stability of electrode material in question is a vital parameter to endure excessive charge-discharge cycles. Thus, a number of theoretical studies already investigated phonon dispersion relations of pristine MXene materials and showed that Sc2C [85], Ti2C [85, 86], Ti3C2 [86, 87], V2C [88], Cr2C [89], Zr2C [85], Nb2C [86], Nb4C3 [86], Mo2C [85, 91], Ta2C [92], W2C [93] are dynamically stable. Furthermore, thermodynamical stabilities of above MXene materials except from Sc2C have been also reported Ti3C [94], Ti2C [94], V2C [94], Cr2C [94], Zr2C [94], Nb2C [94], Nb4C3 [86], Mo2C [60, 91, 94], Hf2C2 [65] Ta2C [94], W2C [93]. We filled the gaps by calculating the phonon dispersion relations with all of the possible M2C and M3C2 type MXenes. The phonon dispersions of monolayer W2C, W3C2, Ti2C, and Ti3C2 are shown in figure 2 as an example.

In general, negative (imaginary) vibrational frequencies are related with dynamical instability in phonon dispersion relations and there is no vital negative frequency observed for the considered MXene systems, but only artificial and negligible negative frequencies around the Γ point as in the case of W2C and W3C2 (see figure 2). Thus, due to the given phonon dispersions, all of the MXene systems can be considered to be dynamically stable. For M2X systems, there are nine modes, among which three of them are acoustic modes and the rest (3 n − 3 = 6, n: number of atoms in the unit cell) are optical modes. On the other hand, there are three acoustic and twelve optical modes for M3X2 systems. In general, for all MXene systems, the in-plane transverse acoustic (TA) and longitudinal acoustic (LA) modes have linear dispersions, whereas that of the out-of-plane acoustic modes (ZA) is quadratic near the gamma point which is known to be a common feature of 2D materials like silicene, germanene, phosphorene, and graphene.

The calculated physical properties of the considered single layer M2C and M3C2 structures are shown in table 3. The optimized geometries show that the lattice constants decrease while increasing the atomic number of transition metal elements in the same row in the periodic table. The optimized thickness of monolayer M3C2 systems was found approximately two times larger than the monolayer M2C systems. On the first sight, C11 and Y values of M3X2 systems are higher than M2X systems, except for Cr2C. This increase in stiffness is somehow expected because of the layer thickness increases for the same metal from M2X to
Mechanical stability of 2D hexagonal crystals was evaluated according to Born criteria \[ \frac{E_c}{E_M} > 0 \] and \[ \frac{E_{coh}}{E_M} > 0 \]. As given in Table 3, all considered pristine MXene systems met these criteria and can be considered as mechanically stable. For most of the MXenes considered, positive Poisson’s ratio was obtained. The only exception is Cr$_2$C, Mo$_2$C, and Ta$_3$C$_2$ monolayers, which can be considered Auxetics materials because of their negative Poisson’s ratio. In general, the elastic constants C$_{11}$ is found much higher than C$_{12}$ due to the hexagonal symmetry. Among the considered MXenes the stiffest crystals were found as W$_2$C and W$_3$C$_2$. The stiffness of W$_3$C$_2$ is much higher than that of monolayer TMDC family (max; W$_5$: 139 N m$^{-1}$) \[ \text{(98)} \] and less than that of graphene (341 N m$^{-1}$) \[ \text{(98)} \] and single layer h-BN (275.9 N m$^{-1}$) \[ \text{(99)} \].

To further investigate and compare the relative stabilities of the 2D MXene materials, well-established indicators such as cohesive energy \( E_{coh} \) and exfoliation energy \( E_{exf} \) can be used. (see Table 4) The cohesive \( E_{coh} \) and exfoliation \( E_{exf} \) energy are usually estimated by the following equations:

\[
E_{coh} = \frac{E_{M+1C} - (n + 1) E_M - (n) E_C}{(n + 1) + n}
\]

and,

\[
E_{exf} = \left( E_{Al} + E_{M+1C} - \frac{1}{2} E_{M+1AlC_n} \right) / \text{Area}
\]

where \( E_{M+1C} \) and \( E_{M+1AlC_n} \) are the total energy values of the corresponding MXene and MAX systems for the metal element M (M: Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W), while \( E_{Al} \) and \( E_C \) are the total energy values of corresponding elements at their preferred bulk phases.
Figure 3. Electronic band structures of monolayer (a) Ti$_2$C, (b) Ti$_3$C$_2$, (c) Sc$_2$C, and (d) Sc$_3$C$_2$ systems.

Firstly, all the cohesive energies of monolayer M$_3$C$_2$ systems were found 0.4–0.6 eV lower than M$_2$C systems as expected, since the average coordination number increases with the additional metal layer. The lowest cohesive energy value was found for Ta$_3$C$_2$ (Ta$_2$C), while the highest was found for Cr$_3$C$_2$ (Cr$_2$C) when changing the metal atom in the MXene system. Note that, all the cohesive energy values are between the values of already synthesized materials such as graphene (~7.906 eV) [100] and silicene (~4.01 eV) [101]. Except for Sc$_2$C, all the calculated cohesive energy values are also lower than that of borophene (5.87 eV) [102] and phosphorene (4.67 eV) [103]. The exfoliation energies of all the MXene materials were found similar and in the range between 0.30–0.45 eV Å$^{-2}$ except for Sc$_2$C and Sc$_3$C$_2$. Noting all graphene, silicene, borophene, and phosphorene were already synthesized, pristine MXene materials could also be achievable due to their similar exfoliation and formation energy values.

4. Properties of pristine MXene monolayers towards LIBs

The cycle characteristics of LIBs are affected by the electronic properties of electrode materials, i.e. the cyclic performance correlates with the conductivity of electrode materials [104, 105]. Therefore, metallic materials with high conductivity are more suitable for LIBs. Note that, Hart et al [80] showed that the termination removal increases the electronic conductivity of MXenes, which makes pristine MXenes desirable. Furthermore, it is also shown that some functionalized MXene structures have semiconducting nature [84, 85]. In that respect, electronic band structures of Ti- and W- based MXenes are given in figure 3 as an example. In these band structures, the Fermi level is fitted to zero eV. The non-zero density of states at the Fermi level shows that all the considered systems were found to be metallic.

A relatively strong Li binding to the metal atoms is a sine qua non in order to be a good anode material. However, too strong binding may also lead to the trapping of the Li-ions. According to table 2, different Li binding energies are reported in literature even for the same systems as in Ti$_2$C [47, 69], Ti$_3$C$_2$ [50, 51] and V$_2$C [54, 55] cases. These type of differences in different computational studies can be caused by (I) the selection of different computational methods or parameters, (II) different system configurations, i.e. different Li adsorption sites, different coverages treated as full coverage (III) unit cell and system sizes, and (IV) different reference systems, for example, whether Li bulk or Li single atom energies are taken into account.

Therefore, here we present the calculated Li binding energy values for all the pristine MXene systems in figure 4 by the following definition of Li binding energy:

$$E_{\text{bind}} = E_{\text{MXene} + \text{Li}} - E_{\text{MXene}} - xE_{\text{Li}}$$

(3)
where $E_{\text{MXene}+\text{Li}_x}$ is the total energy of Li bound MXene system, $E_{\text{MXene}}$ is the total energy of the pristine MXene and $E_{\text{Li}}$ is the total energy of Li atom in a body-centered cubic bulk phase and $x$ is the number of Li atom bound by MXene.

Three possible high-symmetry adsorption sites (A: hcp site; B: atop site; C: fcc site) were considered for the Li adsorption energies on monolayer $M_2C$ and $M_3C_2$ systems. Here, more negative $E_{\text{bind}}$ means energetically more favorable interaction between the Li atom and MXene monolayer. In general, the Li binding energies are very close (within 0.01 eV) for hcp and fcc sites, and the hcp site is slightly more favorable for most of the considered systems. Li adsorption on the atop site, on the other hand, is always the least favorable site by 0.05–0.2 eV.

As depicted in figure 4, Sc$_2$C and Sc$_3$C$_2$ systems have weak Li binding energies which are between $-0.1$ and $-0.5$ eV. The strongest Li binding energies were found for Mo$_2$C, W$_2$C, and Ta$_3$C$_2$ systems, which are lower than $-1.1$ eV. For the rest of the MXene systems, binding energies were found approximately between $-0.7$ and $-1.0$ eV. These results and trends are also compatible with the literature values given in table 2. Note that these binding energy values are for single Li adsorption on MXene systems and generally Li binding energy decreases going from low coverage to higher coverages.

The charge/discharge process of MXene relates to the common half-reaction vs. Li/Li$^+$:

$$(x_2 - x_1)\text{Li}^+ + (x_2 - x_1)\text{e}^- + Li_{x_1}\text{MXene} \leftrightarrow Li_{x_2}\text{MXene}$$

Here, the average voltage of $Li_{x_1}\text{MXene}$ in the coverage range of $x_1 \leq x \leq x_2$ can be estimated by the following equation:

$$V \approx \frac{E_{M_{x_1}X_{x_2}+Li_{x_2}} - E_{M_{x_1}X_{x_2}+Li_{x_1}} + (x_2 - x_1)E_{Li}}{(x_2 - x_1)e} \tag{4}$$

where $E_{M_{x_1}X_{x_2}+Li_{x_2}}$ and $E_{M_{x_1}X_{x_2}+Li_{x_1}}$ are the total energies of the MXene with $x_1$ and $x_2$ Li atom intercalated, respectively. $E_{Li}$ is the total energy of the corresponding bulk phase of the Li atom.

Open circuit voltage is a crucial measure of the performance of an anode material. In general, a negative value of voltage would mean that the Li ions prefer to form clusters instead of adsorbing on the anode surface, and thus when the open-circuit voltage drops to 0 V the material is considered to attain its maximum capacity of Li. On the other hand, to meet the needs of rapid charge and discharge, the open-circuit voltage should not be too high. Usually, the open-circuit voltage decreases with the increasing coverage due to the decrease in Li binding energy, and hence the anode material reaches its storage capacity. However, sometimes the voltage values may start to show an increasing tendency at higher coverages due to the increasing Li-Li interactions.

We checked the open-circuit voltage values at the low and high Li coverage limits (single atom and full coverage) for all the considered MXenes and the lack of negative voltage values even at the high coverage...
Figure 5. Open Circuit Voltage values (eV) for M\textsubscript{2}C and M\textsubscript{3}C\textsubscript{2} systems at low and high Li coverage limits.

| System | $E_{\text{barrier}}$ (eV) | Capacity (mAh g\textsuperscript{-1}) | System | $E_{\text{barrier}}$ (eV) | Capacity (mAh g\textsuperscript{-1}) |
|--------|--------------------------|-----------------------------|--------|--------------------------|-----------------------------|
| Sc\textsubscript{2}C | 0.010 | 526.086 | Sc\textsubscript{3}C\textsubscript{2} | 0.017 | 337.468 |
| Ti\textsubscript{2}C | 0.008 | 497.658 | Ti\textsubscript{3}C\textsubscript{2} | 0.024 | 319.886 |
| V\textsubscript{2}C | 0.010 | 470.790 | V\textsubscript{3}C\textsubscript{2} | 0.025 | 303.202 |
| Cr\textsubscript{2}C | 0.026 | 462.230 | Cr\textsubscript{3}C\textsubscript{2} | 0.034 | 297.873 |
| Zr\textsubscript{2}C | 0.013 | 275.740 | Zr\textsubscript{3}C\textsubscript{2} | 0.011 | 180.118 |
| Nb\textsubscript{2}C | 0.030 | 271.050 | Nb\textsubscript{3}C\textsubscript{2} | 0.054 | 177.115 |
| Mo\textsubscript{2}C | 0.037 | 262.932 | Mo\textsubscript{3}C\textsubscript{2} | 0.042 | 171.913 |
| Hf\textsubscript{2}C | 0.027 | 145.315 | Hf\textsubscript{3}C\textsubscript{2} | 0.027 | 95.837 |
| Ta\textsubscript{2}C | 0.037 | 143.405 | Ta\textsubscript{3}C\textsubscript{2} | 0.055 | 94.590 |
| W\textsubscript{2}C | 0.045 | 141.220 | W\textsubscript{3}C\textsubscript{2} | 0.039 | 93.164 |

Table 5. Diffusion energy barriers ($E_{\text{barrier}}$) and specific capacities of monolayer M\textsubscript{2}C and M\textsubscript{3}C\textsubscript{2} systems for LIBs.

limit indicates that the calculated maximum capacity values should be at reach for all these considered MXene materials (see figure 5). One should also note that the open-circuit voltages do not decrease drastically between low and high coverage limits which indicate these MXene systems are suitable to be anode materials for Li-ion batteries, within the full range of coverages. The highest open-circuit voltage values at high coverage limit is calculated for W\textsubscript{2}C (0.893 eV), Mo\textsubscript{2}C (0.819 eV), W\textsubscript{3}C\textsubscript{2} (0.830 eV), and Mo\textsubscript{3}C\textsubscript{2} (0.823 eV), while the lowest are for Sc\textsubscript{2}C (0.571 eV), V\textsubscript{3}C\textsubscript{2} (0.593 eV), Cr\textsubscript{3}C\textsubscript{2} (0.594 eV) and Sc\textsubscript{3}C\textsubscript{2} (0.505 eV), and Cr\textsubscript{3}C\textsubscript{2} (0.609 eV).

In today’s world, quick charging time is quite desirable for all electrical devices. Thus, fast electron and ion transport are necessary in electrodes for low charge/discharge times in batteries. The key parameter to estimate the charge/discharge rate of a battery is the diffusion energy barrier of lithium-ion on the electrode material. It is already given in table 2 that the pristine MXenes has the lowest diffusion energy barriers than their terminated counterparts but a system by system comparison to determine which MXene could be better is difficult to grab from there. To allow this type of comparison we recalculated Li diffusion energy barriers together with all the missing pristine MXene monolayers. The calculated diffusion energy barriers of M\textsubscript{2}C and M\textsubscript{3}C\textsubscript{2} systems are shown in table 5 and figure 6. When we compare these values with the literature values presented in table 2, the ones for Nb\textsubscript{3}C [67] and Mo\textsubscript{2}C\textsubscript{2} [61] are in good agreement while for the other MXenes exist in literature our calculated barriers are energetically lower. This is probably due to the selection of different calculation parameters and selection of different migration paths that probably goes over higher local energy minimum sites. When we compare the gravimetric capacity values given in table 5 with the literature values in table 2, there is much higher degree of agreement, except for Mo\textsubscript{2}C\textsubscript{2} [60, 61] and V\textsubscript{2}C\textsubscript{2} [54, 55] cases. This is because for these materials the capacity values in literature are calculated for double or triple layer coverages, which is unlikely due to the interlayer spacing between MXene layers.

According to the diffusion energy barrier results, the Ti, V, Zr, and Sc based MXene structures have the smallest values both for M\textsubscript{2}C and M\textsubscript{3}C\textsubscript{2} systems. For the M\textsubscript{2}C systems of these materials, the diffusion barriers are as low as 0.01 eV (Ti\textsubscript{2}C: 0.008 eV, V\textsubscript{2}C: 0.010 eV, Sc\textsubscript{2}C: 0.010 eV, and Zr\textsubscript{2}C: 0.013 eV) while for the rest of the materials it is between 0.026 and 0.045 eV. For M\textsubscript{3}C\textsubscript{2} systems the diffusion energy barriers are slightly higher than M\textsubscript{2}C systems in general, but they are still quite low as below 0.06 eV for every material. The lowest are again Ti\textsubscript{3}C\textsubscript{2} (0.024 eV), V\textsubscript{3}C\textsubscript{2} (0.025 eV), Sc\textsubscript{3}C\textsubscript{2} (0.017 eV) and Zr\textsubscript{3}C\textsubscript{2} (0.011 eV). These
Figure 6. Diffusion energy profiles of M$_2$C and M$_3$C$_2$ systems.

diffusion energy barriers are extraordinarily low when compared to other common 2D materials such as MoS$_2$ (0.25 eV) [106], VS$_2$ (0.22 eV) [106], and graphene (0.33 eV) [57] in literature. Arrhenius law ($D \approx \exp(-E_a/k_BT)$) can be used to roughly compare the mobilities of the lithium atoms at room temperature, where $E_a$ is the diffusion energy barrier, $k_B$ is the Boltzmann constant, and $T$ is the temperature. According to this estimation we expect that the Li mobility on Ti$_2$C, V$_2$C, Sc$_2$C, and Zr$_2$C are at least 2 times more than the other mate-rials and 8 times more than the Ta$_3$C$_2$ which has the highest diffusion barrier energy among the considered MXene materials. Note that even Ta$_3$C$_2$ has much lower diffusion energy than other common 2D materials. Thus, in general we expect a faster Li transport and, therefore higher charge/discharge rates for pristine MXene systems.

In terms of computational science point of view, computational studies are expected to direct experimental work beforehand by selecting promising materials among many others by high throughput screening and thus reduce the workload on the experimental efforts. However, generally it is usually difficult to compare calculated properties in different computational studies as the calculated values are usually affected by the selected approach and calculation parameters. Thus, we believe the trends and relative values of calculated properties among a materials series are more meaningful and helpful than the absolute values of a single material. In this respect, the computational methodologies are pretty standardized for specific purposes such as battery applications, however, a multiscale scale computational approach is necessary in order to describe real devices beyond the model system because of the complexity of the environment and processes [107].

5. Conclusion

Motivated by the importance of 2D MXene materials and their critical role in energy storage technologies we present a review on the current theoretical progress of MXene materials towards Li-ion battery applications.

The electronic band structures of pristine MXenes reveal their metallic properties, whereas the conductivity is showed to be lower for terminated MXenes. The pristine structures also have lower diffusion barriers compared to their functionalized derivatives. Thus, due to their metallic properties and high adsorption capacities, the pristine MXene monolayers are very promising electrode materials for Li-ion batteries. Calculated Open circuit voltage profiles reveal that estimated high capacities can be fully achieved for all considered pristine MXene systems. Stability analyses demonstrate that M$_2$C and M$_3$C$_2$ monolayers...
are dynamically and mechanically stable and hint that pristine MXene systems should be experimentally achievable.

Remarkably, Li migration calculations show that Li-atoms are very mobile on the surface of the M₂C and M₁₇C₈ monolayers with extraordinary low diffusion barriers, which are as low as 0.01 eV for Ti₃C, V₃C, Sc₃C, and Zr₃C. Thus, this work suggests the monolayer transition-metal carbides could be a good alternative for fast charging electrode materials and, in particular, the Sc, Ti, V, and Zr based MXene materials are good candidates for experimental and further theoretical investigations.

6. Computational methodology and details

The calculations were performed by using the Vienna ab initio simulation package (VASP) code [108, 109] which is based on Density Functional Theory (DFT) [110, 111]. The projector augmented wave (PAW) pseudopotentials [112, 113] from the standard distribution were integrated into the calculations together with the van der Waals correction of Grimme [114]. The generalized gradient approximation in its PBE parameterization [115] was used for electronic exchange-correlation functional. An energy cut-off of 600 eV was used for the plane wave expansion. The convergence criterion of the self-consistent field calculations was chosen as 10⁻² eV for the total energy. To prevent interactions between isolated monolayers, a vacuum spacing of at least 15 Å was introduced. For geometry optimizations, the Brillouin-zone was sampled using a Monkhorst-Pack k-point grid 24 × 24 × 1 for the unit cell of MXenes, while the force tolerance is set to 10⁻³ eV Å⁻¹.

The elastic tensor of each system was derived from the strain-stress relationship calculated by considering symmetry inequivalent finite distortions of the lattice as implemented in the VASP code [116]. For this part of the calculations, 600 eV energy cut-off and 30 × 30 × 1 k-points sampling were used. The vibrational frequencies were acquired by using PHONOPY code [117], which can directly use the force constants obtained by density functional perturbation theory [118] provided by the VASP code. Here, 4 × 4 × 1 conventional supercell structures and 6 × 6 × 1 Γ centered k-points grids were considered for all 2D MXene systems. The nudged elastic band (NEB) method as implemented in the VASP transition state tools (VTST) [119, 120] was used to calculate the diffusion barriers. Seven images, including initial and final positions, were used for a single Li atom diffusion on a 4 × 4 × 1 MXene supercell.

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