

Native Vacancy Defects in MXenes at Etching Conditions

Rina Ibragimova, Patrick Rinke, and Hannu-Pekka Komsa*



Cite This: *Chem. Mater.* 2022, 34, 2896–2906



Read Online

ACCESS |



Metrics & More

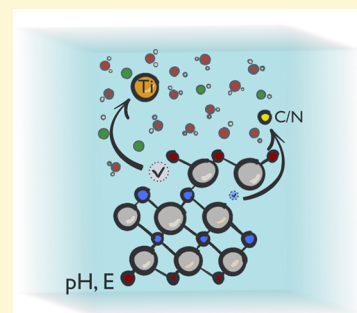


Article Recommendations



Supporting Information

ABSTRACT: Two-dimensional MXenes have recently received increased attention due to their facile synthesis process and extraordinary properties suitable for many different applications. During the wet etching synthesis of MXenes, native defects, such as metal and carbon or nitrogen vacancies, are produced, but the underlying defect formation processes are poorly understood. Here, we employ first-principles calculations to evaluate formation energies of Ti, C, and N vacancies in Ti_3C_2 and Ti_2N MXenes under etching conditions. We carefully account for the mixed functionalization of the surfaces as well as the chemical environment in the solution (pH and electrode potential). We observe that the formation energies of the metal vacancies differ significantly for different types of surface functionalization as well as for different local and global environments. We attribute these differences to electrostatic interactions between vacancies and the surrounding functional groups. We predict that Ti vacancies will be prevalent on bare or OH-functionalized surfaces but not on O-functionalized ones. In contrast, C and N vacancies are more prevalent in O-functionalized surfaces. In addition, our results suggest that the pH value of the etching solution and the electrode potential strongly affect vacancy formation. In particular, the predicted conditions at which abundant vacancy formation is expected are compared to experiments and found to coincide with conditions at which MXenes oxidize readily. This suggests that Ti vacancy formation is a crucial step in initiating the oxidation process.



INTRODUCTION

MXenes are a diverse class of two-dimensional (2D) materials with unique properties, such as extraordinary electromagnetic interference shielding properties, high catalyst activity, sensing properties, and optoelectronic properties, which have consequently made them highly attractive for various applications.^{1–9} The structure of 2D MXenes consists of transition metal (M) and either carbon or nitrogen (X) layers. They are typically synthesized by wet etching from the parent precursor phase (known as MAX phases) with hydrofluoric (HF) acid, during which the surface is passivated by an evenly distributed mixture of functional groups such as O, F, and OH. More recently, HF-free approaches have also been developed, based on, e.g., a combination of LiF and HCl (so-called MILD approach),¹ an electrochemical route,¹⁰ and the molten salt approach.^{11–13} Depending on the synthesis, the type and composition of functional groups can be different^{14–23} and affect the electronic properties of MXenes as well as their stability.

Like any other material, MXenes contain crystalline imperfections in their structure, both native defects and extrinsic defects. These could be inherited from the precursors (bulk MAX phases),²⁴ or they could be introduced during etching. XPS studies revealed, for example, that the bulk MAX phase could be responsible for up to 10% of the carbon vacancies found in MXenes.²⁵ Conversely, scanning transmission electron microscopy studies attribute Ti vacancies to etching.^{24,26–28} The concentration of the observed metal vacancies depends on the acid concentration and the synthesis

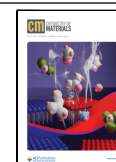
time.¹⁷ Regarding the location of defects, computational studies have shown that defects form more easily in the outer than in the inner layers.^{26,29,30} Defects in the outer layers are in contact with functional groups, who affect their properties. For instance, the formation energy of a metal vacancy in a fully O-functionalized surface is significantly higher (by about 4.5 eV) than that of a fully OH-functionalized surface.^{26,29} Given the size of this difference, it is timely to explain its origin and to study the effects of more realistic, mixed functionalizations.

Another problem pertaining to the previous computational studies is that the reported formation energies of metal and carbon/nitrogen vacancies vary widely.^{8,26,29–32} This variation is due to the different reference chemical potentials used in the formation energy calculations. For instance, in Ti-based MXenes, a common reference for the chemical potential is bulk Ti. Considering that MXenes are known to degrade to TiO_2 ,^{33–36} the reference could be TiO_2 instead, which reduces the Ti chemical potential by about 9 eV. One of these choices of the Ti chemical potential might be valid for certain conditions; however, it does not accurately represent strong acid-based etching conditions. Ti is not a noble metal and is

Received: September 14, 2021

Revised: March 10, 2022

Published: March 28, 2022



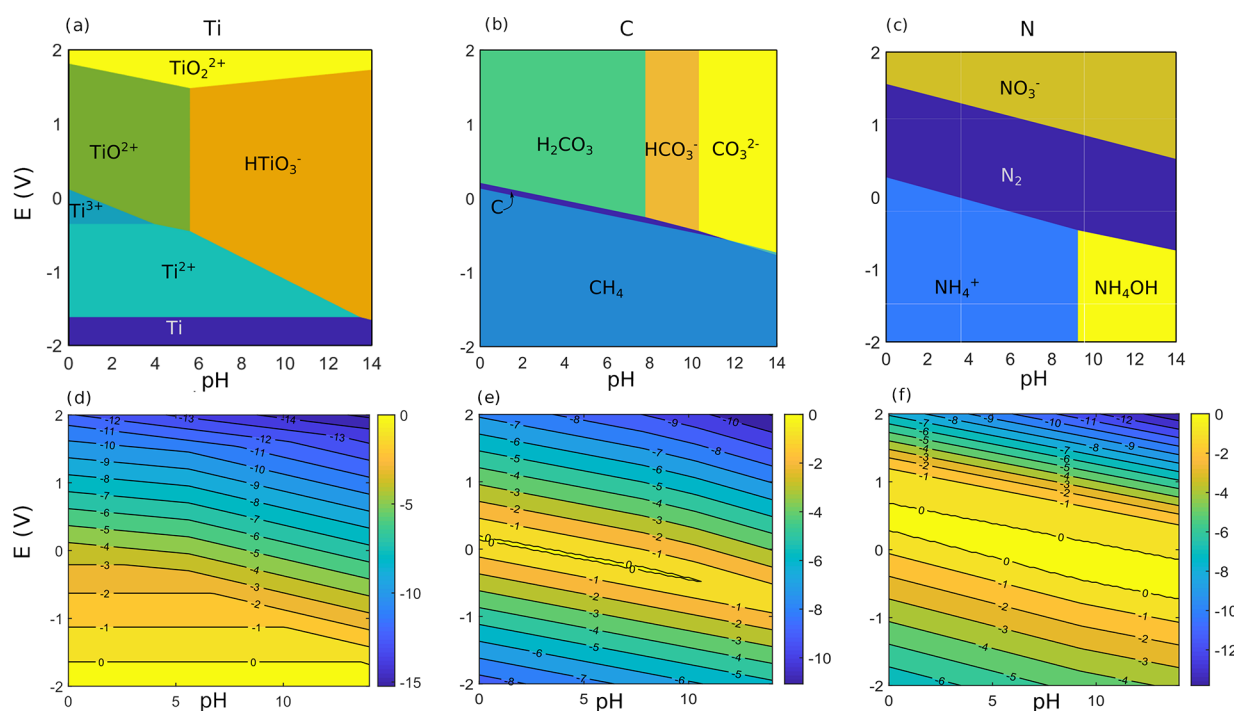


Figure 1. Pourbaix diagram of (a) Ti, (b) C, and (c) N in solution and the corresponding chemical potentials (d) $\Delta\mu_{\text{Ti}}$, (e) $\Delta\mu_{\text{C}}$, and (f) $\Delta\mu_{\text{N}}$ as a function of pH and electrode potential.

thus only stable for certain pH values, electrode potentials, and temperatures in electrochemical experiments. The most stable state of Ti, and correspondingly its chemical potential, depends on these external conditions, which therefore need to be accounted for in first-principles studies.

In this work, we explore the formation of native defects in Ti_3C_2 and Ti_2N MXenes for a range of experimental conditions and with particular focus on the etching conditions. We use the concepts of computational electrochemistry^{37–41} to properly set the chemical potentials in the formation energy calculations of Ti, C, and N vacancies in Ti_3C_2 and Ti_2N . We also investigate the role of functionalization by utilizing our previously constructed models for mixed surface functionalization.^{22,23} Studying the formation energy dependence on the pH and the electrode potential allows us to identify stability regions and, more importantly, find regions where Ti_3C_2 and Ti_2N would decompose as a result of excessive vacancy formation.

METHODOLOGY

To assess equilibrium defect concentrations in a grand canonical ensemble requires evaluating the defect Gibbs free energy of formation. However, since the vibrational contributions in the defective and pristine systems are similar (and small due to the low temperatures during etching), these contributions cancel each other to a good approximation, and it is sufficient to only consider the defect formation energy. For vacancies, the formation energy is given by

$$E_f = E_{\text{def}} - (E_{\text{ideal}} - \mu_i) \quad (1)$$

where E_{def} and E_{ideal} are the total energies of the defective and nondefective system, respectively, and μ_i is the chemical potential of the removed atom ($i = \text{Ti}$ or C/N). The latter is calculated from the Gibbs free energy of formation of the corresponding reservoir. The chemical potential can also be

expressed as $\mu_i = \mu_i^0 + \Delta\mu_i$, where μ_i^0 is the chemical potential of the reference phase (bulk Ti, graphite, and N_2 for Ti, C, and N, respectively).

To include the electrode potential and pH of the solution in the chemical potentials, we used the approaches developed in the theoretical electrochemistry community, combining the grand canonical approach with Pourbaix diagrams, used to study, e.g., the surface structure of metals and defect formation in metal oxides in aqueous solution.^{22,37–42} First, assuming an equilibrium of H and O with water at a given pH and electrode potential, the chemical potential of O is defined as

$$\Delta\mu_{\text{O}} = \Delta_f G_{\text{H}_2\text{O}}^0 - 2\Delta\mu_{\text{H}} \quad (2)$$

where $\Delta_f G_{\text{H}_2\text{O}}^0$ is the Gibbs free energy of formation of liquid water. The chemical potential of H can be expressed as

$$\Delta\mu_{\text{H}} = -E - k_{\text{B}}T \ln 10 \cdot \text{pH} \quad (3)$$

where E is the electrode potential with respect to the standard hydrogen electrode (SHE). The electrode potential can be mapped to the electron chemical potential (w.r.t. vacuum level) μ_e via $E = (\mu_e^{\text{SHE}} - \mu_e)/e$, where $\mu_e^{\text{SHE}} = -4.73$ eV is the theoretical SHE.³⁹ During etching, as there is no electrochemical cell, the chemical potential is not fixed, and it can fluctuate depending on the surface functionalization and defect formation. The exact details are not known, but based on measured work functions and our previous investigations,^{22,43–48} we assume μ_e remains fairly close to μ_e^{SHE} . Nevertheless, in this context, it is more appropriate to denote E as the open-circuit potential rather than electrode potential. In the context of electrochemical cells, the electrode potential can be used to extract the chemical potential from Pourbaix diagrams (cf. below), but it is worth noting that the charging of the MXene sheets and its influence on vacancy formation energies is not included in our calculations.

Second, we constructed the Pourbaix diagrams, taking into consideration the most stable phases of Ti, C, and N and ions in the solution as a function of pH and electrode potential E . All relevant data is taken from the original work of M. Pourbaix.⁴¹ To identify the stable phases of Ti, C, and N, we calculated the Gibbs free energy of formation for all phases and track which phase yields the lowest formation energy at a given pH and E . For example, for dissolved TiO^{2+} , the Gibbs free energy of formation is

$$\Delta_f G_{\text{TiO}^{2+}} = \Delta_f G_{\text{TiO}_2}^0 - \Delta\mu_{\text{Ti}} - \Delta\mu_{\text{O}} - 2E \quad (4)$$

where $\Delta_f G$ is the Gibbs free energy of formation and $\Delta_f G^0$ is the tabulated standard value given with respect to reference phases of Ti and O, at SHE conditions ($\text{pH} = 0$, $E = 0$ V), molar concentration of dissolved species equal to 10^{-6} , room temperature, and atmospheric pressure. E corresponds to the electrode potential. To find the chemical potential of Ti, μ_{Ti} , we assume equilibrium with the considered phase, thus, $\Delta_f G_{\text{TiO}^{2+}} = 0$, which yields

$$\Delta\mu_{\text{Ti}} = \Delta_f G_{\text{TiO}_2}^0 - \Delta\mu_{\text{O}} - 2E \quad (5)$$

$\Delta_f G^0$ is known from the tabulated standard value data, and $\Delta\mu_{\text{O}}$ is found using eqs 2 and 3.

Figure 1a shows the Pourbaix diagram for Ti considering only dissolved forms of Ti as reservoirs for Ti vacancies: Ti, Ti^{2+} , Ti^{3+} , TiO^{2+} , HTiO_3^- , and TiO^{2+} .⁴¹ We also reproduced Pourbaix diagrams for solid and gaseous forms of Ti in Figure S1 of the Supporting Information (SI). The corresponding Ti chemical potential ($\Delta\mu_{\text{Ti}}$) can be derived from equations similar to eq 5 knowing the stable phases and are shown in Figure 1d. Note that when the chemical potential $\Delta\mu_{\text{Ti}} = 0$, the reference phase is the most stable one.

From the Pourbaix diagrams, we extract the formation energies for the experimentally relevant ranges of chemical potentials. For instance, previous defect studies used the bulk Ti chemical potential.^{29,49} According to our Pourbaix diagram in Figure 1a, solid Ti is only stable for high negative electrode potentials $E < -1.6$ V. However, more realistic conditions would correspond to the water stability region (between $E = 0$ V and $E = 1.228$ V at $\text{pH} = 0$), which is clearly above the stability region of bulk Ti. Another common reservoir choice is TiO_2 . The Gibbs free energy of formation of TiO_2 is -9.2 eV,⁴¹ and the same value is obtained for the chemical potential of Ti when O is in the reference phase (O_2). In Figure 1d, corresponding values can be found right at the edge of the water stability region. Overall, the chemical potentials are seen to vary dramatically depending on the adopted choice of Ti reservoir.

In our opinion, realistic chemical potential choices for electrochemical solutions should include stable titanium ions in the water stability region, i.e., dissolved Ti^{3+} , TiO^{2+} , and HTiO_3^- . This would imply significantly different chemical potentials than used in previous publications.

Next, we establish the chemical potential choice for carbon and nitrogen vacancies. A common choice for the carbon chemical potential is graphite, the most stable solid phase of C.³⁰ However, in the Pourbaix diagram (Figure 1b, with the corresponding chemical potentials in Figure 1e), graphite is only stable in a narrow region near $E = 0$ V. Calculations using the graphite reference therefore exclude a large part of the water stability region. More realistic would be to consider a few more stable phases of carbon, which are located above the solid

graphite stability region. Then, carbon dissolves to CO_2 , CO_3^{2-} , and HCO_3^- depending on the pH value, and below it to CH_4 .⁴¹ It is worth noting that CH_4 formation upon Ti_3C_2 oxidation was reported in ref 50.

The Pourbaix diagram of nitrogen is shown in Figure 1c (and the corresponding chemical potentials in Figure 1f), according to which N can dissolve to NH_4^+ , NO_3^- , or NH_4OH . However, since N_2 is fairly stable in water, the corresponding chemical potential sufficiently describes the etching conditions.

The etching is commonly performed at fluorine solutions, but in our approach the effect of fluorine is included only via pH. However, it is also important to consider if titanium fluoride phases might affect Ti chemical potential. We could not find experimental data for solvated TiF_x species, but those for the gaseous phase are available from NIST-JANAF thermochemical tables.⁵¹ The two-component (Ti + F) Pourbaix diagram is a straightforward overlap of the Ti and F diagrams (Figure S2), i.e., that shown in Figure 1a, and HF stable when $\text{pH} > 3.18$ and F^- stable when $\text{pH} < 3.18$. $\text{TiF}(\text{g})$ or $\text{TiFO}(\text{g})$ are not stable. Adding TiF_2O , TiF_2 , TiF_3 , and TiF_4 phases to this diagram is not straightforward due to the difference in the stoichiometries. Since we are mainly interested in the Ti chemical potential, we constructed a Pourbaix-like stability diagram, where we find the phase with the lowest chemical potential of Ti such that the chemical potentials from TiF_x phases are obtained by assuming equilibrium with the stable F phase. That is, e.g., for the TiF_4 phase, $\Delta\mu_{\text{Ti}} = \Delta_f G_{\text{TiF}_4}^0 - 4\Delta\mu_{\text{F}}$, and $\Delta\mu_{\text{F}}$ is taken from the lowest energy phase at that pH and E . Such a stability diagram is shown in Figure 2a, and Figure 2b shows the

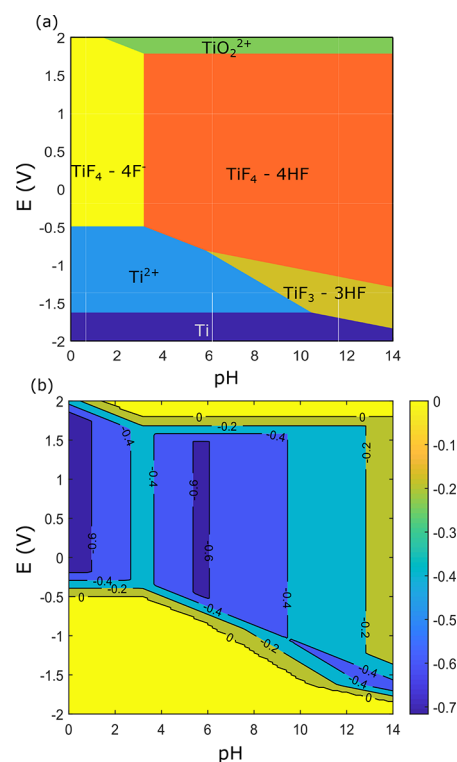


Figure 2. (a) Stability diagram of Ti including metal fluoride phases and (b) the chemical potential difference to Figure 1d as a function of pH and electrode potential.

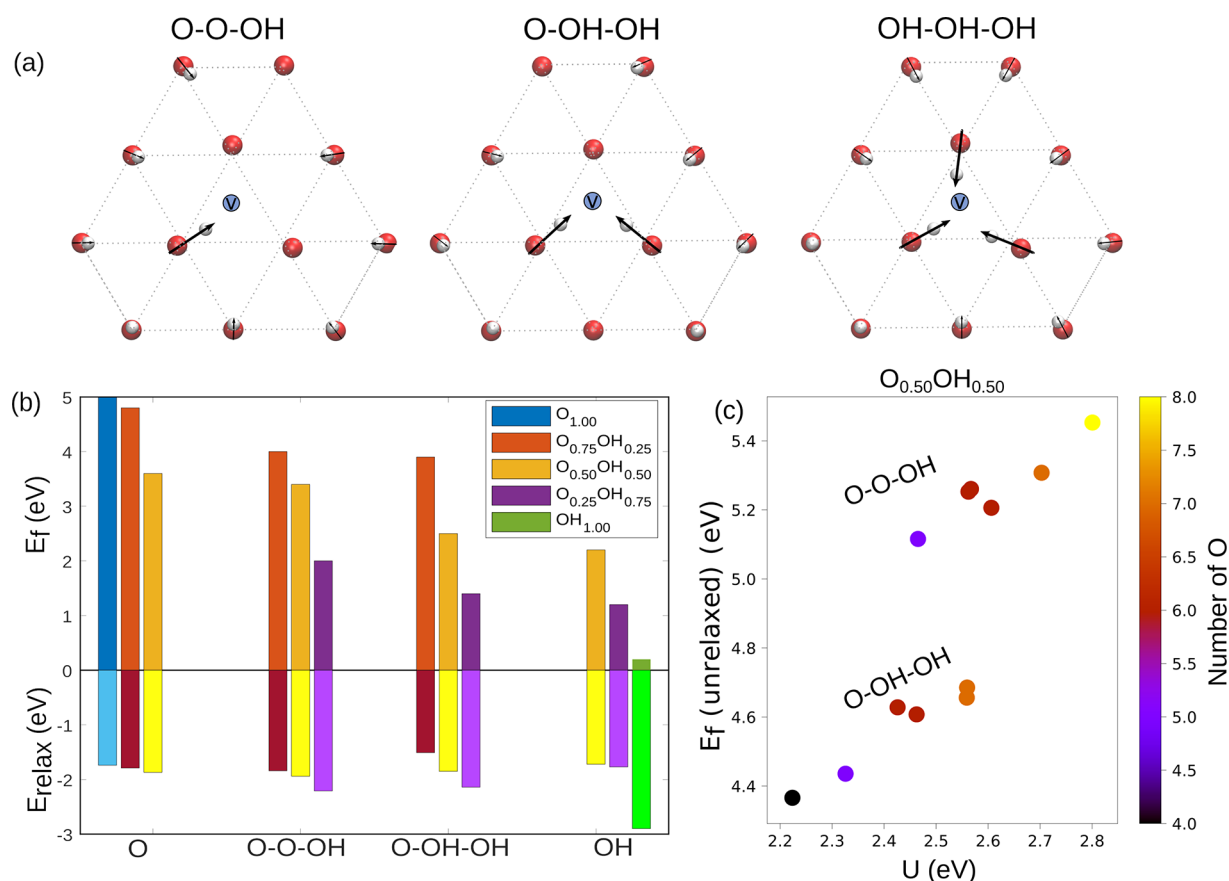


Figure 3. (a) Surface of Ti₃C₂ with different local surroundings of vacancy: O–O–OH, O–OH–OH, and OH–OH–OH. O atoms are denoted as red balls, H atoms are denoted as white balls, and the vacancy site is denoted as a blue circle. The black arrows highlight the direction of OH group tilting. (b) Formation energies and corresponding relaxation energies of the Ti vacancy in Ti₃C₂ for different surface compositions and with different numbers of O and OH groups in the nearest-neighbor sites and (c) formation energy of the Ti vacancy in unrelaxed Ti₃C₂(O_{0.5}OH_{0.5})₂ vs the corresponding electrostatic potential energy, where the number of O atoms in the surroundings up to the third-nearest neighbors is shown via a color code. The data is grouped according to the first-nearest neighbor surrounding of the Ti vacancy: O–O–OH and O–OH–OH.

chemical potential difference to the F-free Pourbaix diagram shown in Figure 1a. Only TiF₄ and TiF₃ are found stable. The area covered by the TiF₄ phase is relatively large, but the chemical potential difference is less than 0.6 eV. Since the energies of solvated TiF species are unknown, it is not clear if there is enough F to form TiF₄, and the energy difference is relatively minor, in the following, we use the Ti chemical potential shown in Figure 1d. If metal fluoride phases are known to be important, the resulting formation energy difference can be extracted from Figure 2b.

All the calculations were performed using the Vienna ab initio simulation package (VASP)⁵² together with the projector augmented plane wave method (PAW).⁵³ We used the Perdew–Burke–Ernzerhof for solids (PBEsol) exchange–correlation functional⁵⁴ throughout, which was selected based on benchmarking of enthalpies of formation in our previous publication.²² The converged plane-wave cutoff energy was found to be 550 eV according to the tests. For the calculation of vacancy formation energies, we utilized the structures with mixed O, F, and OH functional group distributions found in our previous work.^{22,23} The distributions were obtained using a computational multiscale scheme, where energies for different configurations of functional groups were approximated using a cluster expansion approach and then sampled via Monte Carlo simulations. The 4 × 4 supercells minimizing the free energy were then used in modeling the

defective systems. Vacancy formation energy convergence with increasing supercell size (4 × 4, 5 × 5, and 6 × 6), shown in Figure S3, assures us that the 4 × 4 supercell size is sufficient. The adopted k-point sampling was 4 × 4 × 1. In order to include implicit solvent contributions, the final energies of relaxed structures were calculated using VASPsol.^{55,56} The differences between formation energies with implicit solvent and without are listed in Table S1.

RESULTS

Formation Energy Dependence on Surface Functionalization. As alluded to in the introduction, previous studies observed a significant dependence of defect formation energies on the surface termination of MXenes.^{8,26,32} To investigate the effect of mixed functionalizations, we calculated Ti vacancy formation energies for different compositions of O and OH on the surface of Ti₃C₂: O_{1.0}, O_{0.75}OH_{0.25}, O_{0.5}OH_{0.5}, O_{0.25}OH_{0.75}, and OH_{1.0}. The results are shown in Figure 3.

For surfaces with mixed O–OH compositions, the Ti vacancy can be surrounded by different numbers of O and OH groups in the nearest-neighbor sites. We observed that the OH functional groups are always tilted in the vicinity of the Ti vacancy. The orientation of the tilting depends on the distribution of O and OH in the first and second nearest neighbor sites. Examples of several different O–OH surroundings are shown in Figure 3a, while a more complete

illustration of all different surroundings and corresponding OH tilting angles can be found in the SI (Figure S4). Besides tilting, the atomic structure is perturbed fairly little by the Ti vacancy.

The vacancy formation energies are shown in Figure 3b. They gradually decrease with increasing OH content. Moreover, the local surroundings of the defect affect the formation energy. For instance, the vacancy formation energy in $\text{Ti}_3\text{C}_2(\text{O}_{0.5}\text{OH}_{0.5})_2$ is largest for an O–O–O surrounding and decreases with increasing OH content. We deduce, thus far, that the vacancy formation energy depends on (i) the global and (ii) local composition of the surface functional groups.

The degree of structural relaxation around Ti vacancies is quantified Figure 3b. It depends mainly on the amount of OH in the nearest-neighbor sites. The relaxation energy for a Ti vacancy in an O-terminated structure is 1.7 eV, whereas it increases to 2.9 eV in OH-terminated structures. However, the relaxation energy is not the dominating factor in the formation energy variance. For instance, the relaxation energies for the $\text{O}_{0.5}\text{OH}_{0.5}$ surfaces are very similar, regardless of the local O–OH structure, while the formation energy changes by about 1.4 eV. At larger OH concentrations around the vacancy, the OH tilting becomes more pronounced, and the second and third nearest OH groups tilt as well. The tilting leads to the larger relaxation energy and contributes markedly to the low formation energy in purely OH-functionalized surfaces.

Since relaxation is not the dominating factor in the formation energy changes, we hypothesize that the energy difference primarily arises from electrostatic interactions between the functional groups and the defect. Furthermore, tilted OH functional groups toward the Ti vacancy might indicate that the vacancy is charged. We therefore build an electrostatic model where the charges in functional groups and in the defect are replaced by point charges. The electrostatic potential energy stored in a system of point charges is simply given by

$$U_e = \frac{1}{4\pi\epsilon_0} q_i \sum_j \frac{q_j}{r_{ij}} \quad (6)$$

where ϵ_0 is permittivity of vacuum, q_i is the charge of the Ti vacancy, q_j are the point charges of functional group sites j , and r_{ij} is the distance between q_i and q_j .

To decouple the effects of relaxation and electrostatic interaction, we use the atomic distances of the unrelaxed systems and compare them to the formation energies of the unrelaxed systems. We include interactions up to the third nearest neighbor around the vacancy site in the sums in eq 6. We set the charge of the vacancy to -1 , of O to -2 , and of OH groups to -1 . We also tested different values of vacancy charge from -0.5 to -2 , as shown in Figure S6, and find that the electrostatic potential energy increases linearly with the increasing charge. The electrostatic potential energy was calculated for the binary composition of $\text{O}_{0.5}\text{OH}_{0.5}$, where the vacancy was placed on different surface sites with different local O–OH surroundings. Screening of the MXene is approximately included in our model by dividing the electrostatic energy by 30, which yields qualitatively similar energy differences for U and E_f .

To understand the dependence of the formation energy on the local O–OH surroundings of the vacancy, the formation energies and the corresponding electrostatic potential are

compared in Figure 3c. The electrostatic potential for the vacancy in the same global composition of $\text{O}_{0.5}\text{OH}_{0.5}$ clearly depends on the O–OH content in the surroundings. The sets of points with higher and lower formation energies correspond to O–O–OH and O–OH–OH surroundings in the nearest neighbor shell around the vacancy, while the color coding denotes the number of O atoms in the surroundings up to third-nearest neighbors. Within the O–O–OH and O–OH–OH groups, the formation energies of the Ti vacancy linearly depend on the value of the electrostatic potential. Since the electrostatic interaction between the vacancy and O is stronger than the interaction between the vacancy and OH, the contribution from oxygen is much more pronounced. Therefore, the higher the content of O around the vacancy, the higher the electrostatic potential and thus the formation energy. The difference between the two linear correlations in Figure 3c can be explained by the shell effect. Since the electrostatic energy is inversely proportional to the distance between the vacancy and the O charge, lower formation or electrostatic energies correspond to O in the second nearest neighbor shell and higher energies to O in the first nearest neighbor shell. Both global and local effects of the functionalization therefore play a role.

Formation of Vacancies during Etching. *Formation of Ti Vacancies.* Using the Pourbaix diagrams constructed earlier, we now calculate the defect formation energies as a function of solution pH and the electrode potential with respect to the standard hydrogen electrode (SHE). We focus on the defects induced by the synthesis conditions and thus only consider vacancies in the outer layers of Ti_3C_2 and Ti_2N . These materials were selected to represent materials that are easy and difficult, respectively, to synthesize with the common fluorine-etching method.

Since the formation energies significantly depend on the functionalization type and its composition, we show results for four different types of surface functionalization: bare non-functionalized surfaces relevant at the very early stages of etching and fully O- and OH-terminated surfaces to yield the formation energy limits, as well as mixed surface functionalization at typical surface compositions relevant at later stages of etching. For Ti_3C_2 we use the mixed $\text{O}_{0.5}\text{OH}_{0.5}$ composition and for Ti_2N the mixed $\text{O}_{0.75}\text{OH}_{0.25}$ composition, which we found to be the most stable compositions in our earlier studies.^{22,23} Moreover, according to these studies, upon changing the pH or the potential, the surface composition of both materials will vary between those values and the fully O-terminated surfaces, thus providing practical limits. Alternatively, if the composition is known from the experiments, it is straightforward to interpolate the formation energy values from these limits. The location of a vacancy on the surface with mixed functionalization was chosen so that the vacancy formation energy is the lowest. In Ti_3C_2 , the vacancy is surrounded by three OH, whereas in Ti_2N , the vacancy is surrounded by two O and one OH. Since the synthesis mainly occurs near room temperature and the formation energies tend to vary over several electronvolts, the vacancy concentrations calculated from $c \sim \exp(-E_f/kT)$ tend to be very small for positive E_f and very large for negative E_f . Consequently, we mostly focus on the $E_f = 0$ line, which then indicates whether defect formation is energetically favored or not. We also note that, due to the low temperature during etching, defects can form very slowly in the case of small, or even negative, formation energies.

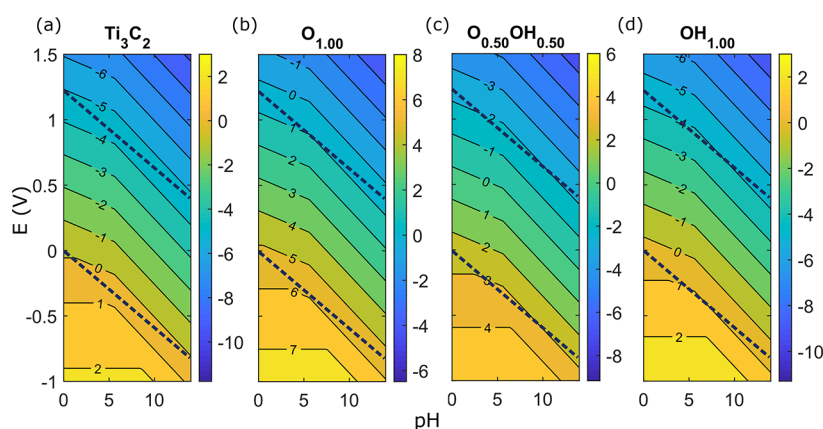


Figure 4. Formation energy of the Ti vacancy as a function of pH and electrode potential for (a) the Ti_3C_2 bare surface, (b) $\text{Ti}_3\text{C}_2(\text{O}_{1.00})_2$, (c) $\text{Ti}_3\text{C}_2(\text{O}_{0.5}\text{OH}_{0.5})_2$, and (d) $\text{Ti}_3\text{C}_2(\text{OH}_{1.00})_2$. The dashed lines represent the water stability region.

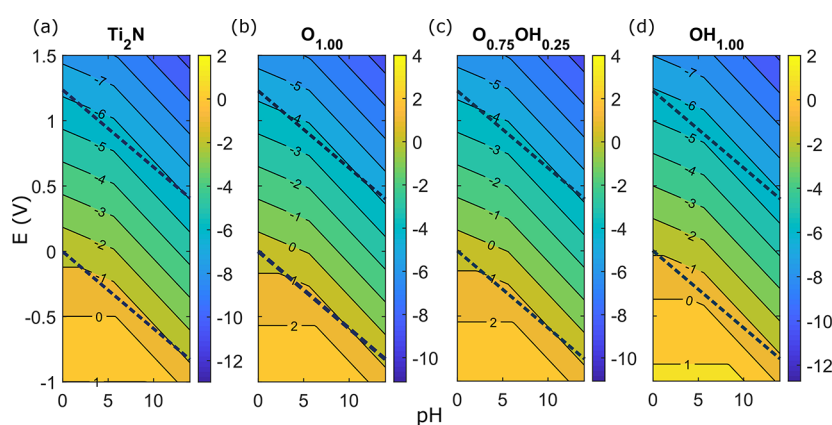


Figure 5. Formation energy of the Ti vacancy as a function of pH and electrode potential for (a) the Ti_2N bare surface, (b) $\text{Ti}_2\text{N}(\text{O}_{1.00})_2$, (c) $\text{Ti}_2\text{N}(\text{O}_{0.75}\text{OH}_{0.25})_2$, and (d) $\text{Ti}_2\text{N}(\text{OH}_{1.00})_2$. The dashed lines represent the water stability region.

The formation energies of Ti vacancies on the surface of Ti_3C_2 are presented in Figure 4 as a function of pH and the electrode potential. The area between the dashed lines highlights the water stability region. At SHE conditions ($\text{pH} = 0$, $E = 0$ V), Ti vacancy formation energies in Ti_3C_2 vary significantly with surface termination. The bare surface possesses the lowest formation energy, where the Ti vacancy formation energy is about 0 eV at the SHE. Moreover, the formation energies for bare Ti_3C_2 are mostly negative in the water stability region, suggesting a spontaneous formation of vacancies at large quantities, and possible material decomposition, under these conditions. In fact, the decomposition of MXene might be anticipated, since Ti metal is not stable at the acidic conditions and dissolves to ions and hydrated oxides (Figure 1b). However, we assume that in aqueous solution the bare surface will be quickly covered by functional groups. These protect the surface from decomposition, which can be seen from the formation energy increase in the presence of functional groups. The pure O-terminated surface has the highest formation energy, which is 5 eV at SHE conditions, and the formation energy gradually decreases to 1 eV with increasing electrode potential or with increasing pH. The $\text{O}_{0.5}\text{OH}_{0.5}$ functionalized surface has a formation energy of 2.5 eV at $E = 0$ V (and $\text{pH} = 0$), but becomes negative (−2 eV) at the top of the water stability region. Finally, the formation energy in the OH-functionalized surface is relatively low (about 0.5 eV) at SHE and decreases with increasing electrode

potential (becomes negative above SHE conditions). The negative formation energies within water stability region suggest decomposition of the material.

Furthermore, formation energies for all systems at a constant electrode potential decrease with increasing pH. The decrement is quite small until $\text{pH} = 7$, and then formation energies decrease much faster at $\text{pH} > 7$. Therefore, in the alkaline solution starting from $\text{pH} = 7$, formation of vacancies is more favorable. For instance, at $E = 0$ V and $\text{pH} = 14$, the formation energy of vacancy in Ti_3C_2 with mixed surface functionalization becomes negative. On the other hand, the surfaces with higher O concentration are still stable. This is an important observation, since the 2D sheets are washed in water after etching and commonly stored in a solution.⁵⁷ However, we find that this step might also involve formation of vacancies. Moreover, since washing decreases the Ti concentration in solution, this in turn can lead to a lower Ti chemical potential and lower vacancy formation energy.

A few earlier computational studies have found that the formation energies of Ti vacancies are higher for fully O-terminated surfaces, whereas OH-terminated surfaces possess much lower formation energy.^{8,26,30,32,49} Our results are qualitatively in agreement with these. However, in order to quantitatively compare our results to the previously reported formation energies, we should compare these with the same reference chemical potential. As seen in Figure 1, solid Ti is stable at $E < -1.6$ V. The formation energy of the Ti vacancy

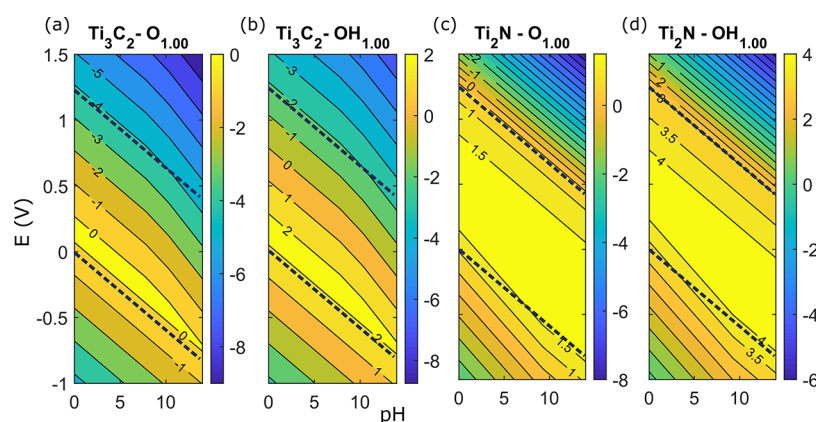


Figure 6. Formation energy of the C and N vacancies for Ti_3C_2 and Ti_2N as a function of pH and electrode potential: (a) $\text{Ti}_3\text{C}_2(\text{O}_{1.00})_2$, (b) $\text{Ti}_3\text{C}_2(\text{OH}_{1.00})_2$, (c) $\text{Ti}_2\text{N}(\text{O}_{1.00})_2$, and (d) $\text{Ti}_2\text{N}(\text{OH}_{1.00})_2$. The dashed lines represent the water stability region.

with respect to solid Ti for the fully O-terminated surface is 8.7, which is in agreement with the value of 8.6 eV reported in ref 49 and higher than the value of 7.7 eV reported in ref 26. Meanwhile, the formation energy of the Ti vacancy for the fully OH-terminated surface is about 3.9 eV, which is in a good agreement with the value of 3.5 eV reported in ref 26 and formation energy of 3.4 eV from ref 49.

The formation energies of the Ti vacancy on the surface of Ti_2N as a function of pH and electrode potential are shown in Figure 5. A bare surface possesses the formation energy of about -1.5 eV at the SHE, and it decreases to -6 eV in the top of the water stability region. Highly negative vacancy formation energies suggest that the material eventually dissolves in the acid. With the presence of O functionalization, the formation energy at the SHE becomes equal to 0.8 eV. However, formation energies become negative with increasing electrode potential to $E = 0.2$ V. In contrast to the case of carbides, Ti_2N with a mixed surface functionalization has a similar vacancy formation energy as the fully O-functionalized surface, due to a high content of O in the $\text{O}_{0.75}\text{OH}_{0.25}$ composition. The formation energy is about 1 eV at the SHE and gradually decreases with increasing electrode potential or pH. Ti vacancy formation energies for the OH-terminated surface are negative throughout the water stability region. The predominance of negative vacancy formation energies for a wide range of conditions suggests that Ti_2N is largely unstable toward Ti vacancy formation.

The formation energies for pure F and mixed $\text{O}_{0.50}\text{F}_{0.50}$ surfaces are given in Figures S7 and S8. The results are similar to those of OH-terminated surfaces, as one might assume due to the same oxidation state of -1 . The values of formation energies are systematically higher by about 0.3 eV in the case of F surface functionalization as compared to OH functionalization. Therefore, F-rich surfaces are also expected to contain more vacancies than O-rich surfaces, and their formation could be further accelerated by the lower Ti formation energy in TiF_x phases (cf. Methodology).

Formation of X Vacancies. We also calculated the formation energies of X vacancies in Ti_3C_2 and Ti_2N . Figure 6a,b shows the formation energies for C vacancies in Ti_3C_2 as a function of pH and electrode potential. Here, we present results only for the pure functionalization $\text{O}_{1.00}$ and $\text{OH}_{1.00}$, assuming that the energies for mixed systems would lie between these limits. Since X atoms are not in direct contact with the functional groups, the vacancy formation energies are

less sensitive to the local distribution of functional groups around the vacancy than in the case of the Ti vacancy. They can, however, be affected by the global functional group composition via changes in the Fermi level position. Indeed, the C vacancy formation energies vary significantly with surface functionalization but clearly less than with Ti vacancies. Moreover, opposite of the Ti case, the formation energies of carbon vacancies are lower for the pure O-terminated system and higher for the OH-terminated system. As discussed earlier, solid carbon (graphite) is relatively stable in solution with a stability window between electrode potential values of -0.5 and 0.2 V. For fully O-functionalized Ti_3C_2 , the carbon vacancy formation energy is 0.2 eV in this window, whereas above and below this window the formation energies become negative. Conversely, for OH-functionalized Ti_3C_2 the formation energy is equal to 2.2 eV in the carbon stability window and decreases above and below the carbon stability window, eventually becoming negative. A comparison to the previously reported formation energies can be carried out for values in the carbon stability region since the reference chemical potential is graphite. In the absence of data for Ti_3C_2 , we compare to the formation energies in Ti_2C from ref 30. The reported values are 0.6 eV for O-terminated Ti_2C and 2.8 eV for OH-terminated Ti_2C ,³⁰ in fairly good agreement with our results.

The formation energies for N vacancies in Ti_2N are shown in Figure 6c,d. For O-terminated Ti_2N , the formation energy at SHE conditions is 1.2 eV. Due to the high stability of N_2 in solution, this phase covers most of the water stability region. Above the window, the formation energies decrease; however, the values remain positive for the whole water stability region. Our results are comparable with earlier reported data using N_2 as the reference. The nitrogen vacancy formation energy of Ti_2NO_2 is 1.9 eV compared to 1.6 eV from ref 49 and 4.1 eV for $\text{Ti}_2\text{N}(\text{OH})_2$ compared to 3.8 eV from ref 49. Slightly different values of formation energies in our calculations compared to previously computed values are likely because of the use of different exchange-correlation functionals and additional implicit solvent correction in our calculations. As shown in Figure S9, the formation energies of F-terminated surfaces are again very similar to those of OH-terminated surfaces.

DISCUSSION

Defects in 2D MXenes have not been systematically studied concerning the influence of the chemical environment and the distribution of functional groups on the surface. It is generally assumed that the formation of defects and functionalization of the surface emerges simultaneously during etching. It is thus important to understand how formation energies depend on surface functionalization. A few earlier computational studies have found that the formation energies of Ti vacancies are higher for fully O-terminated surfaces, whereas OH-terminated surfaces possess much lower formation energies.^{8,26,30,32,49} Our findings not only agree with earlier studies but also extend these results to mixed surface functionalizations, which show strong dependence on the nearest neighbors surrounding the defect. We also showed that a simple electrostatic model can describe these formation energy trends and explain the large difference of ~ 5 eV in the formation energies of O and OH functionalized MXenes.

We further studied the formation of vacancies under synthesis conditions in Ti-based carbides and nitrides. Our results align with earlier experimental results, where the formation of Ti vacancies due to etching in HF aqueous solutions has been demonstrated.^{17,26} Since electroneutrality of the solution and the MXene sheets should be retained during etching, we presume that, upon dissolution of positively charged Ti ions, the negative charge of MXene sheets is compensated by adsorbed H^+ ions that turn O functional groups to OH groups. If MXene sheets cannot easily accommodate more H, H_2 formation would then be expected (taking two electrons from the MXene sheet and two H^+ from the solution). Since the formation energies are lower at higher pH, the sheets are not safe from degradation after etching. In ref 58, Ti_3C_2 and Ti_2C were found to oxidize much faster in basic solutions ($pH > 7$) than in acidic solutions. While the reactive molecular dynamics simulations in ref 58 showed that oxidation of edges becomes faster under basic conditions, our results suggest that also the basal planes become more susceptible to oxidation via vacancy formation. Note that the electroneutrality considerations can be opposite in basic solutions where dissolution of $HTiO_3^-$ would need to be compensated by desorption of H^+ from the MXene sheets.

The formation energies of Ti vacancies depend significantly on the value of the electrode potential. We observe that, at higher E values, the formation energies decrease and become negative, causing thermodynamic instability. In the following we compare our results to those from electrochemical experiments. Although this is not strictly valid since, e.g., the charging of the MXene sheets or electroneutrality of the solution are not included in our computational approach, we think this gives qualitatively correct trends and with it valuable insight. A few experiments with electrochemical setups support our results.^{34,59} In ref 34, partial oxidation started at $E > 0.8$ V and excessive oxidation to TiO_2 was observed at $E > 1$ V (0.1 and 0.3 V vs Hg/Hg_2SO_4 electrode) at low pH. In ref 59, oxidation started at $E > 0.4$ V, peaking at $E = 0.6$ V, at pH 7 (0.2–0.4 V vs $Ag/AgCl$ electrode), and leading to dissolution of the material. Our results for $Ti_3C_2(O_{0.5}OH_{0.5})_2$ and low pH predict that the formation of a large number of vacancies would start at $E > 0.6$ V at low pH and $E > 0.4$ V at pH 7, in a reasonably good agreement with experiments (and assuming that the vacancy formation initiates oxidation). In ref 34, it was also shown that a large amount of oxygen remains on the

surface.³⁴ Since the formation energy of the Ti vacancy varies strongly with the chemical surroundings, areas with a high OH content, or lack of any surface termination, would have more vacancies. Simultaneously, areas with oxygen termination would remain untouched, serving as a protective coating. We also stress that in these experiments Ti_3C_2 is stable at negative potentials. According to the calculations of Ashton et al.,⁶⁰ Ti_2CO_2 (and Ti_3C_2 presumably behaves similarly) would decompose into CH_4 and Ti^{2+}/Ti^{3+} at negative potentials and low pH. This seems to suggest that even when decomposition is energetically favored, it is the Ti vacancy formation that governs the oxidation in practice.

Although it has been shown experimentally that using a high concentration of HF leads to the formation of larger quantities of metal vacancies,^{24,26,28} such a dependence is not evident in our calculations. In our calculations, at constant electrode potential, formation energies are slightly higher at low pH values and lower for increasing pH. This effect is minor at low pH values and more pronounced at $pH > 7$. Higher concentrations of HF in solution lower the pH; however, in practice pH values vary slightly (~ 0 –1) with increasing HF concentration. Thus, most likely the disagreement has kinetic reasons. For instance, etching in stronger HF acid might lead to faster removal of Al from the MAX phase, which increases the number of bare sites and which finally results in a larger number of Ti vacancies.

Formation energies for Ti vacancies in Ti_2N are mostly negative in a wide range of conditions. It is interesting to note that Ti_2N has not been synthesized via HF etching due to partial decomposition of the precursors and formation of TiO_2 .^{61–63} Our negative formation energies suggest that MXene sheets decompose at these conditions, in agreement with the experimental results.

The formation energies of X vacancies also depend on the type of surface functionalization. However, the formation energies of carbon and nitrogen vacancies are lower in the presence of O functionalization and higher for OH functionalization—opposite to the trend seen with Ti vacancies. Therefore, mixed functionalizations are preferential for minimizing the overall defect concentration in these MXenes. Fortunately, this should often be the case due to the higher stability of the MXenes with mixed functionalizations.^{22,23} Moreover, the formation energies are clearly lower for Ti_3C_2 than for Ti_2N . In Ti_3C_2 , formation energies are negative at the top of the water stability region, indicating the formation of carbon vacancies in large quantities, whereas in Ti_2N , formation energies remain positive irrespective of the electrode potential and the type of the surface functionalization. Experimentally, X vacancies are believed to originate from the MAX precursors.^{24,25} However, no experimental data regarding formation of carbon or nitrogen vacancies during etching is available thus far. Naturally, formation of X vacancies should involve large kinetic barriers since X atoms reside inside the MXene sheet, thus reducing the rate of defect formation. Nevertheless, the low formation energy of C vacancies tentatively supports their presence in Ti_3C_2 .

Finally, we note that formation of any type of defect could lead to lowering of the formation energies of other defects in its vicinity, such as vacancies in the functional group sites or in the nearby M or X sites, and thereby defect clustering. However, this is out of scope of the present study, due to the vast number of configurational degrees of freedom.

CONCLUSIONS

We have systematically studied the formation of titanium and carbon/nitrogen vacancies in Ti_3C_2 and Ti_2N . We explored the formation energies of the vacancies in relation to the composition of functional groups and their local surroundings. Our results show that the type and composition of functional groups on the surface strongly affect the formation energies. Abundant formation of titanium vacancies is expected in bare surfaces and in systems with high OH content, while increasing O content tends to protect the surface. We observed that the vacancy formation energies depend on both the local and the global O and OH content around the vacancies. We attribute this behavior to the strong electrostatic interaction between the metal vacancy and the functional groups, which largely depends on the content and distribution of O in the system.

Furthermore, our computational scheme, which involves the selection of the chemical potential according to the Pourbaix diagrams, allowed us to construct formation energy diagrams with explicit dependence on the electrode potential and the pH. From these we could find the conditions under which a large number of vacancies can be expected to form. As the unstable conditions for Ti vacancy in Ti_3C_2 were found to match closely with the experimentally observed conditions at which rapid oxidation starts, we suggest that the titanium vacancy formation is the critical initial step in this process. The Ti vacancy formation energies for Ti_2N were negative irrespective of the conditions, which might explain why it has not been successfully etched using HF.

Our calculations for the carbon and nitrogen vacancies showed the opposite trend, wherein the vacancies are more stable in systems with high OH content. Moreover, Ti_3C_2 was found to be more susceptible to vacancy formation in the X sublattice than Ti_2N .

Our results are expected to be useful in guiding future experimental research, in avoiding excessive defect formation, and even in estimating conditions needed to reach desired defect concentrations. Furthermore, the computational approach presented herein can be readily applied to other MXenes and other defects.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.1c03179>.

Pourbaix diagrams of solid Ti phases; surface geometries of Ti_3C_2 in the presence of Ti vacancy for different mixed functionalizations; effect of vacancy charge to the model electrostatic potential; vacancy formation energies for F-terminated surfaces; and effect of implicit solvent on formation energies (PDF)

AUTHOR INFORMATION

Corresponding Author

Hannu-Pekka Komsa — Department of Applied Physics, Aalto University, 00076 Aalto, Finland; Microelectronics Research Unit, University of Oulu, 90014 Oulu, Finland;
orcid.org/0000-0002-0970-0957; Email: hannu-pekka.komsa@oulu.fi

Authors

Rina Ibragimova — Department of Applied Physics, Aalto University, 00076 Aalto, Finland; Department of Electrical

Engineering and Automation, Aalto University, 00076 Aalto, Finland; orcid.org/0000-0001-5773-3457

Patrick Rinke — Department of Applied Physics, Aalto University, 00076 Aalto, Finland; orcid.org/0000-0003-1898-723X

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.chemmater.1c03179>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge funding from the Academy of Finland under Project No. 311058. We gratefully acknowledge CSC — IT Center for Science, Finland, and the Aalto Science-IT project for generous computational resources.

REFERENCES

- (1) Ghidui, M.; Lukatskaya, M. R.; Zhao, M.-Q.; Gogotsi, Y.; Barsoum, M. W. Conductive Two-Dimensional Titanium Carbide 'Clay' with High Volumetric Capacitance. *Nature* **2014**, *516*, 78–81.
- (2) Zhang, C. J.; Anasori, B.; Seral-Ascaso, A.; Park, S.-H.; McEvoy, N.; Shmeliov, A.; Duesberg, G. S.; Coleman, J. N.; Gogotsi, Y.; Nicolosi, V. Transparent, Flexible, and Conductive 2D Titanium Carbide (MXene) Films with High Volumetric Capacitance. *Adv. Mater.* **2017**, *29*, 1702678.
- (3) Cao, W.-T.; Chen, F.-F.; Zhu, Y.-J.; Zhang, Y.-G.; Jiang, Y.-Y.; Ma, M.-G.; Chen, F. Binary Strengthening and Toughening of MXene/Cellulose Nanofiber Composite Paper with Nacre-Inspired Structure and Superior Electromagnetic Interference Shielding Properties. *ACS Nano* **2018**, *12*, 4583–4593.
- (4) Hantanasirisakul, K.; Zhao, M.-Q.; Urbankowski, P.; Halim, J.; Anasori, B.; Kota, S.; Ren, C. E.; Barsoum, M. W.; Gogotsi, Y. Fabrication of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Transparent Thin Films with Tunable Optoelectronic Properties. *Adv. Electron. Mater.* **2016**, *2*, 1600050.
- (5) Lipatov, A.; Lu, H.; Alhabeb, M.; Anasori, B.; Gruverman, A.; Gogotsi, Y.; Sinitskii, A. Elastic properties of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ MXene monolayers and bilayers. *Sci. Adv.* **2018**, *4*, eaat0491.
- (6) Khaledialidusti, R.; Anasori, B.; Barnoush, A. Temperature-dependent mechanical properties of $\text{Ti}_n\text{+1CnO}_2$ ($n = 1, 2$) MXene monolayers: a first-principles study. *Phys. Chem. Chem. Phys.* **2020**, *22*, 3414–3424.
- (7) Handoko, A. D.; Chen, H.; Lum, Y.; Zhang, Q.; Anasori, B.; Seh, Z. W. Two-Dimensional Titanium and Molybdenum Carbide MXenes as Electrocatalysts for CO_2 Reduction. *iScience* **2020**, *23*, 101181.
- (8) Khaledialidusti, R.; Mishra, A. K.; Barnoush, A. Atomic defects in monolayer ordered double transition metal carbide ($\text{Mo}_2\text{TiC}_2\text{T}_x$) MXene and CO_2 adsorption. *J. Mater. Chem. C* **2020**, *8*, 4771–4779.
- (9) Morales-García, A.; Calle-Vallejo, F.; Illas, F. MXenes: New Horizons in Catalysis. *ACS Catal.* **2020**, *10*, 13487–13503.
- (10) Yang, S.; Zhang, P.; Wang, F.; Ricciardulli, A. G.; Lohe, M. R.; Blom, P. W. M.; Feng, X. Fluoride-Free Synthesis of Two-Dimensional Titanium Carbide (MXene) Using a Binary Aqueous System. *Angew. Chem., Int. Ed.* **2018**, *57*, 15491–15495.
- (11) Li, M.; Lu, J.; Luo, K.; Li, Y.; Chang, K.; Chen, K.; Zhou, J.; Rosen, J.; Hultman, L.; Eklund, P.; et al. Element Replacement Approach by Reaction with Lewis Acidic Molten Salts to Synthesize Nanolaminated MAX Phases and MXenes. *J. Am. Chem. Soc.* **2019**, *141*, 4730–4737.
- (12) Kamysbayev, V.; Filatov, A. S.; Hu, H.; Rui, X.; Lagunas, F.; Wang, D.; Klie, R. F.; Talapin, D. V. Covalent surface modifications and superconductivity of two-dimensional metal carbide MXenes. *Science* **2020**, *369*, 979–983.
- (13) Li, Y.; Shao, H.; Lin, Z.; Lu, J.; Liu, L.; Duployer, B.; Persson, P. O. Å.; Eklund, P.; Hultman, L.; Li, M.; et al. A general Lewis acidic etching route for preparing MXenes with enhanced electrochemical

performance in non-aqueous electrolyte. *Nat. Mater.* **2020**, *19*, 894–899.

(14) Wang, H.-W.; Naguib, M.; Page, K.; Wesolowski, D. J.; Gogotsi, Y. Resolving the Structure of $\text{Ti}_3\text{C}_2\text{Ti}_x$ MXenes through Multilevel Structural Modeling of the Atomic Pair Distribution Function. *Chem. Mater.* **2016**, *28*, 349–359.

(15) Hope, M. A.; Forse, A. C.; Griffith, K. J.; Lukatskaya, M. R.; Ghidui, M.; Gogotsi, Y.; Grey, C. P. NMR Reveals the Surface Functionalisation of Ti_3C_2 MXene. *Phys. Chem. Chem. Phys.* **2016**, *18*, 5099–5102.

(16) Sang, X.; Xie, Y.; Lin, M.-W.; Alhabeb, M.; Van Aken, K. L.; Gogotsi, Y.; Kent, P. R. C.; Xiao, K.; Unocic, R. R. Atomic Defects in Monolayer Titanium Carbide ($\text{Ti}_3\text{C}_2\text{T}_x$) MXene. *ACS Nano* **2016**, *10*, 9193–9200.

(17) Karlsson, L. H.; Birch, J.; Halim, J.; Barsoum, M. W.; Persson, P. O. Å. Atomically Resolved Structural and Chemical Investigation of Single MXene Sheets. *Nano Lett.* **2015**, *15*, 4955–4960.

(18) Urbankowski, P.; Anasori, B.; Makaryan, T.; Er, D.; Kota, S.; Walsh, P. L.; Zhao, M.; Shenoy, V. B.; Barsoum, M. W.; Gogotsi, Y. Synthesis of two-dimensional titanium nitride Ti_4N_3 (MXene). *Nanoscale* **2016**, *8*, 11385–11391.

(19) Djire, A.; Bos, A.; Liu, J.; Zhang, H.; Miller, E. M.; Neale, N. R. Pseudocapacitive Storage in Nanolayered Ti_2NT_x MXene Using Mg-Ion Electrolyte. *ACS Appl. Nano Mater.* **2019**, *2*, 2785–2795.

(20) Djire, A.; Zhang, H.; Liu, J.; Miller, E. M.; Neale, N. R. Electrocatalytic and Optoelectronic Characteristics of the Two-Dimensional Titanium Nitride $\text{Ti}_4\text{N}_3\text{T}_x$ MXene. *ACS Appl. Mater. Interfaces* **2019**, *11*, 11812–11823.

(21) Ghidui, M.; Naguib, M.; Shi, C.; Mashtalir, O.; Pan, L. M.; Zhang, B.; Yang, J.; Gogotsi, Y.; Billinge, S. J. L.; Barsoum, M. W. Synthesis and characterization of two-dimensional Nb_4C_3 (MXene). *Chem. Commun.* **2014**, *50*, 9517–9520.

(22) Ibragimova, R.; Puska, M. J.; Komsa, H.-P. pH-Dependent Distribution of Functional Groups on Titanium-Based MXenes. *ACS Nano* **2019**, *13*, 9171–9181.

(23) Ibragimova, R.; Erhart, P.; Rinke, P.; Komsa, H.-P. Surface Functionalization of 2D MXenes: Trends in Distribution, Composition, and Electronic Properties. *J. Phys. Chem. Lett.* **2021**, *12*, 2377–2384.

(24) Zhang, H.; Hu, T.; Wang, X.; Zhou, Y. Structural defects in MAX phases and their derivative MXenes: A look forward. *J. Mater. Sci. Technol.* **2020**, *38*, 205–220.

(25) Plummer, G.; Anasori, B.; Gogotsi, Y.; Tucker, G. J. Nanoindentation of monolayer $\text{Ti}_{n+1}\text{C}_n\text{T}_x$ MXenes via atomistic simulations: The role of composition and defects on strength. *Comput. Mater. Sci.* **2019**, *157*, 168–174.

(26) Sang, X.; Xie, Y.; Lin, M.-W.; Alhabeb, M.; Van Aken, K. L.; Gogotsi, Y.; Kent, P. R. C.; Xiao, K.; Unocic, R. R. Atomic Defects in Monolayer Titanium Carbide ($\text{Ti}_3\text{C}_2\text{T}_x$) MXene. *ACS Nano* **2016**, *10*, 9193–9200.

(27) Sang, X.; Xie, Y.; Yilmaz, D. E.; Lotfi, R.; Alhabeb, M.; Ostadhosseini, A.; Anasori, B.; Sun, W.; Li, X.; Xiao, K.; et al. In situ atomistic insight into the growth mechanisms of single layer 2D transition metal carbides. *Nat. Commun.* **2018**, *9*, 2266.

(28) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D Metal Carbides and Nitrides (MXenes) for Energy Storage. *Nat. Rev. Mater.* **2017**, *2*, 16098.

(29) He, R.; Wan, Y.; Zhao, P.; Guo, P.; Jiang, Z.; Zheng, J. First-principles investigation of native point defects in two-dimensional Ti_3C_2 . *Comput. Theor. Chem.* **2019**, *1150*, 26–39.

(30) Hu, T.; Yang, J.; Wang, X. Carbon vacancies in Ti_2CT_2 MXenes: defects or a new opportunity? *Phys. Chem. Chem. Phys.* **2017**, *19*, 31773–31780.

(31) Zhou, T.; Zhao, W.; Yang, K.; Yao, Q.; Li, Y.; Wu, B.; Liu, J. Atomic Vacancy Defect, Frenkel Defect and Transition Metals (Sc, V, Zr) Doping in Ti_4N_3 MXene Nanosheet: A First-Principles Investigation. *Appl. Sci.* **2020**, *10*, 2450.

(32) Cui, W.; Hu, Z.-Y.; Unocic, R. R.; Van Tendeloo, G.; Sang, X. Atomic defects, functional groups and properties in MXenes. *Chin. Chem. Lett.* **2021**, *32*, 339–344.

(33) Chertopalov, S.; Mochalin, V. N. Environment-Sensitive Photoresponse of Spontaneously Partially Oxidized Ti_3C_2 MXene Thin Films. *ACS Nano* **2018**, *12*, 6109–6116.

(34) Tang, J.; Mathis, T. S.; Kurra, N.; Sarycheva, A.; Xiao, X.; Hedhili, M. N.; Jiang, Q.; Alshareef, H. N.; Xu, B.; Pan, F.; et al. Tuning the Electrochemical Performance of Titanium Carbide MXene by Controllable In Situ Anodic Oxidation. *Angew. Chem., Int. Ed.* **2019**, *58*, 17849–17855.

(35) Zhang, C. J.; Pinilla, S.; McEvoy, N.; Cullen, C. P.; Anasori, B.; Long, E.; Park, S.-H.; Seral-Ascaso, A.; Shmeliov, A.; Krishnan, D.; et al. Oxidation Stability of Colloidal Two-Dimensional Titanium Carbides (MXenes). *Chem. Mater.* **2017**, *29*, 4848–4856.

(36) Ghassemi, H.; Harlow, W.; Mashtalir, O.; Beidaghi, M.; Lukatskaya, M. R.; Gogotsi, Y.; Taheri, M. L. In situ environmental transmission electron microscopy study of oxidation of two-dimensional Ti_3C_2 and formation of carbon-supported TiO_2 . *J. Mater. Chem. A* **2014**, *2*, 14339–14343.

(37) Persson, K. A.; Waldwick, B.; Lazic, P.; Ceder, G. Prediction of solid-aqueous equilibria: Scheme to combine first-principles calculations of solids with experimental aqueous states. *Phys. Rev. B* **2012**, *85*, 235438.

(38) Hansen, H. A.; Rossmeisl, J.; Nørskov, J. K. Surface Pourbaix diagrams and oxygen reduction activity of Pt, Ag and Ni(111) surfaces studied by DFT. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3722–3730.

(39) Todorova, M.; Neugebauer, J. Extending the Concept of Defect Chemistry from Semiconductor Physics to Electrochemistry. *Phys. Rev. Appl.* **2014**, *1*, 014001.

(40) Todorova, M.; Neugebauer, J. Identification of bulk oxide defects in an electrochemical environment. *Faraday Discuss.* **2015**, *180*, 97–112.

(41) Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; Pergamon Press: 1966.

(42) Huang, L.-F.; Scully, J. R.; Rondinelli, J. M. Modeling Corrosion with First-Principles Electrochemical Phase Diagrams. *Annu. Rev. Mater. Res.* **2019**, *49*, 53–77.

(43) Mariano, M.; Mashtalir, O.; Antonio, F. Q.; Ryu, W.-H.; Deng, B.; Xia, F.; Gogotsi, Y.; Taylor, A. D. Solution-Processed Titanium Carbide MXene Films Examined as Highly Transparent Conductors. *Nanoscale* **2016**, *8*, 16371–16378.

(44) Peng, C.; Wei, P.; Li, X.; Liu, Y.; Cao, Y.; Wang, H.; Yu, H.; Peng, F.; Zhang, L.; Zhang, B.; et al. High Efficiency Photocatalytic Hydrogen Production over Ternary $\text{Cu}/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{Ti}_x$ Enabled by Low-Work-Function 2D Titanium Carbide. *Nano Energy* **2018**, *53*, 97–107.

(45) Kang, Z.; Ma, Y.; Tan, X.; Zhu, M.; Zheng, Z.; Liu, N.; Li, L.; Zou, Z.; Jiang, X.; Zhai, T.; et al. MXene-Silicon Van Der Waals Heterostructures for High-Speed Self-Driven Photodetectors. *Adv. Electron. Mater.* **2017**, *3*, 1700165.

(46) Wang, Z.; Kim, H.; Alshareef, H. N. Oxide Thin-Film Electronics using All-MXene Electrical Contacts. *Adv. Mater.* **2018**, *30*, 1706656.

(47) Schultz, T.; Frey, N. C.; Hantanasirisakul, K.; Park, S.; May, S. J.; Shenoy, V. B.; Gogotsi, Y.; Koch, N. Surface Termination Dependent Work Function and Electronic Properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. *Chem. Mater.* **2019**, *31*, 6590–6597.

(48) Khazaei, M.; Arai, M.; Sasaki, T.; Ranjbar, A.; Liang, Y.; Yunoki, S. OH-Terminated Two-Dimensional Transition Metal Carbides and Nitrides as Ultralow Work Function Materials. *Phys. Rev. B* **2015**, *92*, 075411.

(49) Bandyopadhyay, A.; Ghosh, D.; Pati, S. K. Effects of point defects on the magnetoelectronic structures of MXenes from first principles. *Phys. Chem. Chem. Phys.* **2018**, *20*, 4012–4019.

(50) Huang, S.; Mochalin, V. N. Understanding Chemistry of Two-Dimensional Transition Metal Carbides and Carbonitrides (MXenes) with Gas Analysis. *ACS Nano* **2020**, *14*, 10251–10257.

- (51) Chase, M. W. J. *NIST-JANAF Thermochemical Tables*, 4th ed.; American Institute of Physics: New York, 1998.
- (52) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (53) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (54) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. *Phys. Rev. Lett.* **2008**, *100*, 136406.
- (55) Mathew, K.; Kolluru, V. S. C.; Hennig, R. G. *VASPSol: Implicit Solvation and Electrolyte Model for Density-Functional Theory*. <https://github.com/henniggroup/VASPSol> (accessed March 23, 2019).
- (56) Mathew, K.; Sundararaman, R.; Letchworth-Weaver, K.; Arias, T. A.; Hennig, R. G. Implicit Solvation Model for Density-Functional Study of Nanocrystal Surfaces and Reaction Pathways. *J. Chem. Phys.* **2014**, *140*, 084106.
- (57) Verger, L.; Xu, C.; Natu, V.; Cheng, H.-M.; Ren, W.; Barsoum, M. W. Overview of the synthesis of MXenes and other ultrathin 2D transition metal carbides and nitrides. *Curr. Opin. Solid State Mater. Sci.* **2019**, *23*, 149–163.
- (58) Zhao, X.; Vashisth, A.; Blivin, J. W.; Tan, Z.; Holta, D. E.; Kotasthane, V.; Shah, S. A.; Habib, T.; Liu, S.; Lutkenhaus, J. L.; et al. pH, Nanosheet Concentration, and Antioxidant Affect the Oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x MXene Dispersions. *Adv. Mater. Interfaces* **2020**, *7*, 2000845.
- (59) Lorencova, L.; Bertok, T.; Dosekova, E.; Holazova, A.; Paprckova, D.; Vikartovska, A.; Sasinkova, V.; Filip, J.; Kasak, P.; Jerigova, M.; et al. Electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in aqueous media: towards ultrasensitive H_2O_2 sensing. *Electrochim. Acta* **2017**, *235*, 471–479.
- (60) Ashton, M.; Trometer, N.; Mathew, K.; Suntivich, J.; Freysoldt, C.; Sinnott, S. B.; Hennig, R. G. Predicting the Electrochemical Synthesis of 2D Materials from First Principles. *J. Phys. Chem. C* **2019**, *123*, 3180–3187.
- (61) Soundiraraju, B.; George, B. K. Two-Dimensional Titanium Nitride (Ti_2N) MXene: Synthesis, Characterization, and Potential Application as Surface-Enhanced Raman Scattering Substrate. *ACS Nano* **2017**, *11*, 8892–8900.
- (62) Shao, J.; Zhang, J.; Jiang, C.; Lin, J.; Huang, P. Biodegradable titanium nitride MXene quantum dots for cancer phototheranostics in NIR-I/II biowindows. *Chem. Eng. J.* **2020**, *400*, 126009.
- (63) Abdelmalak, M. N. *MXenes: A New Family of Two-Dimensional Materials and its Application as Electrodes for Li-ion Batteries*. Ph.D. Dissertation, Drexel University, Philadelphia, PA, 2014.

Recommended by ACS

Ultralarge Flakes of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene via Soft Delamination

Mikhail Shekhirev, Yuri Gogotsi, et al.

JULY 25, 2022
ACS NANO

READ 

Construction of an MXene/Organic Superlattice for Flexible Thermoelectric Energy Conversion

Zhiwen Wang, Peng-an Zong, et al.

SEPTEMBER 11, 2022
ACS APPLIED ENERGY MATERIALS

READ 

Scaled Deposition of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene on Complex Surfaces: Application Assessment as Rear Electrodes for Silicon Heterojunction Solar Cells

Erkan Aydin, Stefaan De Wolf, et al.

FEBRUARY 09, 2022
ACS NANO

READ 

MXene-Integrated Metal Oxide Transparent Photovoltaics and Self-Powered Photodetectors

Thanh Tai Nguyen, Joondong Kim, et al.

JUNE 06, 2022
ACS APPLIED ENERGY MATERIALS

READ 

Get More Suggestions >