To my beautiful wife, Nia. You married me while I was making grad student money, so I know it was for love.
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Computational methods centered around density-functional theory (DFT) calculations are performed to discover and characterize a large number of two-dimensional (2D) materials. The first class of 2D materials discussed are the transition metal carbides and nitrides known as MXenes. An investigation into the aqueous electrochemical synthesis techniques used to create MXenes reveals that some MXenes will be easier to synthesize at negative applied voltages, and that nearly all MXenes will be mostly terminated by oxygen immediately upon synthesis. The thermodynamic stability of several MXene compositions is calculated, and many are predicted to be stable that have not yet been synthesized.

Next, a topology-scaling algorithm is used to identify layered bulk materials in the Materials Project online database. More than 800 layered materials were identified by the algorithm, and calculations are performed to determine the energy required to exfoliate a 2D monolayer of each material. It is discovered that more than 600 materials have monolayers with exfoliation energies below that of SnSe, which has already been synthesized in this manner.

A few of the materials identified by the topology-scaling algorithm are then investigated in detail. A family of binary group IV-V 2D materials based on SiP, which was found by the algorithm, have two nearly degenerate polymorphs with significantly different electronic structures. According to their band edge locations, electronic
heterojunctions with minimally defective interfaces might be created by bringing the two polymorphs into contact with one another.

Another group of materials identified in the search are the iron dihalides, which are half-metallic. The magnetic structure of these materials is investigated in detail, revealing that they are $xy$ magnets with Berezinski-Kosterlitz-Thouless transition temperatures between 122 and 210 K. Some spintronic devices that might be possible based on these materials are briefly discussed.
For more than 100 years, Robert Louis Stevenson’s classic *Treasure Island* has captivated readers’ imaginations with its swashbuckling tale of adventure and discovery. No less swashbuckling, one might argue, has been the tale of materials discovery over the last several years. In fact, the quest for materials discovery and the quest for Flint’s treasure have a great deal in common (except, for most research groups, the mutinous betrayal). In the same way that the search in *Treasure Island* begins with a map found by Jim Hawkins, the discovery of new materials has provided researchers with a sort of treasure map which can be used to look for new materials properties. New properties are the treasure in materials research, because they will improve or enable applications society needs or wants. To achieve this, tools are needed not only for discovering new materials, but also for describing them. If materials discovery provides the map, then materials characterization tools are the shovel.

One of the most recently discovered locations on the materials treasure map is the class of two-dimensional (2D) materials, which generally have properties that are markedly different from their three-dimensional counterparts. The canonical example is the graphite/graphene system, but the number and diversity of 2D materials that have been synthesized is quite large and growing. Because of their novelty, a great deal of work remains in completing our understanding of which 2D materials can be experimentally synthesized and what their properties might be.

The rapid growth in 2D materials research over the last ten years has coincided with a number of major advances in the field of computational materials science: a growing number of large and reliable online materials databases, significant upgrades to the processing power in modern supercomputers, and the onset of high-throughput management software packages and tools. These theoretical tools have proven to be one
of the most effective shovels available for digging up new materials properties. Today, computational scientists are able to predict and even characterize new materials before they ever appear in an experimental laboratory. Naturally, these predictions are most powerful when performed together with careful experimental validation, but a great deal of time, money and effort can be spared by starting a materials discovery project with a computer.

Outline

The shared subjects of the present work, discovery and characterization, are broad enough that they probably encompass the entire field of materials research, and therefore deserve some further qualification here.

Discovering, or at least computationally predicting, new 2D materials can be done in a few different ways: 1) finding 2D materials or their precursors that have been “hiding” in existing materials databases, 2) predicting hypothetical materials based on the crystal structures of similar materials already in existence (e.g. substituting other transition metals for Mo in MoS$_2$), and 3) using genetic algorithms or machine learning to predict or design new material structures. All three methods have yielded some important discoveries, but only the first two are discussed and employed in the current work. The use of genetic algorithms or machine learning may well have the most promise for 2D material discovery in the future when database searches and template substitutions have been more or less exhausted, which is not the case right now.

A major aim of the present work has been to develop methods by which one can assert whether or not a 2D material can be created using one experimental synthesis technique or another. This type of analysis is often overlooked in theoretical 2D materials research, which has led to a great deal of research capital being spent on materials that are not likely to ever be synthesized. In particular, two new methods to computationally discover new 2D materials are outlined in this work, which can be thought of as mirroring experimental synthesis techniques. 2D materials can be mechanically exfoliated from
certain layered precursors [1–4], and Chapter 5 details an algorithm to discover and predict which layered compounds in existing material databases could feasibly be exfoliated in this way to form new 2D materials. Other 2D materials can only be obtained by chemically exfoliating bulk precursors [5, 6], and Chapter 3 outlines a framework in which the experimental conditions required to chemically etch and exfoliate a 2D material from a precursor can be determined. Another popular technique to synthesize 2D materials is by deposition on a substrate [7–10]. Established methods already exist for predicting the feasibility of synthesizing a 2D material on various substrates; these methods are mentioned and used but not developed here.

The remainder of this work is arranged as follows: Chapters 2 – 4 are a discussion of the synthesis and properties of MXenes, a class of 2D transition metal carbides and nitrides that are obtainable by chemically exfoliating bulk layered ceramics referred to as MAX phases. Specifically, Chapter 2 investigates the stability of a large number of MAX phases, and those that are stable are used as in Chapter 3 to demonstrate how first-principles calculations can be used to predict which ones can be etched to form MXenes. Then, in Chapter 4, the properties of several MXenes are investigated in detail, especially those properties that are relevant to their application as Li-ion battery anodes.

A large number of novel 2D materials were discovered using the mechanical exfoliation algorithm developed in Chapter 5, and the remaining chapters explain some of the preliminary efforts to characterize them. In Chapter 6, a class of group IV-V 2D materials that was discovered in the search is investigated with an emphasis on its members’ electronic properties for use in heterojunctions and as photocatalysts. Finally, Chapter 7 describes a search through all of the 2D materials identified in Chapter 5 for those with half-metallic band structures. General conclusions are provided in Chapter 8.
CHAPTER 2
SEARCHING THE M_2AX PHASE COMPOSITIONAL SPACE FOR STABLE M_2XENE PRECURSORS

The vision that state-of-the-art computational methods allow the screening of vast compositional spaces for selected properties in a matter of days to weeks is becoming a reality, and can aid experimental efforts. For example, compositions spanning nearly the entire periodic table have been screened for stability and piezoelectric-related properties \[12, 13\], over 2000 compounds have been systematically investigated for their properties as Li-intercalation electrodes \[14\], and the thermal conductivities of 75 compounds were predicted computationally and discovered to correlate linearly with their experimental values \[15\]. In each case, the interpretation of results and design of screening parameters has drawn heavily on experimental knowledge.

The hexagonal layered ceramic compounds known as MAX phases represent one such vast composition space, and one that has proven to be a fertile frontier for materials discovery over the last five decades \[16\]. The flexible \(M_{n+1}AX_n\) formula \((M = Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta; A = Al, Si, P, S, Ga, Ge, As, Cd, In, Sn, Tl, Pb; X = C, N; n = 1, 2, 3)\) is responsible for the large size of the MAX phase family. Over 60 compositions have been synthesized already \[17\], including solid solution mixtures of \(M, A, \) and/or \(X)\) species \[18-24\]. All MAX phases share the same crystal structure, shown in Figure 2-1 for \(V_2AlC\) as an example. The recently reported synthesis of MAX phases with new compositions suggests that the compositional space of MAX phases has not yet been exhausted \[25, 26\]. The list of potential applications for MAX phases is quite long, and includes magnets \[27\], high-temperature protective coatings \[28\], low-friction coatings \[29, 30\], heating elements \[31\], electrical contacts \[32\], radiation cladding \[33, 34\], and

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Figure 2-1. Crystal structure of V$_2$AlC, a representative member of the M$_2$AX phase family.

impact-absorption materials [20], among others. They can even be chemically etched to produce two-dimensional transition metal carbides and nitrides [5, 6, 35], which have shown aptitude for application in ionic battery anodes [36–38].

Considerable work has already been performed to establish the stability of members in the MAX phase family [39–42], but never in the solid solution compositional space, and the selection of competing phases was generally performed in an *ad hoc* manner. The solid solution space is particularly interesting, as solid solutions often provide improved mechanical properties over their end members [20, 43, 44] and in some cases are stable even when neither end member is [45].

The ability to accurately determine phase stability from first-principles calculations hinges largely on our ability to identify the most stable competing phases for each composition. Hand-selecting these phases without error from experimental phase diagrams requires meticulous and time-consuming analysis that is only feasible for a small number of compounds at a time. Screening a large compositional space requires a consistent, systematic approach that lends itself to, and even requires, computation. Here, we extend the use of modern high-throughput screening techniques and first-principles calculations to screen the entire $n = 1$ M$_{n+1}$AX$_n$ phase family (hereafter referred to as M$_2$AX phases) for thermodynamic stability. The $n = 1$ stoichiometry is chosen because it represents the
simplest and smallest unit cell, and includes 49 out of the 61 experimentally synthesized MAX phases, thus allowing our predictions to be readily compared to experimental results. Our strategy can be extended to screen the \( n = 2 \) and \( n = 3 \) \( M_{n+1}AX_n \) stoichiometries in future work.

In this study we apply a high-throughput framework coupled to density-functional (DFT) theory calculation for phase stability, described in Sec. 2, to screen the large number of possible \( M_2AX \) phases for previously unknown compounds. We show in Sec. ?? that all 49 experimentally synthesized \( M_2AX \) phases have low formation energies of less than 30 meV/atom relative to competing phases. Among the 10,530 compositions considered, we identify 3,140 with formation energies below 30 meV/atom and 301 with strong exothermic stability in excess of 100 meV/atom. We identify trends and design rules in Sec. ?? and determine that two Cr-based \( M_2AX \) show ferromagnetic ordering with magnetic moments above 1 \( \mu_B \). Our predictions provide guidance to experimental efforts for the synthesis of previously unknown \( M_2AX \) compounds.

**Computational Approach**

To achieve computational tractability, we limit our search to consider only 50-50 solid solutions for all three of the \( M, A, \) and \( X \) components. Lower resolution stoichiometries would require larger periodic cells. Interestingly, all but one, \((Ti_{0.75}Nb_{0.25})_2AlC\) [18], of the experimentally synthesized solid solution MAX phases are close to 50-50 ratios for the \( M, A \) and/or \( X \) components. In the case of \((Ti_{0.75}Nb_{0.25})_2AlC\), a corresponding \((Ti_{0.55}Nb_{0.45})_2AlC\) MAX phase was also synthesized, indicating that considering only 50-50 solid solutions will still identify most or all compositional systems in which stability is possible. Therefore, a resolution of 0.5/formula unit is chosen for all three of the \( M, A \) and \( X \) sites in the present work. Applying this constraint aids the investigation in two ways: it narrows the number of compositions to 10,530, and enables the use of periodic cells containing only 8 atoms (4 \( M \), 2 \( A \), and 2 \( X \)). Figure 2-2 illustrates the six unique atomic configurations for these 8 atom cells.
Figure 2-2. Structure models for the six unique configurations of an \((\text{MM}'_2\text{(AA')}(\text{CN})\) compound. In configurations 1 and 2, M layers envelop C and N layers, respectively. In configurations 3 and 4, they envelop A and A' layers, respectively. In configurations 5 and 6, M layers alternate with M' layers.

To complete the non-trivial task of selecting the most thermodynamically stable competing phases for these 10,530 compositions, we systematically survey the Materials Project database [46], containing structural and thermodynamic data obtained by DFT calculations for more than 58,000 compounds. The use of this database for thermodynamic screening in similar high-throughput searches has been demonstrated to result in occasional overestimates of thermodynamic stability but only rarely in underestimates [13].

To determine the stability of the \(\text{M}_2\text{AX}\) compounds, we perform DFT calculations for the \(\text{M}_2\text{AX}\) compounds and all competing phases using the VASP package [47, 48], a plane-wave code using the projector-augmented wave method [49, 50]. We select the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation to the
exchange-correlation functional \[51\], which has been widely used in high-throughput DFT calculations \[12, 13, 52\] and shown to accurately reproduce structures and formation energies for solid systems \[53–57\]. A plane-wave cutoff energy of 520 eV and a \(k\)-point mesh with a density of 500 \(k\)-points per atom ensure energy convergence to within 5 meV/atom and cell volumes to within 2.5\% for over 70\% of compounds in a high-throughput test \[52\]. These input settings are based on the default parameters used by the Materials Project structural database \[46, 58\]. The Brillouin-zone integration is performed with the Methfessel-Paxton scheme as implemented in VASP with a smearing of 0.1 eV. To detect magnetic \(M_2AX\) phases, we include spin-polarization in all calculations. The \(M_2AX\) compounds and all competing phases are relaxed until the energy changes by less than \(10^{-4}\) eV.

**Results and Discussion**

To reduce the number of possible configurations that need to be considered, we first identify empirical rules for the most favorable configuration of all compositions in the 8-atom unit cell and then investigate the effect of in-plane mixing on the energy.

For all 10,530 \(M_2AX\) compositions we consider 8-atom unit cells with the characteristic \(P6_3/mmc\) hexagonal \(M_2AX\) phase crystal structure and cell volumes adjusted based on the covalent radii of atoms in the cell. Even for these simple ordered cells, there are several possible atomic configurations for compositions that contain more than one \(M\) and \(A\) element. Specifically, there are 3 unique ways to arrange the atoms for the \((MM')_2AX\) composition, 4 unique arrangements for \((MM')_2(AA')X\) and \((MM')_2A(XX')\), and 6 unique arrangements for \((MM')_2(AA')(XX')\). Optimizing the structures of each of these arrangements would increase the number of calculations from 10,530 to 37,455. To avoid this additional expense without sacrificing accuracy, we identify empirical rules for the most favorable arrangement based on the energy of the 6 possible arrangements shown in Figure 2-2 for the subset of 36 \((MM')_2(AlGa)(CN)\) and 36 \((MM')_2(AlAs)(CN)\) compositions with \(M, M' = Sc, Ti, V, Cr, Zr, Nb, Mo, Hf,\) and Ta.
Figure 2-3. Relative stability of configurations 1 and 2 from Figure 2-2 for 36 (MM’)2(AlAs)(CN) compositions. The x-axis is arranged from left to right in order of decreasing valence difference between M and M’ to show that the preference between configurations 1 and 2 is most marked when the valence difference is large, indicated by the colored regions. All energies are shown relative to the most stable of all 6 configurations, so a positive value of $E - E_{min}$ for both configurations indicates that one of configurations 3-6 is the most stable. These cases are rare, and in all other cases the energies of configurations 3-6 are all between those of configurations 1 and 2.

We find that when the A elements are Al and Ga, either configuration 1 or 2 from Figure 2-2 is always the most favorable. For the more dissimilar A elements Al and As, Figure 6-2 shows the energy of configuration 1 and 2 relative to the lowest energy configuration. We observe that the same trend mostly holds and that the energy difference decreases with the difference in the valences and atomic radii of the two M elements. Moreover, we observe that when the M elements are from different groups in the periodic table, the M element of higher valence preferentially bonds to C. When the M elements are from the same group, the one with the larger atomic radius preferentially bonds to C.

The large energy differences between configurations 1 and 2, particularly for the cases with large difference in valence, suggests that the creation of maximally ionic M-X bonds...
Figure 2-4. Energy per atom of the ordered 8 atom cells (red lines) in relation to the distribution of energies calculated for 40 configurations with random in-plane mixing of the corresponding 32 atom cells (blue histograms). The greatest enthalpy of mixing is observed for \((\text{MoTa})_2(\text{CdPb})(\text{CN})\), at 47 meV/atom. 

is the most important driving factor in determining the optimal configuration, and that the choice of configuration significantly affects the stability of \(M_2AX\) phases with multiple \(M\) and \(X\) elements. These predictions are in agreement with previous calculations, which identify \(M\)-\(X\) bonds as being responsible for close to 50% of the total bond order in \(M_2AX\) phases. [42]

Based on our empirical observations, we assume configuration 2 for all combinations of \(M\) elements is the lowest energy configuration. Based on the energy differences shown in Figure 6-2, we estimate a maximum error of less than 30 meV/atom for every combination of \(M\) elements. The \(M\) element in that configuration is selected as the one of higher valence or with larger atomic radius, if the valences are the same.

To investigate the effect of in-plane mixing on the energy, we create larger \(2 \times 2 \times 1\) cells containing 32 atoms for three \((\text{MM'})(\text{AA'})\)(CN) compounds. Figure 2-4 compares the energy of 40 random configurations of \(M/M', A/A',\) and \(C/N\) atoms on
their respective sites for these three compounds. We find that for two of the compounds, the ordered 8 atom cell is energetically favored over in-plane mixing, while for the third, \((\text{MoTa})_2(\text{CdPb})(\text{CN})\), the in-plane mixing is favored but still within 50 meV/atom of the energy of the ordered 8 atom cell. This value is sufficiently small, such that the ordered 8-atom cell provides a reasonably accurate energy estimate even for cases with in-plane mixing.

To estimate the gain in Gibbs free energy at finite temperature due to in-plane mixing, we apply the regular solution model. This model assumes the ideal entropy of mixing, which provides an upper bound for the configurational entropy. The ideal entropy of mixing per formula unit (f.u.) for the M\(_2\)AX phases is

\[
\Delta S^{\text{mix}} = -k_B \left[ 2 \ln \left( \frac{1}{n_m} \right) + \ln \left( \frac{1}{n_a} \right) + \ln \left( \frac{1}{n_x} \right) \right],
\]

where \(n_m\), \(n_a\), and \(n_x\) are the number of M, A, and X elements (either 1 or 2) in a given composition. For the \((\text{MM}'_2)(\text{AA}'_2)(\text{CN})\) composition, where \(n_m\), \(n_a\), and \(n_x\) are each equal to 2, the entropy of mixing is 0.24 meV/f.u.-K, or 0.06 meV/atom-K. The energies for in-plane mixing of the \((\text{TiNb})_2(\text{AlGa})(\text{CN})\) and \((\text{ScHf})_2(\text{SAs})(\text{CN})\) compounds shown in Figure 2-4 are about 20 and 40 meV/atom, respectively, resulting in critical temperature for complete in-plane mixing of 330 and 670 K, respectively. We expect that many of the \((\text{MM}'_2)(\text{AA}'_2)(\text{CN})\) systems exhibit similar energies of mixing and in-plane disorder at high temperature.

While calculating the enthalpy of in-plane mixing for all M\(_2\)AX phases is outside of the current scope, it is an important consideration for future detailed work on selected compositions.

Next, we determine the stability of the 10,530 possible M\(_2\)AX compositions relative to the competing phases in each system. The structures of the competing phases are obtained from the Materials Project database [46] and optimized using the parameters as described in Sec. 2.
Before asserting its predictive capability, we benchmark the screening method against the experimentally known stable compounds. As mentioned above, 49 M$_2$AX phases have successfully been synthesized, providing the screening with a substantial benchmarking sample size. Figure 2-5 shows the formation energies of all 49 experimentally stable M$_2$AX phases with respect to the most stable competing phases. Eleven of the 49 experimentally stable phases were already reported in the Materials Project database. We predict negative (stable) formation energies for 45 of the 49 stable M$_2$AX phases, with the remaining four (Sc$_2$InC, Nb$_2$SC, Hf$_2$SnN, and Hf$_2$SC) possessing small positive (unstable) formation energies of 8, 23, 26, and 11 meV/atom, respectively.

The slightly positive formation energies for four of the 49 experimentally observed MAX phases indicate that either entropic contributions such as the configurational entropy discussed earlier are important for the stabilization of these compounds or that the choice of exchange-correlation functional affects these energy differences. Slightly
positive DFT formation energies are common across experimentally phases; in fact, nearly 20% of the compounds in the Inorganic Crystal Structure Database [59] have instabilities above 36 meV/atom [60]. To ensure that we do not overlook a viable $M_2AX$ compound, we select a 30 meV/atom cutoff for the formation energies in our study. We furthermore note that even compounds above this cutoff could be stabilized by their configurational entropy of mixing.

We identify 3,140 of the 10,530 $M_2AX$ compositions with formation energies below 30 meV/atom, highlighting the large potential size of this family. Of these 3,140 compositions, 301 have formation energies below $-100$ meV/atom. 27 of these 301 are among the compositions that have already been synthesized. 134 of the 301 contain Ti, 112 contain In, and 261 contain C; these are the elements that are present the largest number of $M_2AX$ compounds for $M$, $A$, and $X$, respectively. All 3,140 stable $M_2AX$ compounds can be found in the MaterialsWeb online database at http://materialsweb.org. The MaterialsWeb database provides the relaxed structures and stability information for all investigated $M_2AX$ compounds.

The four most stable $M_2AX$ phases that were previously unknown are Ti$_2$V$_2$Ga$_2$CN, Sc$_2$Zr$_2$Ga$_2$CN, Zr$_2$Hf$_2$Ga$_2$CN, and Zr$_2$Mo$_2$Ga$_2$CN. All four have $A = Ga$ and $X = C-N$, and $M$ is always a mixture of two metals. This means that mixtures are among the most stable of all $M_2AX$ phases, and that the solid-solution space should certainly be explored in searches for stable $M_3AX_2$ and $M_4AX_3$ phases.

The automatic data-mining approach for the identification of the most stable competing phases minimizes the number of false positives in our study of the $M_2AX$ phase stability. A previous study [39] that relied on manual selection, identified the same competing phases for Sc$_2$AlC, Mo$_2$GeC, and Ti$_2$AsC. However, for Ta$_2$GeC, our data-mining approach identifies competing phases with a combined enthalpy that is 0.3 eV/atom lower than the manually selected ones. This illustrates the power of databases and high-throughput approaches and the importance of exhaustive searches for
competing phases. On the other hand, for V\textsubscript{2}AlC, the manually selected phases are lower in energy by 0.045 eV/atom, since they included the hypothetical V\textsubscript{3}AlC\textsubscript{2} phase, which has not been synthesized and does not currently exist in the Materials Project database.

Several trends emerge from the calculated stability of the 10,530 M\textsubscript{2}AX compositions. The first one is illustrated in Figure 2-6, which compares the distribution of compositions for the predicted highly stable ($\Delta E_F < -100$ meV/atom) and experimentally synthesized M\textsubscript{2}AX phases. In both cases, M\textsubscript{2}AX phases that contain $M = Ti$, $A =$ group 13 elements, and $X = C$ present the largest group of stable M\textsubscript{2}AX phases. Overall, we find a close agreement in the frequency of occurrence for each element in the predicted and experimentally synthesized M\textsubscript{2}AX phases. Our screening indicates that the dearth of experimental Si-, P-, Ge- and As-containing M\textsubscript{2}AX phases is likely due to lack of thermodynamic stability of these phases and not due to kinetics. Previously, a similar thermodynamic argument explained the relatively small number of only 13 stable M\textsubscript{n+1}AX\textsubscript{n} phases with $n = 2, 3$.\cite{27}

For the unstable M\textsubscript{2}AX phases, we find that the stable competing phases, or decomposition products, are generally binary $M$-$X$ compounds with either elemental $A$ and $M$ or $M$-$A$ compounds forming from the excess $A$ and $M$. Experimentally, most M\textsubscript{2}AX phases decompose to highly defective $M$-$X$ compounds, e.g. TiC\textsubscript{0.67}, with elemental $A$ diffusing between the layers at high temperatures. \cite{61}

We predict considerably higher relative numbers of stable Sc- and Cd-based M\textsubscript{2}AX phases than have been created experimentally. This is an interesting result for several reasons. First, it could mean that a large number of Sc- and Cd-containing M\textsubscript{2}AX phases are stable and their synthesis has simply not yet been attempted. Alternatively, it could indicate that there are more stable competing phases for Sc- and Cd-containing M\textsubscript{2}AX phases than the ones presently found in the Materials Project database. If this is the case, careful analysis of the decomposition products after attempted synthesis for these M\textsubscript{2}AX phases could lead to the discovery of new compounds, or at least to the addition of new
Figure 2-6. Frequency of elements occurring in stable M\textsubscript{2}AX phases, that are (a) computationally predicted in this work, and (b) experimentally synthesized. In (a), the number of compositions with formation energies $< 100$ meV/atom that contain a given element is given for all M, A, and X elements. In (b), the number of synthesized M\textsubscript{2}AX phases containing the element is given. Similar trends are found.

compounds to the Materials Project database. Finally, it could be the result of some more complex phenomena governing the stability of these compounds, which are outside the scope of our screening approach. For example, the effect of oxygen incorporation, which is known to occur in MAX phases [62–66], is not considered in our models but could affect the stability of some M\textsubscript{2}AX compounds.

**Summary**

Using a high-throughput framework coupled to DFT, we calculated the formation energies of the 10,530 M\textsubscript{2}AX compositions with the goal to identify thermodynamically stable compositions and aid experimental synthesis efforts. We characterized the crystal structures of solid solution M\textsubscript{2}AX phases and narrowed the number of promising M\textsubscript{2}AX
phases from 10,530 to 3,140. Furthermore, 301 compositions have been identified that should be readily synthesizable, with formation energies below -100 meV/atom relative to their competing phases. All the data generated in this high-throughput screening is available in the database provided at https://materialsweb.org.

The results of this systematic search for stable M_{2}AX phases demonstrate the power of leveraging large-scale computational efforts to discover new compounds, and indicate there is still plenty of room for discovery in this already large family of compounds. We have demonstrated the ability of computational techniques to screen compounds for stability against bulk phases in a framework that can easily be applied to other classes of compounds, including the more elusive \( n > 1 \) M_{n+1}AX_{n} phases.
CHAPTER 3
DISCOVERING CHEMICALLY EXFOLIABLE MATERIALS WITH FIRST-PRINCIPLES POURBAIX DIAGRAMS

Mechanical exfoliation of layered solids may be the most simple and well-known technique to synthesize 2D materials, but the creation of 2D materials from non-dispersion layered solids is possible as well. Acid etching, or immersing a bulk precursor in an acid chosen to selectively remove layers of sacrificial atomic species from between other layers, is one technique to obtain 2D materials that might not have dispersion-bound bulk precursors. During acid etching, the newly exposed surfaces of the remaining layers might be passivated by species in solution [6], and often bind to one another through weak dispersion forces [5, 67], making them exfoliable just like the materials discussed in Chapter 5.

Theory and modeling, which have become indispensible tools for predicting the synthesis of new 2D materials through other methods like exfoliation or deposition, are inhibited in this case by the aqueous environment, which is challenging to simulate accurately in first-principles calculations.

Below, we present a framework in which the etching process of an arbitrary bulk precursor for a 2D material can be broadly characterized by first-principles calculations, and the products of the etching can be predicted under different conditions. Generally, the conditions that can be experimentally controlled are the choice of acid and its concentration, the applied potential in the solution, and the bulk precursor used. As a benchmark and example of the framework’s usage, we investigate the synthesis of several MXenes, one of the more well-known classes of 2D materials that has been synthesized electrochemically.

MAX Phases and MXenes: A Use Case

MXenes are 2D transition metal carbides and nitrides whose bulk precursors are layered ceramics known as MAX phases [16, 18–24, 68]. These ceramics derive their name from their formula $M_{n+1}AX_n$, where $M$ is an early transition metal, $A$ a group 12-16...
Figure 3-1. Illustration of the etching process for the V$_2$AlC M$_2$AX phase. (a) The V$_2$AlC crystal structure is immersed in an aqueous 0.5M HF solution. (b) The F$^-$ ions sever the V-Al bonds and are starting to form new Al-F bonds. (c) The etching is complete, with O atoms bound to the newly exposed V surfaces on the M$_2$Xene and AlF$_3$ salts diffusing out.

element, X carbon or nitrogen, and $n$ generally ranges from 1 to 3 [68]. Figure 3-1(a) shows an example crystal structure for the V$_2$AlC MAX phase.

The unusual bonding in the MAX materials enables the aqueous etching process [69]. When certain MAX compounds are immersed in aqueous HF or other agents with active F$^-$ ions [70, 71], the acid selectively attacks the M-A bonds, forming AF$_n$ compounds, which diffuse out from between M$_{n+1}$X$_n$ layers. These M$_{n+1}$X$_n$ layers are immediately passivated by oxygen coming from the water [6], to form a final stoichiometry of M$_{n+1}$X$_n$O$_2$. At this point during the synthesis, the M$_{n+1}$X$_n$O$_2$, or MXene, layers are held together by dispersion forces, and can be mechanically separated after removal from the solution. Other species can be intercalated after synthesis, including methoxy groups [72] or small ions [73] to expand the interlayer spacing and facilitate the isolation of single MXene sheets. So far, the MXenes that have been successfully synthesized in this way include Ti$_2$CO$_2$, V$_2$CO$_2$, Nb$_2$CO$_2$, TiNbCO$_2$, Ti$_3$C$_2$O$_2$, Ti$_3$CNO$_2$, Nb$_4$C$_3$O$_2$, and Ta$_4$C$_3$O$_2$ [5, 37, 67, 74–76].

Methodological Description of the Framework

Recently, Persson et al. developed a consistent formalism to compare the formation energies of solids, molecules and ions in solution by combining experimental data and DFT [77], which provides a new theoretical microscope for investigations of aqueous etching.
processes. This formalism enables the construction of Pourbaix, or pE/pH phase diagrams, which predict which species dominates in an aqueous solution at a given applied potential and pH. The nature of this formalism is discussed in further detail in the next section, and for a complete discussion along with validation of its accuracy, the reader is referred to the original methodological article [77].

Using this approach, we construct Pourbaix diagrams to investigate the aqueous stability of the 18 non-solid solution \( n = 1 \) MXenes and their corresponding MAX phases, hereafter referred to as the \( M_2 \)Xenes and \( M_2 \)AX phases, respectively. Based on these Pourbaix diagrams, we predict experimental etching solutions with the greatest chance of successful synthesis for selected \( M_2 \)Xenes. In particular, we propose the use of suitable applied electric potentials during synthesis to prevent the undesirable decomposition of \( M_2 \)Xenes into solvated ions.

To generate the Pourbaix diagrams for the \( M_2 \)Xenes and \( M_2 \)AX phases, we select known competing ionic and molecular species that may form in solution from experimental databases.[78, 79] Only molecular and elemental species are considered; solid phases are intentionally left out, since they have been considered as competing phases for MXenes elsewhere [6], and molecular species represent the most kinetically straightforward decomposition products in solution. We utilize the experimental ionic formation energies, obtained from the NIST NBS tables [78], in lieu of DFT-calculated values, as it is computationally very demanding to obtain reliable formation energies for dissolved ions and molecules in standard DFT. For dissolved species for which the NBS tables did not contain data, we use that values from Pourbaix’s 1966 Atlas.[79]
We employ the formation energies for standard conditions, $G_i^0$, to calculate the Gibbs free energy, $G_i$, of each species, $i$ in solution,

$$G_i(c_i, pH, \phi) = G_i^0 + 0.0591 \log c_i - n_O \mu_{H_2O} +$$
$$+ pH(n_H - 2n_O) +$$
$$+ \phi(-n_H + 2n_O + q_i),$$

(3-1)

where $c_i$ is the concentration of species $i$, $n_O$ and $n_H$ are the respective numbers of oxygen and hydrogen atoms in the species, $\mu_{H_2O}$ is set to the formation energy of water of $-2.46$ eV, $\phi$ is the electric potential, and $q_i$ is the species’ charge. For the concentration of the ionic species in solution we select $1 \times 10^{-3}$ M, unless otherwise noted. Eq. (3-1) without the concentration dependent term also describes the Gibbs free energy of the solid phases as a function of pH and applied potential, $\phi$. From the Gibbs free energies of all dissolved species and solid phases $i$ and their dependence on pH and potential, $\phi$, we construct the Pourbaix diagram as the convex hull connecting the formation energies of all compounds and species, just like any other phase diagram.

We calculate the energies of all solid compounds using DFT as it is implemented in the Vienna \textit{ab-initio} Simulation Package, VASP. [48, 80] PBE functionals [51] are chosen for their accuracy in calculating reaction energies, reciprocal spaces are sampled at a density of 500 $k$-points per atom for all compounds, and the plane-wave cutoff energies are set to be 30% greater than the values specified in the pseudopotential files.

For the calculation of the energies of the 2D M$_2$Xenes phases, we employ a 15 Å vacuum spacing between periodic images of the layers [81, 82] to reduce spurious interactions to below 5 meV/atom. However, as mentioned above, immediately upon synthesis, M$_2$Xenes exist as dispersion-bound multilayer structures, and not free-standing nanosheets. Therefore, the binding energies between individual M$_2$Xene sheets are calculated using vdW-opt-B88 functionals, which includes dispersion interactions. These energies are then added to the energies of the free-standing sheets. [83].
To bridge the compatibility gap between experimental formation energies and DFT-calculated formation energies, we employ the linear correction scheme of Persson et al. \[77\]. In this formalism, experimental formation energies of ions are corrected by the difference between the DFT and experimental formation energies of a reference compound (preferably a simple binary oxide) containing the same element as the ion. For example, the correction factor applied to the formation energies of all ions containing Nb is calculated as

$$\Delta \mu_{\text{Nb}_2\text{O}_5}^{\text{corr}} = \frac{1}{2} \left[ E_f^{\text{DFT}}(\text{Nb}_2\text{O}_5) - E_f^{\exp}(\text{Nb}_2\text{O}_5) \right],$$

(3.2)

where \(\text{Nb}_2\text{O}_5\) is the reference compound, and the factor 1/2 normalizes the correction per Nb atom. The experimental formation energies, \(E_f^{\exp}\), are taken for all binary oxides Ref. 84.

To achieve seamless compatibility between experimental and DFT frameworks, the formation energies \(E_f^{\text{DFT}}\) of the reference oxides must be calculated using the same input parameters as for the other compounds, i.e. the M\(_2\)Xenes and M\(_2\)AX phases. Finally, we note that this linear correction scheme is compounding; that is, an ion containing two Nb atoms in its irreducible formula will receive twice the correction of an ion that contains one. Similarly, an ion containing both Nb and C will be corrected for both Nb and C.

The successful synthesis of a M\(_2\)Xene by electrochemical etching of a M\(_2\)AX phase requires two conditions to be fulfilled. First, the solution must be able to etch the A element from the M\(_2\)AX phase. This is observed experimentally by the formation of an insoluble AF\(_n\) salt, which acts as a sink to effectively remove the A ions from the solution and enables the continuous etching of the M\(_2\)AX phase as illustrated in Figure 3-1. Second, the remaining M\(_2\)XO\(_2\) layers must not dissolve in the solution. In other words, the
overall reaction should proceed as

\[
M_2AX + 2H_2O + nHF \rightarrow M_2XO_2(MXene) + AF_n + \left(\frac{4+n}{2}\right)H_2.
\]  

(3-3)

These two criteria can be treated separately by generating two Pourbaix diagrams: one for a bulk M\textsubscript{2}AX phase, and another for its corresponding M\textsubscript{2}Xene. The two Pourbaix diagrams can then be overlaid to look for any solution conditions where the AF\textsubscript{n} salt and the M\textsubscript{2}Xene are both stable as precipitates. This methodology can be generalized to any system for which the sacrificial etching element and the salt it forms in solution are known.

Figure 3-2 illustrates this process for the synthesis of the V\textsubscript{2}CO\textsubscript{2} by electrochemical etching of two different possible M\textsubscript{2}AX precursors. Experimentally V\textsubscript{2}CO\textsubscript{2} has been synthesized by etching V\textsubscript{2}AlC in aqueous HF solutions of 0.5 M concentration, which has a pH of about 1.5.

Figure 3-2(a) and (b) shows the Pourbaix diagrams of V\textsubscript{2}AlC and V\textsubscript{2}SiC, two possible M\textsubscript{2}AX precursors for the V\textsubscript{2}CO\textsubscript{2} M\textsubscript{2}Xene, in an aqueous fluoride solution. At low pH, these precursors lead to stable AF\textsubscript{n} salts. In fact, these are the only precursors that display AF\textsubscript{n} salt as a stable etching product in the Pourbaix diagram. The Pourbaix diagram of the desired product, the V\textsubscript{2}CO\textsubscript{2} M\textsubscript{2}Xene, in Figure 3-2(c) shows a broad region of stability at low potential.

In Figure 3-2(d), these stability regions of the three phases of interest – AlF\textsubscript{3} from (a), SiF\textsubscript{4} from (b), and V\textsubscript{2}CO\textsubscript{2} from (c) – are overlaid in a composite diagram. There is considerable overlap between the stability regions of AlF\textsubscript{3} and V\textsubscript{2}CO\textsubscript{2}, confirming that our method identifies the V\textsubscript{2}AlC M\textsubscript{2}AX phase as a good candidate precursor for the formation of V\textsubscript{2}CO\textsubscript{2}. The results also indicate that applying a small negative potential of −0.1 to −0.3 V during synthesis may increase the V\textsubscript{2}CO\textsubscript{2} yield.
Results and Discussion

In addition to V$_2$CO$_2$, two other M$_2$Xenes (not including the solid solution TiNbCO$_2$ M$_2$Xene) have been synthesized from M$_2$AX phases to date: Ti$_2$CO$_2$ and Nb$_2$CO$_2$.

Both of these were etched from A = Al M$_2$AX phases. Figure 3-3 shows the calculated Pourbaix diagrams for these two M$_2$Xene compounds along with all of their possible M$_2$AX precursors and the resulting composite Pourbaix diagrams.
Figure 3-3. Composite Pourbaix diagrams for (a) Ti$_2$CO$_2$ and (b) Nb$_2$CO$_2$. Significant regions of overlap are observed for Ti$_2$AlC and Nb$_2$AlC etching and their respective M$_2$Xenes’ stability, in agreement with their experimental synthesis.

Figure 3-3(a) shows that Ti$_2$CO$_2$ is stable over a wider range of applied potentials in more basic conditions. Under more acidic conditions, it compete with the relatively stable Ti$^{2+}$ and Ti$^{3+}$ ions in solution. This suggests that if a less acidic agent can be used to exfoliate the Al or other A element from the parent Ti$_2$AC phase, it will likely result in higher Ti$_2$CO$_2$ yields. It should also be mentioned that the stability region is suppressed below the OH$^-$ formation line at low pH in the calculated diagram. The formation of a ternary fluoride compound, Ti$_2$AlF$_9$, is observed experimentally when Ti$_2$AlC is immersed in anhydrous HF [85], suggesting that more complex decomposition processes occur in this system at very low pH.

The Nb$_2$CO$_2$ M$_2$Xene was first reported together with V$_2$CO$_2$[37]. Its composite Pourbaix diagram in Figure 3-3 shows a wide range of possible synthesis conditions.

In agreement with experiment, we observe that A = Al M$_2$AX phases exhibit the greatest probability of successful etching. This is apparently due to the relatively exothermic formation of the AlF$_3$ salt as an etchant product. For all four MXenes discussed thus far, the A = Al M$_2$AX phase is the only precursor with any overlap between the M$_2$AX phase etching region and the M$_2$Xene stability region at ionic concentrations of 10$^{-3}$ M.
Figure 3-4. Composite Pourbaix diagrams for (a) Cr$_2$CO$_2$ and (b) Mo$_2$CO$_2$ showing overlap or near-overlap for the M$_2$AX phase etching and M$_2$Xene stability. The Cr$_2$CO$_2$ M$_2$Xene has not yet been synthesized, and its diagram shows that it is only stable under basic conditions.

Certain experimental subtleties are still not captured by these Pourbaix diagrams. Among these are the effects of varying surface coverage (e.g. species other than oxygen on the M$_2$Xene surface, incomplete surface coverage, or hydration of the surface as a function of pH) or the effects of other species in solution (e.g. the AF$_n$ species generated during M$_2$AX exfoliation) that may passivate M$_2$Xene surfaces, or combine with ions in solution to change the Gibbs free energy of certain regions in the Pourbaix diagram. Each of these effects can be analyzed by detailed calculations, but we emphasize that the aim of this work is to provide a first-pass screening to identify compositions with the greatest likelihood of synthesis.

In the following sections, the Pourbaix diagrams of particularly interesting systems are discussed. All of the materials structures, electronic band structures, and Pourbaix diagrams can be found in our online database at https://materialsweb.org.

Cr$_2$AlC exists as a precursor from which Cr$_2$CO$_2$ could potentially be synthesized. The composite Pourbaix diagram generated for this system in Figure 3-4(a) shows only a very small region of overlap between the M$_2$AX phase etching and M$_2$Xene stability at pH = 8 and applied potentials of $-0.5$ V.
Figure 3-5. Stability regions for Nb$_2$NO$_2$ and Nb$_2$CO$_2$. The dramatically smaller stability region for Nb$_2$NO$_2$ is caused by the formation of NH$_3$ and NH$_4^+$ as competing species.

Very recently, the synthesis of the Mo$_2$CO$_2$ M$_2$Xene was reported [86]. The composite Pourbaix diagram generated for Mo$_2$CO$_2$ in Figure 3-4(b) indeed shows a narrow band of stability straddling the lower edge of H$_2$O stability, and within the region of Mo$_2$AlC etching. However, the synthesis was reportedly carried out using a Mo$_2$Ga$_2$C nanolaminate very similar to a M$_2$AX phase. The exfoliation of this nanolaminate to form a M$_2$Xene nanosheet is a promising result which broadens the possibilities of M$_2$Xene synthesis from off-stoichiometry M$_n$+1AX$_n$ phases. Mo-based M$_2$Xenes have been investigated as possible thermoelectric materials, displaying a high maximum power factor of more than $82\times10^{14}$ W cm$^{-1}$ K$^{-2}$ s$^{-1}$ [87].

The Pourbaix diagrams of nitride, or X = N, M$_2$Xenes are of particular interest because none have been synthesized so far [75]. Additionally, their synthesis via non-aqueous methods, such as chemical vapor deposition on substrates, may be considerably more difficult than for carbides, due to nitrogen’s volatility. Nitride M$_2$Xenes are predicted to have considerably different electronic and mechanical properties from their carbide counterparts [75], meaning that their synthesis would open up a new range of accessible properties in the M$_2$Xene family.
Figure 3-6. Composite Pourbaix diagram for Ti$_2$NO$_2$, showing appreciable overlap (shown in green) between the solution conditions required to etch Ti$_2$AlN and those required to stabilize Ti$_2$NO$_2$. The application of a small negative potential during etching may aid in the synthesis of this M$_2$Xene.

With the exception of Ti$_2$NO$_2$, the stability regions for nitride M$_2$Xenes in their Pourbaix diagrams are dramatically smaller than those of the corresponding carbide M$_2$Xenes. For example, the stability region for Nb$_2$NO$_2$ is shown relative to that of Nb$_2$CO$_2$ from their respective Pourbaix diagrams in Figure 3-5. Analyzing the species surrounding the nitride stability region suggests that the decreased stability of nitride M$_2$Xenes is apparently due to the competition with ammonium cations and ammonia in solution, and, in the case of Cr$_2$NO$_2$, also with N$_2$ gas. The thermodynamic competition of these species in solution helps to explain why it is generally more difficult to synthesize the nitride M$_2$Xenes than the carbide ones.

The only A = Al, X = N M$_2$AX phase that currently exists is Ti$_2$AlN. The other A = Al, X = N M$_2$AX phase precursors that are theoretically stable are V$_2$AlN, Zr$_2$AlN, and Hf$_2$AlN, but there is no overlap between their etching regions and the stability regions of their corresponding M$_2$Xenes. The composite Pourbaix diagram for Ti$_2$NO$_2$ in Figure 3-6 shows some overlap for Ti$_2$AlN etching and Ti$_2$NO$_2$ stability, and applying a negative potential to the solution during etching appears to be one possible route to successfully synthesizing this new M$_2$Xene.
Figure 3-7. Regions of overlap in the composite Pourbaix diagram for Cr₂CO₂ for three different ion concentrations. Each region is labeled for the ion concentration used. As the concentration of ions is increased, the size of the region of suitable etching conditions grows significantly.

The concentration of ions in solutions can provide another control for the electrochemical synthesis of the M₂Xenes. So far, we assumed for all ionic concentrations 10⁻³ M, but this can be changed by the intentional addition or subtraction of ions into the solution. By Le Châtelier’s principle, increasing the concentrations of solvated ions will stabilize a M₂Xene against dissolving to form them, and thereby increase the range of the M₂Xene’s stability.

To probe the effect of changing ionic concentrations during synthesis, we recalculate the Pourbaix diagrams for Cr₂CO₂ and its M₂AX precursors at ionic concentrations of 10⁻⁴, 10⁻², and 1 M. The resulting regions of overlap between the Cr₂AlC phase etching and Cr₂CO₂ stability, shown in Figure 3-7, clearly grows in size as the ionic concentration is increased. The primary ions with which Cr₂CO₂ competes for stability in solution are CO₃²⁻ and Cr(OH)²⁺. Figure 3-7 suggests that increasing the concentrations of these ions in the solution to 1 M will be required to successfully synthesize Cr₂CO₂ in solutions of pH < 4. It should be mentioned that other experimental effects (e.g. pH) have not been considered in our analysis and may have effects of the same order as these ionic concentrations.
No M$_2$Xenes based on the transition metal elements not discussed so far- Sc, Zr, Hf, and Ta- have any stability against dissolution in their Pourbaix diagrams, even at high ionic concentrations. For Sc-based M$_2$Xenes, the Sc atoms dissolve into solution to form Sc$^{3+}$ ions at pH < 4, and ScOH$^{2+}$ ions at pH > 4. Zr atoms from Zr-based M$_2$Xenes are predicted to react and primarily form HZrO$_3$ in solution. Similarly, Hf atoms will react with oxygen to form HfO$^{2+}$ in solution, and Ta atoms will react to form TaO$_2^+$. Each of these dissolution reactions is exothermic enough that it persists even at ionic concentrations up to 1 M. Therefore, none of these M$_2$Xenes are predicted to be synthesizable using aqueous etching, regardless of the acid or the precursor used. This also means these M$_2$Xenes, even if synthesized by alternative means, are unsuitable for aqueous applications, including photocatalysis.

**Summary**

We have set forth a method by which the electrochemical synthesis of MXenes can be predicted using Pourbaix diagrams. This method can be generalized to apply to any class of layered materials under investigation as precursors for etching new 2D materials.

Specifically, the Pourbaix diagrams generated for M$_2$Xenes offer specific solution conditions that may enhance the yields of etching reactions of existing M$_2$Xenes, including Ti$_2$CO$_2$, V$_2$CO$_2$, and Nb$_2$CO$_2$, and may even enable the synthesis of brand new compositions. We recommend using a suitable electrochemical potential as a degree of freedom during attempted synthesis, as most M$_2$Xenes show greater stability against dissolution at negative potentials.

The Pourbaix diagrams generated for nitride M$_2$Xenes show stability regions that are much narrower than those of carbide M$_2$Xenes, providing an explanation as to why none have been synthesized yet. Our calculations show that the addition of NH$_3$ and NH$_4^+$ into solution may be the only way to stabilize certain nitride M$_2$Xenes.

The intentional addition of dissolution products into the solution is also recommended as a possible route to synthesizing Cr$_2$CO$_2$ for the first time. In particular, the addition of
$\text{CO}_2^{2-}$ and Cr(OH)$^{2+}$ into solution should serve to oppose the dissolution of Cr$_2$CO$_2$ into these ions.
CHAPTER 4
CHARACTERIZING THE PROPERTIES AND PERFORMANCE OF MXENES AS LI-ION BATTERY ANODES

Promising End Applications for MXenes

The large number of theoretically possible members of the MXene family and the diversity of properties among the synthesized MXene compounds make these compounds attractive for a number of 2D material-related applications [88]. For instance, MXenes are promising candidates for thermoelectrics [87], electrode materials in high-power lithium ion batteries [5, 36, 37, 67, 89–92], larger and multivalent ion batteries [93], electrochemical catalytic surfaces [94], and hydrogen storage [95]. They are also being investigated as sensors [75] and components in electronic heterojunctions [96].

In each of these applications, knowledge of the chemical termination of the MXene surface is critical to predicting the material’s properties and performance. Because of MXenes’ characteristically high surface-to-volume ratio, the atomic or molecular groups chemisorbed to its surface play a critical role in controlling the overall stoichiometry, stability, and properties of the MXene. For instance, the diffusion barrier for Li on a Ti$_2$C(OH)$_2$ surface (1.02 eV) is almost three times as large as it is on a Ti$_2$CF$_2$ surface (0.36 eV) [89], and MXene band gaps have been shown to depend significantly on the nature of the terminating atoms and molecules [5, 89]. This implies that an ability to control which species bind on a MXene’s surface can be used to design a material with fine-tuned properties for technological applications.

Despite their importance, it is not yet understood precisely which chemical species bind to the MXene surfaces during synthesis, the exact manner in which they contribute to the overall stoichiometry, or the effect they have on the MXene’s thermodynamic

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Figure 4.1. A $\text{V}_2\text{AlC}$ MAX phase (a) from which a $\text{V}_2\text{C}$ MXene (b) can be derived by etching. Surface species have been shown to prefer FCC sites (c) over HCP sites (d) for binding on most MXenes.

stability. In sections 4 and 4 below, DFT calculations are used to address these questions for the 54 unique $M_{n+1}X_n$ compositions ($9 \text{ M elements } \times 2 \text{ X elements } \times 3 \text{ values of } n$).

**Surface Compositions**

Binding energies for molecules and atoms on MXene surfaces are calculated according to

$$E_b = E(M_{n+1}X_nT_m) - E(M_{n+1}X_n) - \frac{m}{2}E(T_2) - m\mu_T$$  \hspace{1cm} (4.1)

where $E(M_{n+1}X_nT_m)$ is the energy of the MXene with the adsorbed atoms or molecules, $E(M_{n+1}X_n)$ is the energy of the bare MXene, $E(T_2)$ is the energy of the adsorbed atoms or molecules in their gaseous reference state ($O_2$, $O_2 + H_2$, or $F_2$) and $\mu_T$ is the chemical potential of the adsorbed atoms or molecules in the solution phase. In Equation 4.1, a negative $E_b$ is indicative of exothermic binding.

To determine the degree of saturation predicted for MXene surface binding sites, $E_b$ is calculated as a function of coverage for O, OH and F on a $\text{Ti}_2\text{C}$ surface using Equation 4.1 with $\mu_T = 0$ eV. For these calculations, we use a $2 \times 2 \times 1$ supercell containing eight MXene formula units. This supercell allows resolution in our values of coverage as low as 0.125 T species per formula unit. Previous work [76, 89, 97, 98] has shown that FCC sites (see Figure 4.1) are the most favorable binding sites for most
Figure 4-2. Binding energy vs coverage for O, OH, and F on a Ti$_2$C surface. The DFT energies of O$_2$, O$_2$ + H$_2$, and F$_2$ are used as reference energies in eq 1, and $\mu_T = 0$ eV. We find that all species exactly saturate the FCC sites, corresponding to an $M_{n+1}X_nT_2$ stoichiometry.

MXene composition. Therefore, our coverage profile begins with occupying FCC sites and includes HCP sites after all FCC sites are filled. During the incremental occupation of FCC sites (and later, HCP sites), the site are filled in such a way as to maximize the distance between neighboring surface groups. This configuration minimizes the ionic repulsion between neighboring species and results in the lowest energy configurations in our calculations. Figure 4-2, which plots the binding energy vs. coverage for all three species, shows a sharp increase in $E_b$ after all FCC sites are saturated, indicating that the system’s surface energy is minimized when all the FCC sites are occupied and the HCP sites are empty. This suggests a general $M_{n+1}X_nT_2$ stoichiometry, in agreement with previous investigations [76].

The abrupt upturn in binding energy for HCP sites can be explained as the result of steric hindrance. In particular, the average O-O distance when all FCC sites and HCP sites are occupied on a Ti$_2$C surface is 0.78 Å, compared to 3.1 Å when only FCC sites are occupied. Treated as point charges, the difference in repulsive force between neighboring O anions is more than an order of magnitude in these two cases and explains why the energy
versus coverage curve in Figure 4-2 increases more rapidly for O than for the other anions of lesser charge.

Binding energies have already been calculated for all M_{2}X compounds using \( \mu_{T} = 0 \) eV \[76\], which physically corresponds to the binding energy if the T species came from a gaseous source, as considered in Figure 4-2. A gaseous reference state is an easy but arbitrary choice within the framework of DFT calculations, and it does not describe the experimental conditions. In fact, it is expected that all three surface groups (shown in bold below) come from liquid sources, following the reactions \[5\]

\[
\begin{align*}
\text{Ti}_{2}\text{C} + 2\text{H}_{2}\text{O} & \rightarrow \text{Ti}_{2}\text{CO}_{2} + 2\text{H}_{2} \quad (4\text{-}2) \\
\text{Ti}_{2}\text{C} + 2\text{H}_{2}\text{O} & \rightarrow \text{Ti}_{2}\text{C(OH)}_{2} + \text{H}_{2} \quad (4\text{-}3) \\
\text{Ti}_{2}\text{C} + 2\text{HF} & \rightarrow \text{Ti}_{2}\text{CF}_{2} + \text{H}_{2} \quad (4\text{-}4)
\end{align*}
\]

and that the chemical potential of each species in solution is a variable that can be experimentally controlled. Reactions 4-2 – 4-4 suggest that the most suitable reference chemical potentials are those of O and OH in H_{2}O and F in HF.

The three chemical potentials \( \mu_{O}, \mu_{OH} \) and \( \mu_{F} \) are not independent of one another and are a function of the value of \( \mu_{H} \) in the solution. The chemical potentials of all three surface groups are inversely related to \( \mu_{H} \), according to the energy required to split the liquid source (H_{2}O or HF) into its components:

\[
\begin{align*}
\mu_{O} &= \Delta G_{f}^{H_{2}O} - 2\mu_{H} \quad (4\text{-}5) \\
\mu_{OH} &= \Delta G_{f}^{H_{2}O} - \mu_{H} \quad (4\text{-}6) \\
\mu_{F} &= \Delta G_{f}^{HF} - \mu_{H} \quad (4\text{-}7)
\end{align*}
\]

The values of \( \mu_{O}, \mu_{OH} \) and \( \mu_{F} \) in Equations 4-5 – 4-7 are substituted for \( \mu_{T} \) in Equation 4-1 for their respective species to calculate the binding energy of that species on
Figure 4-3. Binding energy per single species vs $\mu_H$ for O, OH, and F on a Ti$_2$C surface.

MXene surfaces. Solvated formation energies for the liquids from the gaseous molecules ($\Delta G_f^{H_2O} = -2.71$ eV and $\Delta G_f^{HF} = -2.83$ eV) are calculated using the VASPsol method of implicit solvation in DFT [99] and are in good qualitative agreement with their experimental formation energies ($\Delta G_f^{H_2O} = -2.51$ eV and $\Delta G_f^{HF} = -2.81$ eV) [100–102]. Instead of assuming a single value for $\mu_H$, it is more useful to assume that it is a variable bound by a minimum and maximum in the H$_2$O/HF solution. The maximum value of $\mu_H$ in any solution is equal to its value in H$_2$ gas, which is generally set to be the zero reference, $\mu_H^{H_2} = 0$ eV, and the minimum value of $\mu_H$ is calculated as the value in Equations 4–5 – 4–7 when $\Delta \mu_T$ is set to its own zero reference, $\mu_T^{H_2} = 0$ eV. This gives a minimum value of $\mu_H = -1.35$ eV for Equation 4–5 (H$_2$O), $\mu_H = -2.71$ eV for Equation 4–6 (H$_2$O), and $\mu_H = -2.83$ eV for Equation 4–7 (HF). The shared range for $\mu_H$ among all Equations 4–5 – 4–7, then, is from -1.35 to 0 eV. We calculate $E_b$ in Equation 4–1 for all three species on all surfaces across this range of $\mu_H$, and the results for the Ti$_2$C surface are shown in Figure 4-3.

The binding energies calculated using Equation 4–1 and the values of $\mu_T$ described above indicate that all MXene surface strongly prefer O binding toward the lower limit of $\mu_H$, as shown for Ti$_2$C in Figure 4-3. In fact, all MXenes except those with M = Sc are
predicted to prefer O binding across the entire range of $\mu_H$. For Sc$_2$C, Sc$_3$C$_2$ and Sc$_4$C$_3$, O binding is preferred for $\mu_H < -1.0$, -1.25, and -1.05 eV, respectively, and F binding becomes preferred at higher $\mu_H$. For Sc$_2$N, Sc$_3$N$_2$ and Sc$_4$N$_3$, O binding is preferred for $\mu_H < -0.7$, -0.65 and -0.65 eV, respectively, with F binding again becoming preferred at higher $\mu_H$. The preference for F$^-$ over O$^{2-}$ on Sc surfaces is likely the result of scandium’s 1d valence that is unique among the M elements. The maximum and minimum binding energies for O, F, and OH on all MXene surfaces are listed in the Supporting Information.

It should be noted that when $\mu_H$ is decreased (increased) in solution, the chemical potential for electrons, $\mu_e$ may also need to be suitably decreased (increased) to ensure that H$_2$O remains stable against H$^+$ and OH$^-$ formation. Using an applied electric potential, it has been shown that $\mu_e$ can be varied between the band edges of H$_2$O to stabilize H$_2$O across the range of possible $\mu_H$ [103].

To characterize the chemical bonding between O, OH, F and the MXene surfaces and ensure that the bonds are covalent/ionic and not dispersion-dominated, we calculate the charge transfer using Bader charge analysis [104]. We find that the adsorbed O atoms ionize to charge states between -1 and -1.4, while the F and OH species ionize to states between -0.7 and -1. These findings are consistent with the idea that these chemisorbed atoms and molecules form strong covalent/ionic bonds with MXene surfaces. The degree of ionization of O, OH and F on different MXenes is largely independent of the number of layers, $n$, and the anion species, X, but increases with decreasing electronegativity of the metal element, M.

The enthalpy change described by Equation 4-1 is not the only descriptor required to predict adsorption events. Species leaving a liquid to adsorb on a solid surface, as do the O, OH and F atoms/molecules considered here, will also undergo entropic changes that will influence the overall change in Gibbs free energy,

$$\Delta G = \Delta H - T \Delta S$$  \hspace{1cm} (4-8)
where the enthalpy change $\Delta H$ is equivalent to the value of $E_b$ in Equation 4–1 and $\Delta S$ is the difference in entropy between the solvated and adsorbed states. This difference can be estimated analytically. We expect that vibrational contributions to each atom/molecule’s entropy will be roughly the same in the liquid as on the surface at constant temperature and that the changes in vibrational entropy between the initial and final states will therefore be close to zero. The same assumption cannot be made for configurational entropy, which will be significantly higher in the liquid than on the surface (especially the pristine, saturated surfaces we consider in our calculations, which have no configurational entropy). However, the configurational entropy of each species (O, OH and F) in the liquid will be close to that of each other, as the same large number of configurations are available to each. Therefore, the magnitude of the entropic contribution to the Gibbs free energy will be quite similar for all three species. This assumption is further supported by the small and very similar experimental entropies of aqueous $F^-$ (0.02 eV and 298K) and $OH^-$ (0.03 eV at 298 K) ions [105]. Because our primary interest is in comparing the binding energies of these species against one another, we proceed under the assumption that the enthalpy differences captured by Equation 4–1 will correctly order the overall binding probability of the three species. MXene synthesis is typically carried out near room temperature, so the nature of these adsorption events will most likely be enthalpy-cominated anyway, but it bears mentioning that the lines plotted in Figure 4-3 may be shifted upward slightly by these entropic effects.

**Thermodynamic Stability**

As mentioned before, MXenes exist as dispersion-bound multilayer structures before they are exfoliated into single sheets by ultrasonication and filtering. However, now all MXenes are equally easy to exfoliate. For example, the Nb$_2$C and V$_2$C MXenes have been synthesized as multilayer structures but have not yet been successfully exfoliated [37]. In order to investigate the effect of the three surface terminating groups on MXene exfoliation, the energy required to separate a multilayer MXene into freestanding 2D
Figure 4-4. Exfoliation energies of all six Ti$_2$XT$_2$ MXenes. The exfoliation energy is lowest for $T = \text{OH}$ surfaces and highest for $T = \text{O}$ surfaces, indicating that hydroxylating a MXenes surface can facilitate its exfoliation.

layers is calculated as the difference in energy per unit area between the multilayer structure and the isolated sheet for all six Ti$_2$XT$_2$ MXenes. These calculations require the explicit inclusion of dispersion forces, which are not accounted for in standard DFT, to accurately describe the bonding in the multilayer structure. Therefore, vdW-DF-optB88 dispersion-correction functionals \cite{106} are used to calculate the energies of multilayer and single-layer Ti$_2$XT$_2$, and the resulting exfoliation energies are shown in Figure 4-4.

The exfoliation energies follow the trend $T = \text{O}$, $T = \text{F}$, $T = \text{OH}$ for both $X = \text{C}$ and $X = \text{N}$. The energy differences between the three groups are not large ($< 0.8 \text{ eV/nm}^2$) in relation to the exfoliation energies themselves, but oxygenated surfaces appear to have the strongest interactions. This can be explained by oxygen’s larger ionic radius than the other two species, whose ionic radii are quite similar to one another. This leads to a higher polarizability and, in turn, a stronger dispersion interaction between layers.

These exfoliation energies are high relative to that of graphite ($\sim 1 \text{ eV/nm}^2$) \cite{107}, which may help to explain why the processes required to isolate single layer MXenes, such as intercalation, ultrasonication and filtering, are more involved than those used to isolate graphene.
Figure 4-5. Formation energies for $M_{n+1}X_nO_2$ MXenes relative to the lowest energy mixture of competing bulk phases. The green region highlights the general 0.2 eV/atom threshold observed for 2D material stability, and the yellow region highlights the 0.285 eV/atom formation energy of the $V_2CO_2$ MXene, the highest of those that been synthesized.

The formation energies of the freestanding $M_{n+1}X_nT_2$ nanosheets are then calculated as the difference of the energy per atom for the 2D MXene structure with that of the most stable configuration possible for the same elements with the same stoichiometry [108]. For example, the 2D Ti$_2$CO$_2$ MXene is metastable against the three-dimensional bulk phases of TiO$_2$ and TiC, and the energy difference between the 2D MXene and the competing 3D phases is the formation energy of the MXene. The competing phases for each MXene are chosen from data in the Materials Project database [52] and are listed in the Supporting Information. The formation energies calculated here could be underestimates of the real values if more stable competing phases exist than are present in the Materials Project database [13].

Because all MXenes, except those with $M = Sc$, are predicted to be oxygenated for all possible solution conditions, we report their formation energies only for $T = O$ in Figure 4-5.
We also calculate the formation energies of all six fluorinated M = Sc MXenes and find them all to be less than 0.1 eV/atom, much lower than the formation energies of their oxygenated counterparts. Therefore, etching solutions with higher $\mu_H$ should be used during attempted synthesis of Sc-based MXenes, in order to saturate their surfaces with fluorine. Other experimental factors must be considered as well; for example, MAX phases have been shown to decompose to nanocrystalline ternary fluoride compounds in experiments carried out at low pH [85], and care should be taken to avoid creating these when attempting to synthesize fluorinated M = Sc MXenes.

It is interesting to note that several nitride MXenes are predicted to be stable, as shown in Figure 4-5, although none have yet been synthesized. There could be several reasons for this, but perhaps the most compelling is that aqueous ions and molecules have not been considered as competing species in the calculated formation energies. These aqueous species represent an alternative route for the decomposition of MXenes, which will be quite different for nitrides than for carbides. Other possible reasons are the poor description by DFT of the triple bond in N$_2$, which is a competing phase for several nitride MXenes, or the effect of entropy at elevated temperatures.

In addition, some transition metals (Nb, Ta) are more stable with $X = C$, others (Ti, Zr, Hf) are more or less equally stable for both C and N, and still others (Sc, V, Cr, Mo) are more stable with $X = N$. These three groups roughly correspond to the most common oxidation states of the transition metals: 5+ for Nb and Ta, 4+ for Ti, Zr and Hf, and 3+ for Sc and Cr. Vanadium has several common oxidation states, including 3+. This grouping is intuitive; C accepts more valence electrons than N, and therefore it is the preferred X element for metals of high oxidation, and vice versa.

The MXene formation energies generally follow the trend $M_2XT_2$ $M_3X_2T_2$ $M_4X_3T_2$. This can be understood to be the result of a higher volume to surface area ratio in thicker MXenes. Unfortunately, the reverse trend holds for the bulk MAX phases from which
MXenes are derived, and relatively few unique M and X combinations in M₄AX₃ and M₃AX₂ bulk phases exist from which to synthesize these MXenes [16].

Importantly, of the six MXene compounds that have already been synthesized (Nb₂C, Ti₂C, V₂C, Ti₃C₂, Nb₄C₃ and Ta₄C₃), five have formation energies within the general 0.2 eV/atom threshold observed for freestanding 2D materials’ formation energies [83]. The exception, V₂CO₂, has a formation energies of 0.285 eV/atom, which defines a more generous threshold for the stability of other MXenes. It is proposed that this higher metastability could be accommodated by the more complex pathways for MXenes to their competing 3D phases than those for unary (e.g. graphene) or binary (e.g. MoS₂) 2D materials.

In addition to the six fluorinated M = Sc MXenes, six oxygenated MXenes are predicted to have formation energies below 0.1 eV/atom. A total of 28 MXenes have formation energies below 0.2 eV/atom, and 38 have formation energies below 0.285 eV/atom. The synthesis of MXenes with formation energies below 0.285 eV/atom is predicted to be possible from a thermodynamic perspective, revealing that this family of 2D materials remains a rich frontier for materials discovery. The existence of unique M-X combinations in existing MAX phases, however, will dictate which of these compositions can be immediately investigated for synthesis.

**Computational Details**

The DFT calculations have been performed using the Vienna *ab initio* Simulation Package (VASP) [48], which employs a plane-wave basis and the projector-augmented wave method. Starting geometries and bond lengths for each MXene compound are estimated based on the covalent radii of M and X atoms and employ the characteristic hexagonal layered P3m1 MXene space group. Unit cells of two formula units are used for all calculations unless otherwise indicated. The PBE functional [51] and the conjugate-gradient algorithm are used to obtain accurate relaxed structures during structure optimization for each MXene. PBE functionals are chosen for their ability
to accurately reproduce both structural parameters and structural energy differences [53–57]. For a numeric demonstration of the agreement between the PBE-generated and experimental formation enthalpies of selected transition metal oxides, for example, the reader is directed to the Supporting Information. The use of higher order methods, such as hybrid functionals, for describing correlation in MXenes has been shown to be unnecessary [97]. The geometry optimizations were performed with a 12 × 12 × 1 k-point mesh and a 15 Å vacuum to prevent interlayer interaction [81, 82]. At this spacing, the total energy of a single MXene layer is converged to within 1 meV/atom of its value with a 30 Å vacuum, and its treatment is computationally much cheaper. The energy is converged to below 1 meV/atom for a cutoff energy of 520 eV, and geometric optimizations are stopped after Hellman-Feynman forces on all atoms are less than 1 meV/atom and the stresses on the unit cell are below 0.1 GPa in the x and y directions. To preserve the vacuum spacing, the z components of cell vectors are not optimized, but atomic positions are optimized in all directions. Spin-polarized calculations are performed for all systems to capture any magnetic contributions to the overall energy. All M elements are initialized with large magnetic moments (5 μB) and all other elements are initialized with small magnetic moments (0.6 μB).

Lattice parameters of geometrically optimized MXene structures are found to be within 2% of the only experimental data available [109], which is calculated for Ti3C2T2 using pair distribution function analysis, and within 5% of other calculated DFT values where available [5, 110].

To ensure internal consistency between calculated energies, the VASPsol method [99], which effectively fill the vacuum space around a molecule or between slabs with a dielectric continuum, is used to calculate the energies of all compounds. The default dielectric constant (ε = 80.0), which corresponds to that of water, is used in all calculations. The dielectric constant of the experimental H2O/HF solution is expected to be quite close
to this value, as the dielectric constant of HF is nearly the same ($\epsilon = 83.6$) as that of water.

**Characterizing the Battery-Related Properties of Multilayer MXenes**

The lithium ion battery (LIB) is the preferred technology for modular energy storage, and its usage will grow as the demand for applications such as electric vehicles and rechargeable electronic devices increases. These applications require batteries with large reversible capacities, high power, and good cyclability. Current LIBs perform well in all these areas, but the demand for lighter, more powerful, and more durable LIBs has produced a corresponding demand for new electrode materials capable of delivering such performance. For the last three decades, graphite has been the dominant anode material in state-of-the-art LIB’s [111][112], and the cathode material is typically a layered transition metal oxide or phosphate compound [113] that enables minimally inhibited Li uptake and diffusion.

Perhaps the fastest route to improving the state-of-the-art in LIB electrode performance is through the discovery of new materials, such as the family of MXenes, which already show aptitude for use as LIB electrode materials [93][114][92]. Their dispersion-bound scaffold structure enables the same low-voltage, non-destructive Li intercalation and diffusion mechanisms [36][73] as the most common incumbent electrode materials (graphite or layered oxides) [14][115][116][117][118]. Recent calculations of reasonable gravimetric capacities [93] and low Li diffusion barriers [89] in certain monolayer MXenes indicate that these materials may, indeed, be suitable candidates for electrodes in high-power LIBs. A few compositions have also been experimentally and computationally investigated for their ability to intercalate multivalent ions [114][73][119]. The calculated properties of **monolayer** MXenes, however, cannot be straightforwardly compared with the properties of the **multilayer** compounds with which they will technologically compete. In particular, diffusion barriers for Li through a multilayer
structure, critical for predicting the rate performance of an anode, have not yet been
determined and are expected to vary significantly from those on a monolayer.

First-principles calculations are performed using DFT in the Vienna *ab initio*
Simulation Package (VASP) [48], with the projector augmented wave method [49] and
the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [51]. Dispersion
forces, necessary to describe the interlayer interactions in MXenes, are included with
the vdw-DF2 method [120]. Of the many available methods to include dispersion in
DFT [106, 107, 120, 121], vdw-DF2 has been shown to accurately reproduce dispersion
interaction energies and geometries at little additional computational expense [122]. For
consistency, the energies reported for all compounds in this work are obtained using the
vdw-DF2-PBE functionals and methods described above.

The reciprocal space integration for all calculations is performed with a Monkhorst-Pack
[123] *k*-mesh density of 1000 points per atom for each MXene structure. A 10 Å vacuum is
included above the top layer to reduce the interaction between the layer and its periodic
image in the *z*-direction. These structures are optimized until changes in each system’s
energy are less than 1 meV/atom and stresses on cell vectors are below 0.1 GPa in
the *x* and *y* directions. The cell vectors are fixed in the *z*-direction, to preserve the
overlying vacuum, but the atomic coordinates are allowed to relax in all directions. The
plane-wave cutoff energy is 520 eV for all calculations. Spin polarization is included such
that transition metals are initialized with large magnetic moments (6 $\mu_B$) and all other
elements are initialized with small magnetic moments (0.5 $\mu_B$). No experimental data
are available to which the computed interlayer spacings for non-intercalated MXenes
can be compared, and very limited experimental data are available to which the in-plane
geometric parameters can be compared. The in-plane geometric parameters we calculate
are in very close agreement with DFT work on monolayer MXenes [5][97].

The present investigation focuses on multilayer MXenes of the 4*d* transition metals,
for their high theoretical gravimetric capacities. The investigation is further focused
on oxygen-functionalized MXenes, which are predicted to have the highest gravimetric capacities of all functionalized MXenes [93], and carbide MXenes, which are the only type to be synthesized to date. All Sc\(_{n+1}C_nO_2\) and Cr\(_{n+1}C_nO_2\) MXenes have formation energies in excess of 200 meV/atom, making them thermodynamically unstable [6][108]. This leaves Ti\(_{n+1}C_nO_2\) and V\(_{n+1}C_nO_2\) MXenes \((n = 1, 2, 3)\) for a total of six compositions to investigate. The stacking sequence and geometric parameters of these mutilayer MXenes have been previously determined [124] and will provide the starting structures into which Li will be intercalated.

To accurately reproduce the minimum energy multilayer stacking sequence while preserving computational tractability, bilayer structures (containing four formula units) arranged in stacking sequences that maximize interlayer O-O distances are used in lieu of fully periodic multilayer cells that require many more atoms; both models are illustrated in Figure 4-6. The binding energy for Li between layers in the bilayer structure is found to be within 1 meV of its energy between layers in a fully periodic structure, demonstrating that using the bilayer model does not introduce significant errors to the calculations.

To inexpensively characterize the static potential energy surface (SPES) for a Li atom located between MXene layers, we perform single-point calculations for a Li atom at evenly spaced locations on a lateral 10 \times 10 grid between MXene layers. When lithiated bilayer MXene models are fully geometrically optimized, the \(z\)-coordinates of the Li atoms are found to be halfway between the two MXene layers. Additionally, calculations of Bader charges show that half of each intercalated Li atom’s charge is transferred to each MXene layer. These data suggest that Li atoms interact equivalently with both overlying and underlying layers in multilayer MXenes. Therefore, when characterizing the potential energy landscape, the \(z\)-coordinate of the Li atom is held fixed at a distance exactly halfway between the layers. Figure 4-7b shows the resulting SPES for the Ti\(_2CO_2\) MXene. The overall shapes of the landscapes generated for the other five compositions are similar.
Figure 4-6. Multilayer MXene structures used in the DFT calculations. (a) Side view of a bilayer structure (28 atoms) of Ti$_3$C$_2$O$_2$, (b) Side view of the fully periodic structure (42 atoms, not used for calculations), (c) Top down view of Li site filling order in multilayer Ti$_3$C$_2$O$_2$, where the overlying layer is removed for clarity. Li 1 and Li 2 are directly above carbon atoms in the underlying layer; Li 3 and Li 4 are directly above titanium atoms in the underlying layer. The atomic layers in the boxed region in (a) are the only MXene atoms allowed to relax during CI-NEB calculations of diffusion barriers.

The calculated minimum energy pathway (MEP) directions indicate that lithium diffusion in multilayer MXenes occurs along different directions than on monolayer MXenes. The MEP for lithium in MXenes, whether monolayer or multilayer, is determined by maximizing Li-O distances at all positions. This results in diffusion along [1100] and [0200] directions for Li diffusion on monolayer MXenes [89]. In multilayer MXenes, these paths are interrupted by the presence of O atoms in the overlying MXene layer, and diffusion is instead restricted to the [1000] and [0100] directions. The different diffusion paths on monolayers and multilayers can be seen in Figure 4-7b.

Lithiated MXene formation energy profiles are calculated by intercalating Li atoms one at a time into the geometrically optimized MXene structures, re-optimizing the lithiated structures, and calculating the formation energy as to that of Ti$_2$CO$_2$; only the energies themselves differ because they possess similar surface structures [97][98][87].
Figure 4-7. Equivalent minimum energy intercalation sites for Li (yellow circles) for (a) monolayer MXenes based on previous calculations [89] and (b) multilayer MXenes based on this work. For reference, the paths and sites in (b) are shown on top of the static potential energy surface calculated for Li in Ti$_2$CO$_2$. Hash lines represent the locations of saddle points, black circles represent O atoms in the underlying MXene layer, and in (b), O atoms in the overlying MXene layer are represented as white circles. The minimum energy paths for Li diffusion in both cases are determined by maximizing Li-O distances, which results in diffusion along [1100] and [1 200] directions for monolayer MXenes, and along [1000] and [0100] directions for multilayer MXenes.

$$\Delta E_f = -\frac{E(M_{n+1}X_nO_2Li_x) - E(M_{n+1}X_nO_2) - xE(Li)}{3 + 2n + x}$$ (4-9)

where $E(M_{n+1}X_nO_2Li_x)$ is the energy of the lithiated MXene, $E(M_{n+1}X_nO_2)$ is the energy of the bare MXene, and $E(Li)$ is the energy per atom of metallic Li in its native BCC structure, and $3 + 2n + x$ is the total number of atoms in the lithiated MXene. The Li stoichiometry, $x$, changes from 0.5 for a single Li atom between the layers to $x = 2$ for the fully charged materials with four intercalated Li atoms. The locations at which Li is intercalated for each value of $x$ are indicated in Figure 4-6 and correspond to the blue basins in Figure 4-7. At intermediate values of $x$, higher Li-Li distances result in lower energies. The voltage difference $V$ between two Li concentrations $x_1$ and $x_2$ can then be calculated as [125]
Figure 4-8. Formation energy profiles (a) and corresponding voltage profiles (b) for multilayer Ti_{n+1}C_nO_2 and V_{n+1}C_nO_2 MXenes. Compositions lying above the convex hull in (a) have been excluded from the developed voltage profiles.

\[
V = -\frac{E(M_{n+1}X_nO_2Li_{x_1}) - E(M_{n+1}X_nO_2Li_{x_0})}{x_1 - x_0} \quad (4-10)
\]

The overall stoichiometry of the lithiated bilayer structure is not identical to that of a lithiated bulk multilayer structure. In the bilayer model, there are two MXene layers with only one layer of Li between them, whereas in the fully periodic multilayer structure, each MXene layer has Li intercalated above and below it, i.e., the ratio of the number of MXene layers to Li layers is 1 in the bulk and \( \frac{1}{2} \) in the bilayer (see Figure 4-6). For comparison with bulk lithiation, the atoms of the overlying MXene layer are not counted in the stoichiometries reported here, and \( x \) is the number of Li atoms per formula unit in the bulk structure.

Figure 4-8 shows the formation energy \( \Delta E_f \) versus the amount of Li inserted for all six compositions along with the corresponding voltage profiles.

Thermodynamically, it is required that the shape of \( \Delta E_f \) remains convex across the entire lithiation profile. Energies lying above this convex hull will decompose to a compositionally equivalent mixture of the endpoints on the line directly below. The
voltage profiles in Figure 4-8b are calculated based only on the compositions lying on the convex hull.

We estimate that the maximum reversible capacity is achieved close to \( x = 1 \) for all three Ti-based compositions, and close to \( x = 1.5 \) for \( V_4C_3O_2 \). The maximum reversible capacity appears to be \( x = 2.0 \) for \( V_2CO_2 \) and \( V_3C_2O_2 \). However, sever lengthening of the surface M-O bonds and shortening of Li-O bonds are predicted for \( V_2CO_2Li_x \) and \( V_3C_2O_2Li_x \) for \( x \gt 1.5 \). This behavior is characteristic of an irreversible reaction caused by supersaturation of the surface with electron density \([93]\). Therefore, we interpret their reversible capacities as \( x = 1.5 \), no \( x = 2 \).

The theoretical gravimetric capacity is calculated for each composition using the maximum value of \( x \) and the equation

\[
Q = \frac{x F}{m_{M_{n+1}X_nO_2}} \tag{4-11}
\]

where \( Q \) is the capacity, \( F \) is the Faraday constant, and \( m_{M_{n+1}X_nO_2} \) is the mass of the MXene formula unit. We also compute the volumetric capacity of each MXene. The values of Equation 4-11 computed for each multilayer composition are provided in Table 4-1. The values calculated for multilayer MXenes are lower than those calculated for monolayer MXenes, primarily because the calculated capacities of monolayer MXenes assume that for each MXene layer there are two layers of lithium (one on either surface of the monolayer) \([93][89]\). For multilayers, the ratio of Li layers to MXene layers is 1 to 1.

There is better agreement between the calculated reversible capacity for multilayer \( V_2CO_2 \) (276 mAhg\(^{-1}\)) and the experimental reversible capacity of the \( V_2CO_2 \) MXene (260 mAhg\(^{-1}\)) \([37]\) than there is between the experimental value and the value previously calculated for a monolayer (335 mAhg\(^{-1}\)) \([93]\). This is reasonable, as the majority of the experimental anode in Ref. \([37]\) was non-exfoliated multilayer \( V_2CO_2 \). Therefore, comparison with experiment is more sensible for the multilayer value obtained here than for the previously calculated monolayer value. The computed value for Ti\(_2\)CO\(_2\) (192
Table 4-1. Calculated properties of all six Ti$_{n+1}$C$_n$O$_2$ and V$_{n+1}$C$_n$O$_2$ MXenes. Theoretical capacities are calculated using Equation 4-11 and $x=1.5$. Diffusion barriers calculated using the climbing image nudged elastic band method (CI-NEB) are quantitatively more accurate than those calculated from the static potential energy surface (SPES), but both methods are found to reproduce the same qualitative trends.

<table>
<thead>
<tr>
<th>MXene</th>
<th>Gravimetric Capacity (mAhg$^{-1}$)</th>
<th>Volumetric Capacity (AhL$^{-1}$)</th>
<th>Volume Expansion (%)</th>
<th>Diffusion Barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$CO$_2$</td>
<td>192</td>
<td>346</td>
<td>0.32</td>
<td>0.63 0.91</td>
</tr>
<tr>
<td>Ti$_3$C$_2$O$_2$</td>
<td>134</td>
<td>240</td>
<td>-0.1</td>
<td>0.60 0.82</td>
</tr>
<tr>
<td>Ti$_4$C$_3$O$_2$</td>
<td>103</td>
<td>187</td>
<td>0.34</td>
<td>0.73 1.09</td>
</tr>
<tr>
<td>V$_2$CO$_2$</td>
<td>276</td>
<td>379</td>
<td>2.82</td>
<td>0.82 1.15</td>
</tr>
<tr>
<td>V$_3$C$_2$O$_2$</td>
<td>192</td>
<td>263</td>
<td>1.93</td>
<td>0.52 0.81</td>
</tr>
<tr>
<td>V$_4$C$_3$O$_2$</td>
<td>148</td>
<td>205</td>
<td>1.64</td>
<td>0.42 0.48</td>
</tr>
</tbody>
</table>

mAhg$^{-1}$) is still much higher than the experimental value (110 mAhg$^{-1}$) [36], though it is also much closer than the monolayer value (372 mAhg$^{-1}$). Because our models represent ideal intercalation/discharge phenomena, some overestimation of the reversible capacity is to be expected. This overestimate could be explained by the presence of other surface functional species, such as OH, which has been shown to reduce a MXene’s capacity [93][92][89], or the irreversible reaction of Li with the electrode and/or electrolyte. The close agreement between the calculated theoretical capacity for multilayer V$_2$CO$_2$ and its experimental value indicates that these detrimental phenomena are not as significant in V$_2$CO$_2$.

All six compositions display high maximum potentials between 2.5 and 3.7 V. This is consistent with experimentally measured maximum voltages for V$_2$CO$_2$ and Ti$_2$CO$_2$ anodes of 3.0 V and 2.5 V, respectively [37][36]. All MXenes retain a voltage above 2 V for $x < 1$, followed by a drastic drop for higher stoichiometries, suggesting that multilayer MXenes intercalate and discharge most of their capacities at voltages above 2V. Voltages below 1V are desirable to prevent plating during intercalation, and we predict that the voltage windows of all three V$_{n+1}$C$_n$O$_2$ MXenes overlap this range for close to 33% of
their capacity. This is in close agreement with experimental observations for $V_2CO_2$; approximately 67% of their capacity is intercalated above 1.5 V, with the rest intercalating at lower voltages [37].

The volume expansion $\Delta V/V_0$ between the maximally lithiated bilayer structure and the $x = 0$ bilayer structure is calculated as the percent difference in volume between $M_{n+1}C_nO_2Li_x$ and $M_{n+1}C_nO_2$

$$\Delta V/V_0 = \frac{V(M_{n+1}X_nO_2Li_x) - V(M_{n+1}X_nO_2)}{V(M_{n+1}X_nO_2)} \times 100 \quad (4-12)$$

where the volume of the overlying vacuum for each bilayer structure is neglected. Values of Equation 4-12 are also reported in Table 4-1.

These values are not expected to quantitatively reflect the experimental volume changes, as electronic-scale DFT calculations do not account for large-scale phenomena, such as Li clustering and the presence of water or other species that can contribute to the overall electrode swelling [126]. For example, the Ti$_3$C$_2$O$_2$ MXene has been experimentally observed to swell 10%-20% upon Li intercalation [73], while the calculations predict a contraction in volume. By comparison, graphite electrodes swell approximately 10% upon lithiation [127] and silicon anodes swell by nearly 300% [128]. The large difference between the calculated volume expansion and the experimental volume expansion for Ti$_3$C$_2$O$_2$ suggests that there are, indeed, other processes than Li intercalation occurring experimentally during charge/discharge cycles in MXenes that contribute to the swelling.

Following the thermodynamic considerations of MXene lithiation, we now determine the kinetics of lithiation by calculating the diffusion energy barrier of Li in multilayer MXenes. To accurately determine the locations and energy barriers of saddle points along the diffusion paths for Li, we use the climbing-image nudged elastic band (CI-NEB) method [129]. Initial and final locations for Li, along with the linear MEP, are extracted from the SPES, as shown in Figure 4-7.
CI-NEB calculations are initialized with three transition state images between the final and initial states. To simulate the compressive effect of additional layers above and below they bilayer model and to accelerate convergence, only M and O atoms in the four atomic layers nearest the Li (see boxed region in Figure 4-6a) are allowed to optimize their positions during the CI-NEB calculations. Table 4-1 compares the energy barriers calculated from the CI-NEB method with the simple SPES estimate. As expected, relaxations in the CI-NEB method lower the energy barrier compared to the static energy landscape estimate. Interestingly, the simple static estimate predicts the same ordering of the barriers across all compounds, indicating that the SPES provides an efficient materials descriptor that could be used for high-throughput approaches where accurate predictions of trends for diffusion barriers are sought over quantitative accuracy.

The V₄C₃O₂ MXene exhibits the lowest barrier for Li diffusion between layers. Thus, although this composition has the highest specific mass and lowest gravimetric capacity of all those considered, it may find application in high-power, non-portable batteries.

The diffusion barriers determined using CI-NEB for Tiₙ₊₁CₙO₂ multilayer MXenes are roughly twice as large as those predicted for Ti-based monolayer MXenes [89], due to the geometric constraint of the Li traversing between two surfaces in the multilayer structure instead of diffusing on top of a single surface for the monolayer case. None of the diffusion barriers are below that of graphite (∼0.3 eV), suggesting that to be competitive as anodes in high-power batteries, Tiₙ₊₁CₙO₂ and Vₙ₊₁CₙO₂ MXenes may first need to be exfoliated into monolayers and dispersed in some other medium instead of being preserved as multilayer structures.

The lithium ion battery-related properties of six promising Tiₙ₊₁CₙO₂ and Vₙ₊₁CₙO₂ multilayer MXenes have been determined and compared using DFT calculations. Voltage profiles in good agreement with experiment are found for the Ti₂CO₂, Ti₃C₂O₂ and V₂CO₂ MXenes. Calculations show that multilayer vanadium acrbide MXenes can thermodynamically accomodate up to 1.5 Li atoms per formula unit, resulting in
reasonable reversible capacities, though not as high as that of graphite (372 mAhg$^{-1}$). The calculated capacity of the multilayer $V_2CO_2$ MXene (276 mAhg$^{-1}$) is close to its experimental value (260 mAhg$^{-1}$).

Li diffusion is predicted to occur along the [1000] and [0100] directions in multilayer MXenes. Among the six MXenes studied, the reversible capacity is largest for $V_2CO_2$, which is also the MXene with the highest diffusion barrier, suggesting it may be suitable for lightweight, high capacity batteries in applications that do not require high power. Conversely, the $V_4C_3O_2$ MXene is predicted to have the lowest reversible capacity and the fastest diffusion rate, suggesting it may be useful for high-power batteries that need not conform to any weight restrictions. The $V_4C_3O_2$ MXene has not yet been formed experimentally, but the $V_4AlC_3$ MAX phase from which it could possibly be etched has been synthesized [130]. The $Ti_2CO_2$ MXene offers a potential useful compromise between reversible capacity (192 mAhg$^{-1}$) and diffusion barrier (0.63 eV). Additionally, small ($< 3\%$) ideal volume changes during charge/discharge cycles are predicted for all six compositions. These small volume changes imply that the 10%-20% experimental swelling observed for the $Ti_3C_2O_2$ MXene is the result of some processes beyond Li intercalation.
Challenges to Previous 2D Material Searches

In an effort to discover novel 2D materials, Lebègue et al. recently scanned the inorganic crystal structure database (ICSD) in search of compounds with large interlayer spacings, which are characteristic of weak interlayer bonding that could be overcome by mechanical exfoliation [132]. They used the intuitive criteria of a low packing fraction based on the covalent radii of the atoms and an interlayer gap larger than the sum of the covalent radii of atoms at the layers’ surfaces along the $c$-axis to identify layered compounds in the ICSD. They discovered 92 layered phases, nearly half of which had monolayers that had not been the subject of any prior publications.

Here, we extend their method to identify a large number of layered compounds that were missed using the packing factor and $c$-axis interlayer gap criteria. We further add the constraint that a bulk material must be thermodynamically stable to be of interest during our search. Therefore, we use the Materials Project (MP) database [133], an online repository of crystallographic and thermodynamic data for over 65,000 compounds calculated with DFT.

Description of the Topology-Scaling Algorithm

Our algorithm is designed to correctly identify additional layered materials by handling four different cases that are illustrated in Fig. 5-1: (a) materials whose layers are not perpendicular to unit-cell axes or parallel to unit cell surfaces, (b) materials with corrugated layers that therefore lack a planar interlayer spacing, (c) materials with very thick layers that exceed the packing factor normally observed for layered materials, and

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Figure 5-1. Examples of structure types that challenge the search for layered materials by exhibiting a) layers along an axis other than the $c$-axis, b) corrugated layers, c) thick layers, and d) molecular (non-bonded) layers. Each of these examples is correctly classified with the present method.

Each of these cases is correctly classified using our topology-scaling algorithm (TSA) to identify layered compounds. The first step in the TSA is to isolate bonded clusters of atoms in the structure, where a bond is defined as an overlap in the covalent radii of two neighboring atoms plus a small tolerance. If all atoms in the structure are in the same cluster, the structure is classified as a conventional bulk compound. If not, we count the number of atoms in a single cluster, create an $n \times n \times n$ supercell of the original structure, and group all atoms into bonded clusters again. The scaling of the cluster size with supercell size, $n$, determines the dimensionality of the structure as illustrated in Fig. 5-2. If the number of atoms in the original cluster does not change with supercell size (zeroth order scaling), the cluster is an isolated molecule or atom. If the number of atoms scales linearly with $n$, the cluster is a one-dimensional chain. If it scales as $n^2$, it is a true layered...
solid. If it scales as $n^3$, it is most likely an intercalated solid (e.g. a lithiated zeolite) composed of a three-dimensional bonded network structure with intercalated atoms or molecules.

Here, we use the TSA to identify layered solids, but its ability to simultaneously identify bonded networks of any dimension is what allows it to systematically classify structures in large materials databases. Correctly distinguishing between molecular, intercalated, and layered solids is crucial, since there are large numbers of molecular and intercalated structures in most materials databases.

The strength of the TSA is that it discovers structural motifs that are separated from each other by distances larger than the bond length of atoms within the motifs. The search for bonded clusters employs a range of bond-length tolerances between 100% and 135% of the summed covalent radii [134]. A few compounds are only identified as layered for a small range of tolerances; these are visually examined.
Figure 5-3. Distribution of (a) stoichiometries of the 826 layered compounds, and comparison of the compositional complexity among (b) the stable layered materials identified by this work and (c) all materials in the Materials Project database. The top 5 stoichiometries (ABC, AB\textsubscript{2}, AB, AB\textsubscript{3}, and ABC\textsubscript{2}) represent half of all compounds. In general, the relative abundance of a given stoichiometry scales inversely with the formula’s complexity. We observe that the percentage of binary compounds among layered materials is significantly higher than among all materials, suggesting that binary compounds (one cation and one anion) are particularly conducive to creating interlayer dispersion interactions.

**Results of Searching the Materials Project Database**

Our algorithm identifies 1560 layered materials, 509 of which have zero distance to their respective thermodynamic convex hulls, and hence are predicted to be stable compounds. Another 590 materials are metastable by less than 50 meV/atom, 206 by between 50 and 100 meV/atom, and 255 are unstable by more than 100 meV/atom. Here, we focus on the stable and metastable materials with distances to the hull of less than 50 meV/atom. Additionally, several of the 1560 layered materials are simply different stacking sequences of the same monolayer. These duplicates are filtered out using symmetry analysis resulting in 826 unique monolayers for further investigation.

These 826 materials can be grouped according to their stoichiometric ratios. Fig. 5-3(a) shows that 50% of the layered materials are represented by just five stoichiometries. These five – AB\textsubscript{2}, ABC, AB, AB\textsubscript{3}, and ABC\textsubscript{2}, in decreasing order of frequency – mostly reflect the abundance of known 2D materials with simple cation/anion stoichiometries.
However, the large variety of 102 unique stoichiometries indicates that the family of potentially exfoliative layered compounds is much more diverse than the simple compositions typically considered as 2D material candidates.

Figure 5-3(b) and (c) compare the percentages of unary, binary, ternary, etc. stable layered compounds in the MP database with the percentages of all stable (distance to hull $< 50$ meV/atom) compounds in the MP database. Binary, ternary, and quaternary compounds comprise 98.2% of the stable layered compounds. The percentages of unary and ternary compounds among layered materials are very close to their percentages among all materials in the MP database. However, binary compositions are clearly overrepresented among layered materials, while quaternary and quinary compositions are underrepresented. This indicates that compounds of two or three species can more easily form low-energy structures that exhibit dispersion-bound layers.

These materials can be further classified according to their crystal structures, which has implications for future searches for 2D materials based on chemical substitutions and genetic algorithms [135, 136]. The crystal structures represented by each stoichiometry can be used as templates for these searches, which require viable crystal structures as the initial parent structures to seed the algorithm. The use of a larger number of seed structures increases the likelihood that a given search will identify the global minimum of a composition’s high-dimensional phase space. The complete set of the structural templates for all stoichiometries identified by our algorithm is available online in our database at https://materialsweb.org.

An example of structural templates is given in Fig. 5-4, which shows all 15 unique crystal structures identified for the AB stoichiometry. These 15 structures can either augment or stand alone as the parent generation in future searches for 2D materials of AB composition. These various structures will likely possess a wide variety of properties, even for the same A and B elements. For example, buckled structures, such as structures (i) and (m) in Fig. 5-4, are uniquely interesting because their broken inversion symmetry
Figure 5-4. Side views of the 15 unique structural templates identified for monolayers of AB stoichiometry, labeled according to prototypical compounds possessing that crystal structure. The symmetries of structures a) and b) are related by a broken inversion symmetry, in the same way that the well-known 1T and 2H monolayer structures are related. Other structural pairs, such as h), i) and j), k), are related to one another by simple distortions.

could lead to piezoelectricity [137–141] or, given sufficiently large spin-orbit coupling, to Rashba spin splitting [142, 143]. For lubricating applications, flat monolayers like structures (f) and (h) may exhibit lower friction coefficients than strongly buckled monolayers, like structures (c) and (o).

**Calculating the Layered Materials’ Exfoliation Energies**

We re-optimize the structures of all 826 stable layered materials and the single monolayers from each structure with DFT using VASP [47, 80, 144, 145]. We employ the dispersion-corrected vdW-optB88 exchange-correlation functional [106, 122, 146, 147] to accurately account for interlayer dispersion interactions. We compare the resulting exfoliation energy of the single monolayer materials, given by the energy difference between the monolayer and the bulk solid, with that of free-standing monolayers that have
Figure 5-5. Histogram of calculated exfoliation energies for all 826 layered materials compared to the range of calculated exfoliation energies for already synthesized 2D materials. Because of their relatively weak interlayer forces, most compounds found in our search exhibit low exfoliation energies (< 100 meV/atom), indicating the ease of exfoliation.

previously been synthesized. As an upper bound, 2D SnSe has been synthesized [148, 149] and has an exfoliation energy close to 150 meV/atom. The most promising 2D material candidates will have much lower exfoliation energies, but monolayers with exfoliation energies below 150 meV/atom may be feasible for synthesis [83, 136].

Fig. 5-5 shows the distribution of calculated exfoliation energies for all 826 compounds with respect to the exfoliation energies of known 2D materials. A large majority of 680 compounds have exfoliation energies below 150 meV/atom, and most (612) have exfoliation energies below 100 meV/atom.

Isolating Interesting Materials from the Search

We find that C, P, As, Sb, and Bi are the only elements that have pure layered forms. Of those five, Sb and Bi share the same structure, as do P and As, leading to the three unique unary layered crystal structures shown in Fig. 5-6. Graphene (C), phosphorene (P), arsenene (As), and antimonene (Sb) have all been reported as 2D materials experimentally and/or theoretically [150–153], but very little work has been done to isolate or characterize bismuthene (Bi) nanosheets. The exfoliation energy of bismuthene is 273 meV/atom,
Figure 5-6. Side views of monolayers for the five elemental layered materials in the Materials Project database.

similar to that of 2D Sb (236 meV/atom). Both are above the 150 meV/atom threshold of exfoliation energies for experimentally existent materials, but still much more stable than silicene [108, 154], which has been stabilized on substrates. Thus, 2D bismuthene, if not stable as a free-standing monolayer, may be stabilized on a suitable substrate [155, 156].

To illustrate the variety of properties accessible among the 826 2D materials we have identified, 182 are predicted to exhibit magnetic moments larger than 1 \( \mu_B/\text{unit cell} \) and 519 display band gaps at the PBE level. Only ferromagnetic configurations were considered; more detailed analysis will be required to determine which magnetic 2D materials have antiferromagnetic or more complex orderings. CaClF and MgCl\(_2\) have the largest band gaps at the PBE level of both 6 eV. Their inexpensive constituent elements and relatively substrate-agnostic interlayer interactions make CaClF and MgCl\(_2\) particularly interesting candidates for thin transparent dielectrics in electronic device technologies.

Structural information, band gaps and magnetic moments are listed for all materials in Table S1 in the Supplement. Magnetic 2D materials with distinct band gaps for each of their spin channels have both gaps listed. To view interactive and downloadable information for all structures, including exfoliation energies, input files used for calculations, band structures, and calculated Pourbaix diagrams, the reader is again referred to our online database at https://materialsweb.org.
In summary, we predicted the stability of more than 600 potential 2D materials, including bismuthene, which may be the most stable elemental 2D material left to be synthesized. The synthesis and further characterization of these materials could, in turn, unearth a commensurate wealth of materials properties. Additionally, the monolayer structures identified in this search can serve as viable structural templates for theoretical searches for 2D materials, such as genetic algorithm and chemical substitution searches, that may lead to the discovery of many more stable 2D materials.
Motivating the Discovery of Group IV-V 2D Materials

The discovery of two-dimensional (2D) materials composed of earth-abundant elements is an endeavor with promising implications, especially for the marketability of these materials in sustainable large-scale device manufacturing. Many of the earth-abundant 2D materials that have already been discovered are metallic, and the discovery of semiconducting earth-abundant 2D materials is critical for the next generation of electronic devices.

Recent studies have shown that several of the relatively abundant elements from groups III through VI can exist quite flexibly in several 2D crystal structures. Group III-V 2D materials with AB stoichiometries have been predicted to crystallize on substrates in either a tetragonal litharge or hexagonal crystal structure [82, 108]. Group IV-VI AB materials have also been predicted to be metastable in the litharge structure, as well as a distorted rocksalt structure [135]. In general, these materials are semiconducting and could be useful in nanoscale gates or heterojunctions. 2D silicon (silicene) and 2D phosphorus (phosphorene) have also been synthesized, and both are under investigation for their potential application as transistor materials, although silicene is only stable as a thin film on a substrate [158–161].

The discovery of these low-energy 2D materials prompted a recent investigation into the stability of a variety of silicon phosphide nanosheets, in which a stable \( P6m2 \) structure was predicted for SiP using particle swarm optimization [162]. This structure and others identified for varying \( \text{Si}_x\text{P}_y \) stoichiometries were all found to be semiconducting, and each had markedly different band structures. This suggests that the silicon phosphide

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Figure 6-1. Crystal structures of two-dimensional SiP in (a) the $Cm$ crystal structure predicted in this work, and (b) the $P\bar{6}m2$ crystal structure previously predicted.

phase space is a potentially rich reservoir of unique 2D material properties. Later, the same crystal structure was investigated for other IV-V compositions, as well as for several III-VI and II-VII compositions [163], many of which were predicted to have reasonably low formation energies with respect to their bulk competing phases.

In this letter we investigate the bulk structure of SiP as a possible precursor to readily obtain a 2D SiP structure of space group $Cm$, which is different from but related to the $P\bar{6}m2$ structure identified previously [162]. Fig. 6-1 illustrates both 2D structures. Similar to the famously exfoliable graphite/graphene system [150], the layers in bulk SiP are separated by a large distance of 2.8 Å, characteristic of van der Waals (vdW) interactions, and SiP is therefore expected to display weak interlayer interactions.

The structure of this bulk SiP compound is shared by a small class of other group IV-V compounds (SiAs, GeP, and GeAs) [58, 59, 133]. This motivates our investigation of the stability of all 16 group IV-V MX compounds ($M = Si, Ge, Sn, Pb; X = P, As, Sb, Bi$) in the 2D $Cm$ and $P\bar{6}m2$ crystal structures. We note that we also considered carbon and nitrogen as M and X elements, respectively, but found that these compounds were highly unstable.

For the compounds we predict to be stable as 2D materials, we investigate their electronic properties, with a particular emphasis on the heterojunctions formed at the interfaces of the $Cm$ and $P\bar{6}m2$ phases. Additionally, 2D materials’ characteristically
high surface area to weight ratio makes them interesting for application as photocatalysts; therefore, we also determine their band edge positions relative to the stability region of water, and generate Pourbaix diagrams to determine their stability against forming solvated ions in aqueous conditions.

**Computational Details**

DFT calculations are carried out using the Vienna *ab initio* Simulation Package (VASP) [80, 144, 145] to obtain geometrically optimized structures and reaction enthalpies. To account for important dispersion interactions we employ the non-local vdW-optB88 exchange-correlation functional [106, 122, 146, 147]. The structures are optimized until the forces on all atoms are less than 0.01 eV/Å and stresses smaller than 0.05 kbar. The calculations for the 2D materials employ a 20 Å vacuum spacing between periodic layers to reduce interlayer interaction energies to about 1 meV/atom. All calculations are performed with cutoff energies 30% higher than the value specified in the pseudopotential files, and with *k*-mesh densities of 1000 *k*-points per atom. To accurately estimate the band gaps and band edge positions of the 2D materials, we calculate their electronic band structures using the HSE06 hybrid functional that includes a fraction of exact Hartree-Fock exchange [164, 165].

Formation energies are calculated as the difference in energy per atom between the 2D material and its most stable competing 3D bulk phases [6, 11, 82]. The most stable competing phases are selected from the Materials Project database, which currently contains structural and thermodynamic data for over 66,000 compounds [58, 133]. If the most stable bulk phase is the layered precursor, as is the case for the SiP, SiAs, GeP, and GeAs systems, the formation energy can be conceptualized as the energy required to exfoliate a single layer from the bulk structure. For the other materials, which do not naturally exist in this layered crystal structure, and for the *P*6*m*2 2D structure, the formation energy represents the enthalpic tendency for these 2D materials to decompose to bulk phases.
Results and Discussion

Fig. 6-2 shows the calculated formation energies of all 16 2D materials. For comparison, graphene has a formation energy of 70 meV/atom relative to its graphite bulk structure as calculated using the parameters described above. In fact, a threshold formation energy of < 200 meV/atom has been empirically observed for experimentally produced free-standing 2D materials [83, 136].

Interestingly, the four compounds with existing layered bulk precursors all have formation energies below 100 meV/atom, indicating that the ease of their exfoliation should be comparable to that of graphene. Five additional compounds, SnSb, GeSb, SnAs, SnBi and SnP, fall within or very nearly within the empirical 200 meV/atom threshold, and are therefore also expected to be synthesizable as free-standing films. In general, the compounds with smaller M (Si, Ge) and X atoms (P, As) tend to be more stable, as do compounds with M and X atoms of similar size, such as SnSb.

The difference in formation energies between the \( Cm \) and \( P\tilde{6}m2 \) structures are in most cases less than 10 meV/atom, indicating that some polymorphism should be
Figure 6-3. Comparison of the band edge positions of the 9 stable group IV-V 2D materials with the redox potentials of water, relative to the vacuum level.

expected upon synthesis. The near degeneracy of these two structures is likely because their similar bonding environments; namely, each M atom is always bonded to one other M and 3 X atoms. While we expect that the Cm crystal structure will be exclusively obtained by exfoliation of the bulk precursor, synthesis via deposition and self-assembly may result in the higher symmetry P6m2 crystal structure when its periodicity is commensurate with the substrate. Experimental work will be required to assert which crystal structures each composition assumes during growth on a given substrate.

Figure 6-3 indicates that the band edges of several of the nine stable 2D group IV-V compounds straddle the redox potentials of water, making them possible candidates for photocatalytic water splitting. The locations of the band edges are relative to the vacuum level and have been calculated using the hybrid functionals described above. Incidentally, four of these compounds are the most stable 2D group IV-V compounds considered, and the only four that can be obtained by exfoliation from the layered bulk crystal structures.

For all nine stable 2D compounds, the band edges of the P6m2 structure are below those of the Cm structure. This can be explained by the difference in surface dipoles between the two structures, which leads to a shift in the local electrostatic potential. The top and bottom surfaces of the P6m2 structure may be thought of as continuous dipole
Figure 6-4. Planar-averaged potentials plotted along the direction normal to the 2D material for SiP in the two crystal structures. The local potential in the interior of the Cm structure (left) is lower than that on the interior of the P6m2 structure (right), explaining the relative offsets in their band edges.

sheets, with the partial positive charge lying on the M atoms within the interior of the material, and the partial negative charge on the X atoms. This partial positive charge inside the material lowers the potential of negatively charged electrons, thereby lowering the band edge positions. Similarly oriented dipoles exist at the Cm surfaces; however, the dipoles are weakened by the lower symmetry, resulting in higher band edge positions. This effect is illustrated in Fig. 6-4, which shows the planar-averaged electric potential relative to the vacuum level as a function of z-coordinate in the computational cells of SiP in both crystal structures.

This feature makes these materials interesting for use in heterojunctions. If both structures can be independently stabilized and brought into contact with one another, a Type II heterojunction with a clean interface seems feasible. Additionally, the band gaps of the Cm structures are usually larger than those of their P6m2 counterparts by close to 15%. In the case of SiP, the Cm and P6m2 band gaps are 2.83 eV and 2.46 eV, respectively. As a point of interest for optoelectronic applications, the band gaps of the Sb-containing 2D materials in the Cm structure are the only ones predicted to be direct.
To be used as photocatalysts, these compounds must be stable not only against bulk phases, but also against dissolving into ions in an aqueous solution. The aqueous stability of each compound depends on the pH, voltage, and concentration of ions in the solution, and is best illustrated by Pourbaix diagrams. We generate these diagrams following the procedure of Persson et al. [77], which combines DFT formation energies and adjusted experimental ionic formation energies to reproduce experimental Pourbaix diagrams and determine the conditions required for aqueous stability.

Fig. 6-5 shows the Pourbaix diagrams created for the 6 compounds with photocatalytically favorable band edges. Because their formation energies are nearly degenerate with those
Figure 6-6. Band structures of (a-b) GeAs and (c-d) SnAs in the \textit{Cm} and \textit{P6m2} structure calculated with the HSE06 functional. Each band is colored according to the character of its states as projected onto each element in the compound.

of the corresponding \textit{P6m2} structures, and therefore their stability regions are nearly identical, only the Pourbaix diagrams of the \textit{Cm} structures are provided. A high ionic concentration of 1M is required to illustrate those compounds with any stability in suitably tailored solutions. We observe that neither SiP nor SiAs have any appreciable stability against forming ions in solution, and are therefore not promising for use in photocatalysis or any other aqueous applications. While none of the other four compounds have any stability within the water stability region either, the Pourbaix diagrams suggest that GeAs and SnAs may be sufficiently metastable to kinetically stabilize in water and that GeP and SnP should be relatively stable in humid air.

To characterize the bonding in the group IV-V 2D materials, we analyze the electronic structure and determine the charge transfer between the elements. Fig. 6-6 shows the band structures calculated with the HSE06 functional for GeAs and SnAs in the \textit{Cm} and \textit{P6m2} structures. The projection of the bands onto the elements in the compound illustrates that both element contribute nearly equally to the valence and conduction bands. The Bader charges \cite{104,166} show a small charge transfer from Ge to As of about 0.25 and 0.3 electrons in the \textit{Cm} and \textit{6m2} structure, respectively.
SnAs, the charge transfer is a bit larger with 0.45 and 0.6 electrons in the two structures, respectively. This slight increase is a result of the higher electronegativity difference between Sn and As than between Ge and As. The similarity in the Bader charges and the equal contributions of the two elements to the valence and conduction bands shows that the bonding in these compounds is largely covalent in nature.

**Summary**

In summary, we have predicted a new class of 9 stable group IV-V 2D materials in two different crystal structures ($Cm$ and $P\bar{6}m2$) with nearly degenerate energies. The four compounds SiP, SiAs, GeP, and GeAs should be readily exfoliable in the $Cm$ structure from existing bulk precursors. All 9 have band alignments such that type II heterojunctions with minimally defective contacts may be formed by bringing the $Cm$ and $P\bar{6}m2$ structures into contact with one another. The calculations indicate that GeAs and SnAs may be used as photocatalysts, as they have band edges that straddle the redox potentials of water, and are possibly metastable against dissolution in aqueous environments. In particular, we recommend experimental efforts to exfoliate 2D layers from bulk GeAs to investigate their aqueous stability and photocatalytic activity. The crystal structures, band structures, and Pourbaix diagrams of all compounds can be found in our online database at [https://materialsweb.org](https://materialsweb.org).
Spin-based, or spintronic, logic circuits have long held promise for commercial applications [167]. However, the limited number of materials available for various device components presents clear challenges to the design of spintronics devices. Materials for spintronics applications require a suitable combination of magnetic and semiconducting properties at both small scales and room temperature. For near term applications, these materials must also be compatible with commercially used substrates and mature device architectures [168]. Hard disk drives rely on read head sensors based on either giant magnetoresistance spin valves or magnetic tunnel junctions where the magnetic leads are not fully spin polarized. This mixed spin current can limit the overall magnetoresistance and reduce the signal to noise ratio. In magnetic tunnel junctions with high tunneling magnetoresistance (TMR) values [169], this issue is partially mitigated by the effective spin filtering of the MgO complex band structure. However, in GMR structures, the incomplete spin polarization has provided a significant obstacle for high magnetoresistance values.

Magnetic materials that exhibit half-metallicity, or a metallic density of states at the Fermi level for one spin channel and a simultaneous band gap for the other spin channel, show great promise as an ideal electrode for spintronic devices. Half metal electrodes could provide fully spin polarized currents and large magnetoresistance in GMR and TMR devices. A representative magnetic tunnel junction is illustrated schematically in Fig. 7-1, in which a magnetic field is used to switch the magnetization in one layer of the junction between parallel (low-resistance) and antiparallel (high-resistance) states with the other layer [170, 171]. For such a tunnel junction with half-metal electrodes, the absence of minority spin carriers in both electrodes would lead to high tunneling resistance in the antiparallel configuration. In addition, these fully spin polarized electrodes could
Figure 7-1. (Color online) Magnetic tunnel junction design based on half-metallic 2D FeBr$_2$ (bottom) and FeCl$_2$ (top). A magnetic field can be used to re-orient the magnetization in the top layer, while the magnetization in the bottom layer is pinned by a substrate. This leads to two states for the spin current in the device: “on” when the magnetizations are parallel to one another, and “off” when they are antiparallel.

potentially provide efficient spin injection into semiconductors and graphene, opening the way for more exotic applications, including spin-based transistors, diodes, and spin Seebeck devices. Recent studies have identified a number of half-metallic bulk compounds, including Heusler alloys [172, 173], double perovskites [174–176], transition metal oxides [177, 178], and transition metal chalcogenides and pnictides [179–181]. Spintronic devices based on these materials have been proposed [182] and realized [183, 184], but integrating them with Si or other substrates without introducing site disorder and strain defects during deposition and processing and modifying their electronic properties still presents an ongoing challenge [185]. In the case of Heusler alloys, like Co$_2$Mn$_{1-x}$Fe$_x$Ge, atomic disorder at the sublattice sites can lead to the loss of the ordered L2$_1$ or partially ordered B2 crystal structures and the destruction of the half-metal character [186]. While higher annealing temperatures (~500 °C) can ensure proper crystallization, this is outside of the practical temperature range (≤300 °C) for sensor and device fabrication. This dilemma has led to the development of alternative techniques [187] to improve B2 ordering at lower annealing temperature. However, there is still strong interest in identifying robust half-metals that can be easily fabricated at standard processing temperatures.
Two-dimensional (2D) materials offer an alternative route to circumvent this challenge. 2D materials generally lack dangling bonds at their surfaces and interact with substrates and other 2D materials via weak van der Waals (vdW)-type dispersion forces. This minimizes the effect of interfaces on their electronic structure [188] and makes them uniquely suited for vertical heterostructures with materials of incommensurate in-plane lattice constants [189]. It was recently discovered that applied electric fields [190] and edge modifications [191–194] can create half-metallic currents in graphene nanoribbons, which could make them candidate materials for this kind of application. However, removing the need for electric fields during device operation is a major objective of spintronics, and edge modifications add challenges to the synthesis process. Consequently, 2D materials with intrinsic half-metallicity remain an important frontier for discovery.

In this letter, we systematically search the more than 600 2D materials of the MaterialsWeb online database [131] to identify and characterize 2D materials possessing half-metallic band structures. The MaterialsWeb database contains the atomic structure, electronic band structure, band gaps, and Pourbaix diagrams calculated with density-functional theory (DFT) of each of its materials. Most of the 2D materials in this repository are monolayers that are exfoliated from corresponding vdW-layered bulk precursors in the Materials Project Database [133], so they should exhibit sufficiently weak interlayer interactions to be stable as isolated layers or on substrates. We predict that the family of FeX$_2$ compounds with X = Cl, Br, I are 2D half-metals with high magnetic moments of 4 $\mu_B$ and large spin gaps of $>4$ eV. These exceptionally large gaps promise to be useful for spintronic devices that are sensitive to spin leakage.

Methods

The DFT calculations are performed using the projector-augmented wave method [49, 195] as implemented in the Vienna \textit{ab-initio} Simulation Package (VASP) [196]. The 2D structures in the MaterialsWeb database were geometrically optimized with the vdW-corrected optB88 exchange-correlation functional [106, 122, 146, 147] and no further
geometric optimization has been performed in this work. We first calculate the electronic and magnetic structures of all materials in this work using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional \[51\] followed by calculations with the more accurate but computationally demanding HSE06 hybrid functional \[197\]. To determine the magnetocrystalline anisotropy, we perform calculations including spin-orbit coupling.

**Searching for 2D Half-Metals**

The magnetic moment in any half-metallic material must be a non-zero integer. The search of the MaterialsWeb database results in 124 2D materials with non-zero integer magnetic moments. Among those we find that 30 2D materials exhibit half-metallic band structures as calculated with the PBE functional. Since only ferromagnetic (FM) ordering was considered in the MaterialsWeb database, we calculate the energy of the most likely antiferromagnetic (AFM) phase possible (either a striped or checkerboard pattern) and compare it with the FM energy to discern the most stable magnetic configuration for each material. We find that the AFM configuration is favored or nearly degenerate with the FM configuration for ten of the 30 materials: MnCo$_3$O$_8$, VBrO, UTe$_5$, HfFeCl$_6$, Co$_2$NiO$_6$, U$_3$, UIN, UTeN, TiBr$_3$ and VCIO. Naturally, these materials do not behave as half-metals in their AFM state.

The PBE functional is well suited for the rapid screening of materials because of its efficiency and accuracy for structural energies, but it systematically underestimating band gaps in materials. Therefore, we evaluate the electronic band structures of the remaining 20 materials with the HSE06 hybrid functional \[197\], which includes a percentage of exact exchange to improve the accuracy of the band structures. Interestingly, 17 of the 20 materials that are predicted to be half-metals at the PBE level become insulators with band gaps in both spin channels for the HSE06 functional. These 17 are Cr$_3$O$_8$, EuBrO, ScCl, TiCl$_3$, NpIO, CrP$_2$S$_7$, UTe$_3$, CeBrO, CoO$_2$, MnCo$_2$O$_6$, NpI$_3$, CrS$_2$, RuCl$_3$, VCl$_3$, U$_2$Te$_5$, VOF, and V$_2$H$_3$O$_5$. For the remaining three 2D materials, FeCl$_2$, FeBr$_2$ and FeI$_2$, the half-metallicity persists at the HSE06 level.
Figure 7-2. (Color online) Top and side views of the 2D iron dihalide structure shared by FeCl$_2$, FeBr$_2$ and FeI$_2$.

2D Structure

Figure 7-2 shows that the three 2D iron halides are isostructural to the 1$T$ structure common in many transition metal dichalcogenides [82]. In the 1$T$ structure of the iron dihalides, the Fe ions are located in the center plane of the 2D materials and bonded in an octahedral configuration to six neighboring halide ions, which form the top and bottom layer of the material. The exfoliation energies of FeCl$_2$, FeBr$_2$, and FeI$_2$ are 70, 75, and 83 meV/atom, comparable to graphene with an exfoliation energy of 66 meV/atom, indicating that these single-layer materials can be exfoliated from their bulk counterparts.

The in-plane lattice constants are 3.49 Å for FeCl$_2$, 3.70 Å for FeBr$_2$ and 3.98 Å for FeI$_2$. These are relatively large compared to the lattice constants of most metallic contact materials, which are often below 3 Å. Because these are vdW layers, this mismatch is not as likely to cause interfacial defects as it would be for a covalently bonded interface. However, it may still create certain interfacial states that could trap or otherwise alter the transport of spin-polarized currents through interfaces between these half/metals and conventional metal contacts.

Electronic Properties

Following our search for half/metals among 2D materials, we now discuss first their electronic and then their magnetic properties of importance for their application in spintronics devices. Figure 7-3 shows the electronic band structure of the half-metallic 2D materials with spin gaps ranging from 4.0 eV for FeI$_2$ to 6.4 eV for FeCl$_2$ at the HSE06
level. The PBE functional underestimates the spin gaps by 30-45% relative to HSE06, which is similar to the difference in the conventional band gaps for HSE06 and PBE of bulk compounds. As apparent in Figure 7-3, the spin gaps of FeCl\textsubscript{2} and FeBr\textsubscript{2} are direct and occur at \textit{\Gamma}, while the spin gap in FeI\textsubscript{2} is indirect from \textit{\Gamma} to \textit{M}. The 6.4 eV spin gap in FeCl\textsubscript{2} is the largest in any material identified so far.

By projecting the band structures from Figure 7-3 onto atomic orbitals, we determine that the two bands crossing the Fermi level have mostly Fe \textit{d}\textsubscript{xz} and \textit{d}\textsubscript{yz} character; the partially in-plane \textit{d}\textsubscript{z\textsuperscript{2}} and the in-plane \textit{d}\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}} and \textit{d}\textsubscript{xy} orbitals are higher in energy as they are further from the over- and underlying halogen anions. These two bands are plotted throughout the 2D Brillouin zone in Figure 7-4. From the plot, it is easy to see that higher energy band (shown in yellow) leads to a continuous Fermi surface in all directions of the 2D BZ zone. This band is also fairly parabolic so electronic transport due to this band should be isotropic in all directions. The second band (shown in blue) leads to additional Fermi surfaces that arc around the \textit{K} symmetry points and it is absent at the \textit{M} symmetry points. These Fermi surface pockets could lead to some asymmetry in the overall electrical conductivity.

The slopes of the bands crossing the Fermi level along high-symmetry paths in Figure 7-3 correspond to Fermi velocities between 1.2\(\times\)10\textsuperscript{5} and 3.4\(\times\)10\textsuperscript{5} m/s along these directions. These values are within an order of magnitude of the Fermi velocity in graphene [198–200], suggesting that electron transport in these materials will be relatively facile.

**Magnetic Properties**

Next, we investigate the magnetic properties of the 2D half metals. Bulk FeCl\textsubscript{2} and FeBr\textsubscript{2} are known to behave as Ising metamagnets [201–204], exhibiting both FM and AFM couplings. This unusual magnetic behavior is the result of a vertically stacked AFM configuration; there is an FM ordering of the Fe atoms within each layer, the direction of which alternates in alternating layers. This ordering, which is
observed experimentally \cite{201,205} and supported by our calculations for all three materials, suppresses any net spin polarization and is not half-metallic. Therefore, the half-metallicity identified in the 2D iron dihalides is apparently strictly contingent on their single-layer thicknesses.

All three 2D iron dihalides exhibit a magnetic moment of 4 $\mu_B$ per Fe atom. This indicates that the Fe atoms are in their high-spin octahedral $d^5$ state with four unpaired electrons per atom. This spin state is typical for Fe$^{2+}$, which agrees with the oxidation state found on each Fe atom in all three materials using Bader charge partitioning \cite{166}.

The character of the ferromagnetic ordering in 2D materials at low temperature is determined by the magnetocrystalline anisotropy energy (MAE) \cite{206–208}. The Mermin-Wagner theorem \cite{209} prohibits ferromagnetic order in 2D materials that have continuous spin symmetries. This means that 2D materials with an easy magnetization plane do not exhibit a ferromagnetic phase transition but instead a Berezinskii-Kosterlitz-Thouless (BKT) transition to a quasi-long range ordered low-temperature phase with a power-law decay of the correlation function \cite{206,207,210}. In contrast, magnetic 2D materials with an easy magnetization axis possess a ferromagnetically ordered low-temperature phase \cite{208}.

To determine the MAE of the 2D half-metals, we calculate how the direction of the spin of the Fe atom affects the energy with spin-orbit coupling interactions included. Fig. 7-5 illustrates the angular dependence of the MAE for FeCl$_2$. A similar strong dependence of the MAE on the out-of-plane angle of the magnetic moment is observed for the other two dihalides. Hence, all three 2D iron dihalides exhibit an easy magnetization plane, i.e. the rotation of the magnetic moment within the plane of the 2D layer requires no energy. While these 2D half metals do not demonstrate perpendicular magnetic anisotropy, a preferred in-plane magnetic orientation could be introduced through the use of shape anisotropy (e.g. nanoribbons) or the use of an anti-ferromagnetic pinning layer.
We proceed to estimate the critical temperature of the BKT transition. The combination of local magnetic moments and easy magnetization plane implies that the 2D iron dihalides belong to the category of $XY$ magnets. The critical temperature, $T_c$, of the BKT transition can be estimated by

$$T_c = \frac{0.89 \Delta E_{\text{mag}}}{k_B},$$

where $\Delta E_{\text{mag}}$ is the energy difference between the FM and AFM state and $k_B$ is the Boltzmann constant [207, 211]. We compute the energy difference, $\Delta E_{\text{mag}}$, between the AFM and FM configurations using the PBE functional to be 128, 95, and 163 meV per Fe atom for FeCl$_2$, FeBr$_2$, and FeI$_2$, respectively. This yields a critical temperature of 165, 210, and 122 K for the three half-metals, respectively.

**Spintronics Applications**

Two-dimensional half metals with large spin gaps can serve as the most desirable contacts for efficient spin injection and spin detection in a wide variety of spintronic devices. As shown in Figure 7-6, the half-metallic spin gaps of FeCl$_2$, FeBr$_2$, and FeI$_2$ cover the energy ranges of the conduction and valence bands of MoS$_2$ and phosphorene, which can be exploited to achieve efficient spin injection and detection into these intensively studied 2D semiconductor materials.

Recent realization of the valley Hall effect in MoS$_2$ transistors has relied on polarized lights to generate valley polarization [212]. Because the spin and valley polarizations are coupled in the bandstructure of common MX$_2$ materials [213], half metallic 2D materials can be used for electrical injections of spin and valley polarization favorable for all-electric control and high integration density.

Furthermore, the extremely long spin diffusion length in graphene [214], combined with 2D half metals, could be used to fulfill essential components in the “all-spin logic” device based on 2D materials [215, 216].
As shown in Figure 7-1, by vertically stacking the layered 2D materials with BN layers sandwiched between half metal contacts, magnetic tunnel junctions can be formed. The 100% spin polarizations of 2D FeCl$_2$, FeBr$_2$, and FeI$_2$ are advantageous for achieving large magnetoresistance. In addition, half metal materials are most desirable as the contacts in Datta-Das spintronic transistors, which can be formed by the half metal 2D material contacts with a graphene channel and a ferromagnetic dielectric gate insulator [217]. Alternatively, the use of an insulating layer with strong spin-orbit coupling will lead to a spin transistor with high transmittivity [218–220].

Future first-principles electronic transport studies will be required to determine the impact of interface resistance, tunneling through evanescence states, and Fermi level shifts due to interactions with the substrates and metallic leads in contact with these 2D half metals.

**Summary**

Through a systematic search of all layered bulk compounds, we identified a family of three half-metallic 2D materials, FeCl$_2$, FeBr$_2$, and FeI$_2$, and explored their electronic and magnetic properties for application in magnetoresistive spintronic devices. We anticipate modeling and experimental testing of the transport and switchability of spin valves and magnetic tunnel junctions based on these 2D materials to further investigate their technical viability.

Our results demonstrate that 2D FeCl$_2$ is of special interest for experimental investigations, as its predicted BKT transition temperature is estimated to be above 100 K and it has the largest spin gap of the three dihalides at 6.4 eV. All three 2D half metals are predicted to have Fermi level electron densities that compare well with typical metals, suggesting good on/off ratios in devices based on these materials.

The geometrically optimized structures of all materials discussed in this work can be found in the MaterialsWeb 2D materials repository at https://materialsweb.org.
Figure 7-3. (Color online) Spin-polarized band structures of the 2D materials (a) FeCl$_2$, (b) FeBr$_2$ and (c) FeI$_2$ obtained with the HSE06 functional. For each material, the majority spin bands are shown in blue and the minority in red. The relative size of each point indicates the elemental projection of the eigenvalue, with larger points being projected onto Fe and smaller points onto the halogen.
Figure 7-4. (Color online). The two bands crossing the Fermi level in FeCl$_2$ plotted throughout the 2D Brillouin zone. The fermi level is shown as a black line. A contour plot of the bands’ intersections with the fermi plane is provided on the right.

Figure 7-5. (Color online) Magnetocrystalline anisotropy in FeCl$_2$. The radial distance and color saturation of each point indicate the relative increase in energy required to rotate the magnetic axis through that point. Surfaces of the same shape are observed for FeBr$_2$ and FeI$_2$. 
Figure 7-6. (Color online) Locations of the spin gap edges and Fermi levels (white lines) for the free-standing half-metallic 2D materials relative to the vacuum level obtained with the HSE06 functional. The total spin gap of each material is labeled above the CBM edge. For reference, the band edge locations of well-known 2D insulator/semiconductors BN, MoS$_2$ and P (phosphorene), and the Fermi level of C (graphene) are also shown.
CHAPTER 8
CONCLUSIONS

The methods and tools for materials discovery and characterization presented here represent a step forward in the effort to understand the unique properties of 2D materials and their applications. This work has outlined standard computational procedures to guide and predict the outcome of experimental synthesis efforts of new 2D materials. These procedures include a method to predict the electrochemical conditions required to successfully acid etch a 3D precursor to form a 2D material, as well as a topology-scaling algorithm to identify bulk layered solids that can be mechanically exfoliated to form new 2D materials. In fact, it is expected that the topology-scaling algorithm will remain useful in the future for classifying materials in large databases according to the dimensionality of their bonded atomic networks.

Many of the new 2D materials predicted by the topology-scaling algorithm have been investigated in their own chapters here. For example, a relatively large family of group IV-V 2D materials with at least two degenerate crystal phases were identified as candidates for electronic heterojunctions with the two phases potentially enabling junctions with very good interface quality. Some of the Ge- and Sn-based materials from this family are stable or nearly stable in water, indicating they might be of use in photocatalytic junctions as well.

Another set of materials that merited special investigation were the iron-dihalides FeCl$_2$, FeBr$_2$ and FeI$_2$, which were predicted to possess half-metallic band structures. This makes them acutely interesting for use in spintronic devices, and provides fundamental insight into the complex magnetic structure observed for their corresponding bulk phases. According to the calculations performed here, layered stacks of these iron dihalides are expected to be half-metallic if and only if the number of layers is small and odd, as the magnetization directions in even-numbered stacks will compensate one another in an AFM ordering. We investigated the fermi level and band edge locations of these half-metals,
and predict that they can be useful components in a number of devices, including spin valves and magnetic tunnel junctions. A major reason these materials might be useful in spintronic devices is their vdW interlayer interactions, which make them adaptable to vertical stacks and substrates that do not exactly share their lattice parameters. Additional calculations of the transport properties across vertical stacks with these materials, similar to what would be in a spin valve, are currently in progress.

The impacts of this work are expected to last well into the future, with the primary contribution being the computational prediction of more than 600 new stable 2D materials from layered bulk precursors. A great deal of detailed future work investigating these 2D materials remains to be done and is in fact already underway. In addition, the software tools developed and used in each chapter are distributed as part of the MPInterfaces Python package, which is under the MIT free software license. MPInterfaces can be viewed and installed from https://github.com/henniggroup/MPInterfaces.

2D materials are already starting to find their way into several commercial markets, a process which can only be expected to accelerate with the ability to rapidly discover and predict their properties. The discovery and characterization of the many 2D materials presented here, as well as the designed recyclability of the tools presented to discover and characterize them, have advanced the overarching effort to map and understand the unique properties of 2D materials.
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BIOGRAPHICAL SKETCH

Michael Ashton was born in Florida’s space coast, where he spent the first seven years of his life before moving to Colorado with his parents, brother and sisters. The first chance he got, he moved back to Florida for college, where he enrolled in the materials science department. He fell in love with a girl toward the end of his bachelor’s degree, so he decided to stay in Gainesville to marry her and to complete the doctoral work you are looking at right now. He loves to play the guitar, especially when his wife will sing along with him. Jesus has been changing his life since 2006.