Ion Intercalation into Two-Dimensional Transition-Metal Carbides: Global Screening for New High Capacity Battery Materials

Christopher Eames and M. Saiful Islam*

Department of Chemistry, University of Bath, Bath, BA2 7AY, United Kingdom

E-mail: m.s.islam@bath.ac.uk

Abstract

Two-dimensional (2D) transition metal carbides (termed MXenes) are a new family of compounds generating considerable interest due to their unique properties and potential applications. Intercalation of ions into MXenes has recently been demonstrated with good electrochemical performance, making them viable electrode materials for rechargeable batteries. Global screening of the capacity and voltage for a variety of intercalation ions (Li$^+$, Na$^+$, K$^+$ and Mg$^{2+}$) into a large number of M$_2$C-based compounds (M=Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta) with F, H, O and OH functionalized surfaces has been performed using density functional theory methods. A greater gravimetric capacity of Li$^+$ or Mg$^{2+}$ can be intercalated into an MXene than Na$^+$ or K$^+$, which is related to the size of the intercalating ion. Variation of the surface functional group and transition metal species can significantly affect the voltage and capacity of an MXene, with oxygen termination leading to the highest capacity. The most promising group of M$_2$C materials in terms of anode voltage and gravimetric capacity (>400

*To whom correspondence should be addressed
mAh/g) are compounds containing light transition metals (e.g. Sc, Ti, V and Cr) with non-functionalized or O-terminated surfaces. The results presented here provide valuable insights into exploring a rich variety of high capacity MXenes for potential battery applications.

### 1. Introduction

Two-dimensional (2D) materials such as graphene are currently a topic of intense interest. A significant recent discovery is the new family of 2D early transition metal carbides, which are often termed “MXenes” to indicate their structural similarities with graphene; a range of favorable properties have been investigated for possible applications. One such application is energy storage, which is critical in achieving the important goal of clean sustainable energy. It is clear that major advances in electrochemical energy storage for portable electronics, electric vehicles and electricity grid systems will depend on the discovery and optimization of new high performance materials. Recently, intercalation of ions onto the functionalized surfaces of MXenes was demonstrated with a high rate capability, high storage capacity and low intercalation voltages, which make them promising materials for both supercapacitors and ion intercalation batteries.

MXenes form a 2D layered structure with the general formula $M_{n+1}X_n$ (where $M=$Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta; $X=C, N$ and typically $n=1,2$ or 3). The $M_2C$ structure is shown in Fig. 1 and comprises a central hexagonal graphene layer capped on both sides by a transition metal layer. Naguib et al. shown that selective etching of the A group from MAX phases (e.g. Ti$_2$AlC) results in the formation of 2D carbides such as Ti$_2$C. During synthesis, contact with hydrofluoric acid (HF) leads to functionalization of the MXene surface by O, OH and a small amount of F. For this reason MXenes are usually labelled $M_{n+1}X_nT_x$ where $T_x$ denotes the mixture of functional groups that terminate each surface. Numerous compositions have been synthesized and ion intercalation onto the surfaces of Nb$_2$C, Ti$_2$C, V$_2$C and Ti$_3$C$_2$ has been achieved by experiment.
Computational modelling\textsuperscript{11,15-23} has provided key insights into a number of aspects of MXenes including the atomic and electronic structure, elastic properties, surface functionalization and the formation of nanoscrolls from the rolling of the MXene layers. The functional group attachment sites across the series have been identified.\textsuperscript{11,18} Tang et al.\textsuperscript{17} have also examined the favorable sites for Li insertion into functionalized Ti\textsubscript{3}C\textsubscript{2}X\textsubscript{2} and revealed that the functional group affects both the voltage and the capacity of the system. Crucially, the calculated formation energies of possible MXenes that have not yet been synthesised suggest that many more MXene compositions may be energetically stable.

Figure 1: The two-dimensional M\textsubscript{2}C structure (a) view from above down c-axis (b) side view. Key: green - intercalant, red - functional group, blue - transition metal, grey - graphitic C. In the top view the 1x1 unit cell is outlined in black and for clarity only the first four layers are shown.

In the context of energy storage, lithium-ion batteries have helped power the revolution in portable electronics due to their high gravimetric energy density,\textsuperscript{24-28} with growing use in electric vehicles. Recently, there has been renewed interest in alternatives to lithium. Sodium\textsuperscript{29,30} offers a more abundant, lower cost and electrochemically comparable option to lithium-based counterparts, but the graphite anode is problematic for Na-ion batteries. Divalent intercalating ions such as Mg\textsuperscript{2+} are also attractive\textsuperscript{31,32} since the intercalation of each
ion is a two electron process that effectively doubles the capacity per formula unit. However, magnesium-based batteries have presented formidable obstacles, such as compatible electrolytes, which have prevented their use, and the intercalation of divalent ions in typical 3D intercalation compounds is poorly understood. For the 2D MXenes, intercalation occurs directly from solution, resulting in a higher rate capability than that observed for typical 3D intercalation hosts; intercalation of Mg\(^{2+}\) in MXenes was also recently demonstrated.\(^3\)

A key property of an energy storage material is the gravimetric capacity. MXenes have been reported with reversible capacities of 170 and 260 mAh/g for Nb\(_2\)C and V\(_2\)C-based electrodes respectively in Li-ion battery cells.\(^{33}\) These values are not as high as that for the dominant anode material, graphite,\(^{24}\) at around 350 mAh/g. The capacity thus needs to be improved. However, an extensive range of MXene compositions has not been fully explored. Computational methods based on atomistic potentials and density functional theory (DFT) now play a vital role in characterizing and predicting the properties of new promising materials.\(^{28}\)

In this work we use DFT methods to perform a global search across the M\(_2\)Xene family via a combinatorial screening process of over 300 compounds to identify those with a high intercalation capacity and favorable voltage. Common monovalent (Li\(^+\), Na\(^+\), K\(^+\)) and divalent (Mg\(^{2+}\)) intercalating ions have been intercalated into M\(_2\)C-based compounds (M=Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta) capped with F, H, O, and OH surface functional groups. The present study plays a predictive role in suggesting promising new battery materials for future synthesis and electrochemical work to add to the limited M\(_2\)C phases that have been tested so far.

2. Methodology

DFT and Structure Simulation. Since our study is based on well-established DFT techniques that have been applied to other battery materials\(^{28,34-40}\) and high throughput
searches\textsuperscript{41–45} a brief overview is presented here. Relaxed atomic structures and total energies were computed using the plane-wave DFT based code VASP\textsuperscript{46}. Core electrons were treated using PAW pseudopotentials\textsuperscript{47} and electron correlation was treated using the Perdew Burke Ernzerhof (PBE) generalized gradient approximation.\textsuperscript{48} Xie and Kent have shown that for MXenes higher order treatment of correlation effects is unnecessary.\textsuperscript{18} A 600 eV cutoff energy for the plane wave basis set together with a $12 \times 12 \times 1$ reciprocal space sampling mesh was found to adequately converge the stress for cell shape relaxation. Atomic positions and in-plane lattice parameters were relaxed until the stress was converged to better than 0.05 GPa and the atomic forces were below 0.005 eV/Å. Fully delaminated MXenes are used since these offer a higher rate capability and this was achieved by fixing the $c$ axis of all cells at 50 Å. We have focused on the M$_2$X phases which have the lowest mass per formula unit and hence the highest gravimetric capacity. The starting point for all structural optimizations was the comprehensive set of calculated lattice parameters of Ti$_2$C reported by Xie and Kent.\textsuperscript{18} Functional groups were added in the three-fold hollow site above the three neighbouring C atoms in the graphitic central layer. Several studies have shown that for the majority of MXenes this is the most favorable location.\textsuperscript{11,17,18,21} Two Li, Na, K or Mg atoms were inserted per formula unit at the surface in the site directly above the central C atoms after Tang et al.\textsuperscript{17} The intercalated geometry is a single monolayer on each surface of the MXene slab in a $1 \times 1$ unit cell (see Fig. 2). We emphasize that our aim is global screening; the finer details of the most promising compounds are intended for future work.

A complete set of structural parameters for all compounds is contained in the Supporting Information (SI). There is very limited experimental data on the in-plane lattice parameter ($a$) of MXenes for direct comparison since the nanocrystalline nature of the material makes this difficult to obtain. So far, in-plane lattice parameters have only been reported via pair distribution function analysis for pristine and intercalated Ti$_3$C$_2$Tx, and no data is reported for the M$_2$X phases.\textsuperscript{49} We note, however, that our calculated data is in excellent agreement with other computational studies, giving us confidence in the structural reproduction.
Figure 2: Schematic of an intercalation reaction using lithium insertion in Ti₂CO₂ as an example. Key: green - lithium, red - oxygen, blue - titanium, grey - graphitic C. The unit cell is outlined and extends to 50 Å along the c axis.

One noteworthy structural change that we observe on intercalation is a change in the in-plane lattice parameter. In general, the in-plane lattice parameter increases upon intercalation. A clear relation between this \( a \) parameter expansion and the ionic radius of the intercalating ion is present. For example, after intercalation the Ti₂C lattice parameter of 3.082 Å increases to 3.117 Å (+1.1%) for Mg\(^{2+}\), 3.115 Å (+1.0%) for Li\(^+\), 3.205 Å (+4.0%) for Na\(^+\) and 3.334 Å (+8.5%) for K\(^+\) and the respective ionic radii are Mg\(^{2+}\) (72 pm), Li\(^+\) (76 pm), Na\(^+\) (102 pm) and K\(^+\) (138 pm). The implication is that the larger ions experience greater lateral electrostatic repulsion when intercalated due to their outer electron shells being closer together, leading to larger in-plane lattice constants. A small number of functionalized MXenes undergo a slight contraction of the \( a \) lattice parameter on intercalation such as Li₂Ti₂CO₂ where the lattice parameter reduces from 3.032 Å to 3.018 Å (-0.5%), which may be caused by reduced lateral interactions between the surface functional groups due to changes in charge distribution after intercalation.

**Capacity and Voltage.** To determine which intercalating species offers the most favorable energy storage properties we have computed the theoretical capacity and cell voltage for intercalation of a full monolayer coverage on each MXene surface, which corresponds to
two Li\(^+\), Na\(^+\), K\(^+\) or Mg\(^{2+}\) per formula unit (Fig. 2). The theoretical gravimetric capacity, \(Q\), is determined from

\[
Q = \frac{nF}{M_f}
\]  

(1)

where \(n\) is the number of electrons transferred per formula unit (in this case two for Li\(^+\), Na\(^+\), K\(^+\) and four for Mg\(^{2+}\)), \(F\) is the Faraday constant and \(M_f\) is the mass of the formula unit. The current is assumed to be at a 1C rate (full charge/discharge in 1 hour). For the following general intercalation reaction (using Li as the example intercalating ion):

\[
\text{M}_2\text{CT}_x + 2\text{Li} \rightarrow \text{M}_2\text{CT}_x\text{Li}_2
\]  

(2)

the voltage is computed using a well-established approach\(^{50}\) according to the formula:

\[
V = -\frac{1}{2}[E(\text{M}_2\text{CT}_x\text{Li}_2) - E(\text{M}_2\text{CT}_x) - 2\mu(\text{Li})]
\]  

(3)

where \(E(\text{M}_2\text{CT}_x)\) is the total energy of the MXene compound, \(E(\text{M}_2\text{CT}_x\text{Li}_2)\) is the total energy of the MXene after intercalation of two atoms per formula unit and \(\mu(\text{Li})\) is the chemical potential of the intercalating species. Equation 3 is defined such that a positive voltage indicates energetically favorable intercalation. Such computational methods have been applied successfully to a range of Li- and Na-ion battery materials.\(^{28,34–43}\)

3. Results and discussion

3.1 Global Screening of Voltage and Capacity

In recent experimental work, the voltage of a few MXenes is observed to change during intercalation, which is behavior typically associated with the formation of a solid solution. For example, at the start of charge, Nb\(_2\)CT\(_x\) has a voltage of around 2.4 V, which falls to
about 0.4 V after intercalation at 100 mAh/g and to 0 V at 250 mAh/g; this shows a non-linear variation with two-thirds of the capacity removed below 1V.\textsuperscript{33} These electrochemical experiments indicate that a voltage window is obtained (rather than a specific voltage) and it is therefore not valid to compare average voltages computed by DFT with the voltage measured at 50% of the reversible capacity. It is for this reason that we have compared our computed average voltages with observed voltage windows.

In first assessing the validity of our DFT approach it is found that the trend in experimental voltages for Li-ion cells is reproduced by our calculations. Nb$_2$C is observed to intercalate two-thirds of its capacity below 1V\textsuperscript{33} and our calculations predict an average voltage of 0.89V; for V$_2$C an average voltage of 1.43 V\textsuperscript{33} is calculated and from experiment two-thirds of the capacity is above 1.5 V; Ti$_2$C intercalates 50% of its capacity above 1V and the calculated average voltage is 1.22 V.\textsuperscript{5} These calculated values are for oxygen termination, whereas in the electrochemical work a variety of surface functional groups are possible. Nevertheless, the general good agreement between the calculated and experimental voltage trends provides further support to the screening approach used here. We note that recent DFT work of Xie et al.\textsuperscript{51} on lithium intercalation into MXenes complements the results of our study; they consider three M$_2$C-based compounds at slightly different stoichiometries containing less oxygen than the compositions here. Although our focus has been on the carbides, it is worth commenting that we have also performed similar calculations for a wide range of M$_2$N based compounds; the resulting data is presented as Supporting Information and in general indicate slightly lower capacities than the M$_2$C-based compounds.

In addition to voltages we also analyzed how the maximum theoretical capacities compare to practical measured capacities that are currently available. The electrochemical properties of three M$_2$C phases that have so far been reported\textsuperscript{5,33} to successfully cycle Li$^+$ are listed in Table 1. As noted, experiments indicate that MXenes are terminated mostly by oxygen, and so we have used our data for oxygen terminated systems for comparison. The data indicates that, at most, 78% of the theoretical capacity is reached. A number of factors are known to
contribute including: particle size in which smaller particles offer a higher reversible capacity due to greater penetration between the MXene layers during cycling (e.g. in V\textsubscript{2}C, milled samples show a reversible capacity of 290 mAh/g versus 210 mAh/g in unmilled samples\textsuperscript{33}); solid electrolyte interphase (SEI) formation; solvation effects in which intercalation occurs from solution, and the possibility of intercalation of solvated ions onto the MXene surface.\textsuperscript{51}

Table 1: Current experimental data on reversible capacities for Li/MXenes and their maximum theoretical capacity (based on monolayer intercalation and oxygen termination).

<table>
<thead>
<tr>
<th>MXene</th>
<th>Experimental Reversible Capacity (mAh/g)\textsuperscript{5,33}</th>
<th>Theoretical Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb\textsubscript{2}CO\textsubscript{2}</td>
<td>170</td>
<td>250</td>
</tr>
<tr>
<td>V\textsubscript{2}CO\textsubscript{2}</td>
<td>260</td>
<td>335</td>
</tr>
<tr>
<td>Ti\textsubscript{2}CO\textsubscript{2}</td>
<td>110</td>
<td>350</td>
</tr>
</tbody>
</table>

The data in Table 1 shows that the theoretical capacity is a useful guide to the practical capacity and suggests correctly that V\textsubscript{2}CO\textsubscript{2} should have a higher capacity than Nb\textsubscript{2}CO\textsubscript{2}. We note that the earlier data reported for Ti\textsubscript{2}CT\textsubscript{x} represents only 30% of its theoretical capacity, whereas the more recent data for Nb\textsubscript{2}CT\textsubscript{x} and V\textsubscript{2}CT\textsubscript{x} achieves 72% and 87% respectively of the theoretical capacity. It is of interest whether this is due to fundamental differences in electronic structure and/or solid solution behavior or simply an improvement in the sample preparation procedure.

We then used DFT methods to perform a global search across the M\textsubscript{2}Xene family via a combinatorial screening process encompassing more than 300 compounds to identify those with a high intercalation capacity and favorable voltage. The computed results for all M\textsubscript{2}C phases are presented in Fig. 3. The results reveal two main features. First, it is clear that a wide range of electrochemical properties are present in this family of compounds and that these are sensitive to the intercalating species. Second, a number of Li\textsuperscript{+} and Mg\textsuperscript{2+} intercalated MXenes possess highly desirable electrochemical properties. A suitable voltage for an anode material is in the range 0.2 to 1.0V, which will enable a high energy density but prevent lithium plating. Ideally, the capacity should be greater than that of graphite
(372 mAh/g), which is currently the dominant anode in rechargeable Li-ion batteries. This window of desirable voltages and capacities is indicated by a dashed box in Fig. 3 and a number of MXenes are found in this region.

Figure 3: Cell voltage and theoretical gravimetric capacity for intercalation of two ions of Li\(^+\), Na\(^+\), K\(^+\) or Mg\(^{2+}\) per formula unit into \(\text{M}_2\text{CT}_2\) MXenes (where M refers to the transition metal and T to the surface functional group O, OH, H or F). The dashed box indicates an approximate window of desired voltages (0.2 to 1.0 V) and capacities (> 400 mAh/g).

The voltages computed are for single layer MXenes and we also investigated whether these are different for multilayer structures. Table 2 contains voltages computed for lithium intercalation into MXenes of compositions \(\text{Ti}_{n+1}\text{C}_n\) and \(\text{Nb}_{n+1}\text{C}_n\) \((n=1,2,3)\) with H and O functional groups. The voltages do not undergo significant changes in most cases as the MXene is made thicker. For example, in \(\text{Ti}_{n+1}\text{C}_n\) the voltage is 1.22V for a single layer MXene and 1.28V and 1.27V for bilayer and trilayer structures respectively. Although the calculated voltages in O-terminated \(\text{Nb}_{n+1}\text{C}_n\text{O}_2\) are very similar, the voltage for \(\text{Nb}_4\text{C}_3\text{H}_2\) is lower than those for \(\text{Nb}_2\text{CH}_2\) and \(\text{Nb}_3\text{C}_2\text{H}_2\). It is entirely possible that for multilayer MXenes the surface termination and intercalation sites will differ to those for monolayer and bilayer MXenes. A full exploration of this is required in future work. Nevertheless, the data in Table 2 suggest that the overall trend for monolayer MXenes is applicable to the multilayer structures.

To further understand the cause of the optimal electrochemical properties shown in Fig. 3 and also the wide variation seen across the MXenes, we turn our attention to the effect of
Table 2: Cell voltage for lithium intercalation into Ti- and Nb-based multilayer MXenes surface functionalized with H and O.

<table>
<thead>
<tr>
<th>MXene</th>
<th>Voltage (V)</th>
<th>MXene</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$CH$_2$</td>
<td>-0.11</td>
<td>Nb$_2$CH$_2$</td>
<td>+0.19</td>
</tr>
<tr>
<td>Ti$_3$C$_2$H$_2$</td>
<td>-0.09</td>
<td>Nb$_3$C$_2$H$_2$</td>
<td>+0.16</td>
</tr>
<tr>
<td>Ti$_4$C$_2$H$_2$</td>
<td>-0.14</td>
<td>Nb$_4$C$_2$H$_2$</td>
<td>-0.02</td>
</tr>
<tr>
<td>Ti$_2$CO$_2$</td>
<td>+1.22</td>
<td>Nb$_2$CO$_2$</td>
<td>+0.89</td>
</tr>
<tr>
<td>Ti$_3$C$_2$O$_2$</td>
<td>+1.28</td>
<td>Nb$_3$C$_2$O$_2$</td>
<td>+0.79</td>
</tr>
<tr>
<td>Ti$_4$C$_3$O$_2$</td>
<td>+1.27</td>
<td>Nb$_4$C$_3$O$_2$</td>
<td>+0.90</td>
</tr>
</tbody>
</table>

each individual component of the composition.

### 3.2 Trends in Voltage and Capacity with MXene Composition

**Intercalating Ion.** The most significant component in terms of the electrochemistry is the intercalating species. In Fig. 3 it can be seen that there is a strong dependence of the capacity on the intercalating species, with Mg$^{2+}$ based compounds generally offering a higher gravimetric capacity than Li$^+$, Na$^+$ or K$^+$ intercalated compounds. Although Mg$^{2+}$ has a mass about 3.5 times that of Li$^+$, the two electron redox chemistry offered by each Mg$^{2+}$ ion results in a large capacity. This data suggests that experimental efforts to intercalate Mg$^{2+}$ into MXenes are worthy of future investigation.

Besides the capacity, there is also a trend in the voltage with the intercalating species. In general, Li$^+$-intercalated MXenes have the highest voltages, followed in sequence by Mg$^{2+}$, Na$^+$ and K$^+$. Indeed, most of the K$^+$ compounds have a negative average voltage at the theoretical capacity indicating that intercalation of two K$^+$ ions per formula unit is unfavorable. This result is consistent with current experimental reports, which do not show high levels of K$^+$ intercalation into M$_2$C-based compounds.

According to equation 3, as the enthalpy change upon intercalation becomes smaller, the voltage will approach zero and can even become negative if the enthalpy change is negative. Low voltages thus indicate structures which are high in energy after intercalation. Factors that will affect the energy after intercalation are the ionic radius and ion-ion interactions of
the intercalating species. Greater lateral electrostatic repulsion is expected between K$^+$ ions than Li$^+$ ions, with an increased total energy and hence lower voltage. Further support for this is found in the expansion of the in-plane lattice parameter, where the K$^+$ intercalated compounds undergo a larger lateral expansion than the Li$^+$ intercalated compounds. Other factors that influence the intercalated energies of each MXene are outlined in the next section.

**Transition Metal Species and Surface Functional Group.** To isolate the effect of the transition metal species and the surface functional groups the data in Fig. 3 is presented separately for Li$^+$, Na$^+$ and Mg$^{2+}$ in Fig. 4, where the transition metals and surface functional groups are indicated explicitly (data for K$^+$ is in the SI due to their low capacities). Three main results emerge.

The first feature is the variation of the capacity with the transition metal species. As expected, the MXenes containing the lighter period IV (3d) transition metals (Sc, V, Ti, Cr) offer a larger gravimetric capacity than those composed of heavier period V (4d) and VI (5d) transition metals (Nb, Mo, Hf, Ta). The range of voltages does not show a clear variation with the period of the transition metals. For example, in the lithium intercalated MXenes (Fig. 4(a)), the transition metals of each period consistently give rise to voltages in the approximate range of -0.2V to 2.0V. This would suggest that the d-block chemistry for each MXene is largely comparable.

A second feature, present for F-, H- and non-functionalized MXenes, is a correlation between the voltage and the transition metal species. As the transition metal species becomes more electropositive (e.g. Sc-Ti-V-Cr) the voltage increases. For example, Li$^+$ intercalation in H-functionalized compounds gives voltages of -0.30V, -0.11V, +0.20V and +0.35V for Sc, Ti, V and Cr respectively.

The third feature is the effect of the surface functional group. For the light transition metals (Sc, Ti, V, Cr) the general picture that emerges in Fig. 4 is that the voltage is typically 0.0-1.0V for no functional groups, >0.5 V for oxygen termination, negative for H or OH termination, and a range of values for F termination. A key question then is why
Figure 4: Cell voltage and gravimetric capacity for intercalation of two ions per formula unit into M\textsubscript{2}C phases containing various surface functional groups. (a) Li\textsuperscript{+} intercalation, (b) Na\textsuperscript{+} intercalation, (c) Mg\textsuperscript{2+} intercalation.
does a change in the functional group cause such a wide variation in the voltage for the same
transition metal and intercalating species? A useful tool to illustrate the changes in the
electronic structure and bonding that occur on intercalation is the charge density difference.
By subtracting the charge density before intercalation from that after intercalation one can
visualize any charge transfer on intercalation. Using Ti$_2$C as a model system the charge
density difference is shown in figure 5 for Li intercalation in MXenes terminated with oxygen
or hydrogen.

Three main features are found. First, for both Ti$_2$CH$_2$ and Ti$_2$CO$_2$ there is a prominent
increase in the charge density in the surface layer, which is associated with the delocalized
electron density donated to the surface by Li. Second, for Ti$_2$CH$_2$ there is a slight increase
in charge density between the Ti and C layers, but otherwise no significant charge transfer
occurs in the central region of the 2D structure. This result suggests that the intercalation
 mechanism for H-termination can be considered as a simple inductive attraction between the
Li$^+$ ion and the delocalized electrons it transfers onto the surface. The unfavorable voltage
of -0.11V for Ti$_2$CH$_2$Li$_2$ indicates that the surface cannot accommodate large amounts of
electron density, which limits the amount of lithium that can be intercalated. Third, for
Ti$_2$CO$_2$ there is extensive charge transfer around the sites within the Ti/C layer (shown in
Fig. 5b), suggesting a change in the Ti-O and Ti-C bond hybridization (3d-2p mixing). The
higher voltage (and therefore higher energy density) for Ti$_2$CO$_2$Li$_2$ might be related to the
ability to accommodate more electron density and thus a greater quantity of intercalated
lithium.

This example clearly illustrates the significant changes in intercalation behaviour caused
by different functional groups, which will lead to a range of voltages. It is worth noting
that these results are consistent with recent DFT work$^{17,18,51}$ on the electronic and surface
properties of related MXenes.

As outlined earlier, the computed voltages represent an average over the theoretical
capacity range. As such, compounds with average voltages close to or below zero would be
Figure 5: Charge density difference in (110) section after Li intercalaction into (a) Ti$_2$CH$_2$ and (b) Ti$_2$CO$_2$. Key; red - decrease in charge density, dark blue - increase in charge density, green - lithium, blue - titanium, grey - C. Element symbol shows location of obscured H and O atoms. Isovalue 0.0016.
expected to reach approximately half their theoretical capacity since intercalation beyond this would occur at a negative voltage. This suggests that for high capacity MXenes, oxygen functionalization should be encouraged. The large variation in voltage and capacity with the surface functional group demonstrated here shows how alternative surface terminations would lead to MXenes with highly tunable electrochemical properties. The current synthesis method for MXenes involves treatment with hydrofluoric acid and it is difficult to see how O, OH, H and F terminations can be avoided. Nevertheless, a significant improvement in the capacity might be possible if alternative synthesis routes can be found.

Finally, an intercalation mechanism has been suggested based on Coulomb attraction between an induced positive charge on Li$^+$ and the negative functional species. Typical induced charges observed in our calculations are Li $^{+0.7}$, Na $^{+0.85}$, K $^{+0.4}$ and Mg $^{+1.65}$, and we note the two electron process apparent in the case of the Mg ion (see SI for complete data). No clear relation between the voltage and the induced charge could be discerned. However, most MXenes are metallic and in such materials linking delocalized electrons with particular species using techniques such as Bader analysis is problematic. Furthermore, the strong dependence, seen in Fig. 4, of the voltage upon the functional group and the transition metal species suggests that the redox activity and bond rehybridization of the transition metal must also be considered in any mechanism along with the precise electronic structure. Generally, great care must be taken when attributing voltages to any single factor. It is well known, for example in polyanionic lithium battery materials, that numerous interconnected factors can contribute towards the voltage of an electrode, including the crystal structure, redox potentials, inductive effects and Li-Li electrostatic interactions.

To summarize, the most promising group of materials in terms of anode voltage (0.2 $< V < 1.0$V) and gravimetric capacity (>400 mAh/g) are MXenes containing light transition metals with non-functionalized or O terminated surfaces. In particular, we recommend the compositions Li$_2$M$_2$CO$_2$, Li$_2$M$_2$C (M = Sc, Ti, V, Cr) and Mg$_2$M$_2$CO$_2$, Mg$_2$M$_2$C (M = Ti, V, Cr, Nb, Mo) for attention in future work. We recognize that there are challenges in
reaching the theoretical capacity of these compositions related to synthesis, processing and
electrochemistry. We stress that there are inherent difficulties in validating the calculated
voltages with the few measured voltage windows and that the solid solution behavior may
vary considerably between the various compounds. In unique cases, the theoretical capacities
presented here may not be a precise prediction of the practical capacity. Nevertheless, our
focus has been on analyzing favorable electrochemical properties by the systematic screening
process to find candidate battery materials. Future computational work will address related
questions on ion diffusion barriers for rate behavior, extra layers of intercalating ions and
solid-solution effects.

4. Conclusions

The electrochemical properties of a large number of new 2D transition metal carbides (‘MX-
enes’) have been surveyed systematically by DFT methods. Promising materials for energy
storage have been identified by examining the intercalation of Li\(^+\), Na\(^+\), K\(^+\) and Mg\(^{2+}\) into
M\(_2\)C-based compounds (M=Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta) capped with F, H, O, and OH
surface functional groups. These simulations reproduce the observed trends in voltages from
current experimental reports on lithiated V\(_2\)C, Ti\(_2\)C and Nb\(_2\)C. From our global screening
process the following main results emerge:

1. A greater gravimetric capacity of Li\(^+\) or Mg\(^{2+}\) can be intercalated into an M\(_2\)C MXene
   than Na\(^+\) or K\(^+\), which is related to the size of the intercalating ion. Compounds
   based on Mg\(^{2+}\) generally exhibit a higher (theoretical) gravimetric capacity than Li\(^+\)
   intercalated compounds as the two electron redox chemistry offered by the divalent
   Mg\(^{2+}\) prevails over its heavier mass.

2. Variation of the surface functional group and transition metal species can significantly
   affect the cell voltage and gravimetric capacity of an MXene. Surface termination by
oxygen tends to promote the highest capacity, whereas termination by H and/or OH should be avoided if possible since they result in a lower capacity.

3. The most promising group of materials in terms of anode voltage (in the range 0.2-1.0V) and gravimetric capacity superior to graphite (>400 mAh/g) are M$_2$C compounds containing light transition metals with non-functionalized or O-terminated surfaces. We recognize that there are challenges in reaching the full theoretical capacity of these compositions related to their synthesis, processing and electrochemistry. Overall, we recommend the compositions Li$_2$M$_2$CO$_2$, Li$_2$M$_2$C (M = Sc, Ti, V, Cr), Mg$_2$M$_2$CO$_2$ and Mg$_2$M$_2$C (M = Ti, V, Cr, Nb, Mo) for particular attention in future investigations.

In general, the results presented here provide valuable guidelines for exploring a rich variety of high capacity M$_2$C-based MXenes for potential use in rechargeable batteries.

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**Supporting Information Available**

Optimized structures and associated electrochemical properties of all MXene compounds considered. This material is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).
References


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Graphical TOC Entry