On the Use of Ti$_3$C$_2$Tx MXene as a Negative Electrode Material for Lithium-Ion Batteries

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**ABSTRACT:** The pursuit of new and better battery materials has given rise to numerous studies of the possibilities to use two-dimensional negative electrode materials, such as MXenes, in lithium-ion batteries. Nevertheless, both the origin of the capacity and the reasons for significant variations in the capacity seen for different MXene electrodes still remain unclear, even for the most studied MXene: Ti$_3$C$_2$T$_x$. Herein, freestanding Ti$_3$C$_2$T$_x$ MXene films, composed only of Ti$_3$C$_2$T$_x$, MXene flakes, are studied as additive-free negative lithium-ion battery electrodes, employing lithium metal half-cells and a combination of chronopotentiometry, cyclic voltammetry, X-ray photoelectron spectroscopy, hard X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy experiments. The aim of this study is to identify the redox reactions responsible for the observed reversible and irreversible capacities of Ti$_3$C$_2$T$_x$-based lithium-ion batteries as well as the reasons for the significant capacity variation seen in the literature. The results demonstrate that the reversible capacity mainly stems from redox reactions involving the $T_x$-Ti-C titanium species situated on the surfaces of the MXene flakes, whereas the Ti-C titanium present in the core of the flakes remains electro-inactive. While a relatively low reversible capacity is obtained for electrodes composed of pristine Ti$_3$C$_2$T$_x$, MXene flakes, significantly higher capacities are seen after having exposed the flakes to water and air prior to the manufacturing of the electrodes. This is ascribed to a change in the titanium oxidation state at the surfaces of the MXene flakes, resulting in increased concentrations of Ti(II), Ti(III), and Ti(IV) in the $T_x$-Ti-C surface species. The significant irreversible capacity seen in the first cycles is mainly attributed to the presence of residual water in the Ti$_3$C$_2$T$_x$ electrodes. As the capacities of Ti$_3$C$_2$T$_x$, MXene negative electrodes depend on the concentration of Ti(II), Ti(III), and Ti(IV) in the $T_x$-Ti-C surface species and the water content, different capacities can be expected when using different manufacturing, pretreatment, and drying procedures.

**INTRODUCTION**

MXenes constitute a novel class of two-dimensional materials which has obtained its name from the fact that they are produced from MAX phases (where M is a transition metal, A is an A-group element, and X is N and/or C) by etching away the A metal (e.g., Al). As a result, MXenes are 2D transition-metal nitrides or carbides with the general chemical formula M$_n$I$_1$X$_n$T$_{n'}$, where $n$ is 1–4, and T is the surface termination (e.g., O, OH, F, or Cl). Since their discovery in 2011, MXenes have been shown to exhibit several interesting properties, including high electronic conductivity and high surface area. MXenes are therefore promising for applications involving energy storage, mainly as electrode materials for supercapacitors but also as negative electrode materials for lithium-ion batteries.

To be used as a lithium-ion battery material, it is, however, not enough that the material has a high electronic conductivity and a high surface area. A good negative electrode material also needs to undergo a reduction during the lithiation step and an oxidation during the subsequent delithiation step. The redox reactions, which should be reversible and occur in a suitable potential region (e.g., between 2.5 and 0 V vs Li$^+$/Li$^-$), should involve the full volume of the material rather than merely the surface of the material (as for a supercapacitor material). To be able to use an electrode material properly, the composition of the material, its capacity, as well as the redox reactions responsible for the capacity all need to be known. Ideally, the specific capacity of a negative electrode material should be higher than 372 mA h g$^{-1}$, that is, the specific capacity of graphite, which is the most commonly used negative electrode material at present. Many MXene-based materials do not fulfill these requirements, at least not yet, as the origins of the obtained capacities remain unclear and as the capacities have...
been found to depend significantly on the experimental conditions used to manufacture the MXene materials. Ti$_3$C$_2$Tx is an MXene that has been frequently studied as a negative lithium-ion battery material. Although the experimentally found capacity of Ti$_3$C$_2$T$_x$ has been suggested to be due to a lithium-based intercalation reaction, it is still not clear which titanium species are responsible for the obtained capacity. Moreover, as significantly different capacities have been reported for different Ti$_3$C$_2$T$_x$-based electrodes, it can also be suspected that the capacities depend on the processes used to manufacture the MXene material and/or the employed electrodes. Freestanding Ti$_3$C$_2$T$_x$ electrodes have, for example, been found to exhibit specific capacities of 410 mA h g$^{-1}$ at a 1C cycling rate and 110 mA h g$^{-1}$ at a rate of 36C$^\text{x}$ when cycling between 2.5 and 0.05 V versus Li$^+$/Li. In another study, a capacity of about 35 mA h g$^{-1}$ was, on the other hand, obtained when cycling freestanding 5 μm thick multilayered Ti$_3$C$_2$T$_x$ electrodes at a rate of 0.5C between 3.0 and 0.01 V versus Li$^+$/Li. The different capacities have been proposed to be due to different degrees of restacking of the Ti$_3$C$_2$T$_x$ flakes inside multilayered freestanding electrodes, making it difficult to access all of the material. To circumvent this problem, approaches aimed at chemical modifications of the Ti$_3$C$_2$T$_x$ material or structural modifications of the Ti$_3$C$_2$T$_x$ electrodes have been developed. These have involved, for example, chemical etching, oxidation with KOH, as well as modifications of the structure of freestanding electrodes via the incorporation of carbon nanotubes. A capacity of 110 mA h g$^{-1}$ at a rate of 0.5C was, for example, obtained when increasing the porosity of the Ti$_3$C$_2$T$_x$ material through chemical etching. A freestanding Ti$_3$C$_2$T$_x$ electrode containing 10 wt % of CNT was found to have a capacity of 220 mA h g$^{-1}$ at 0.5C, whereas a capacity of 500 mA h g$^{-1}$ at 0.5C was found when using a composite film prepared by combining the chemical etching of the Ti$_3$C$_2$T$_x$ powder with the addition of 10 wt % of carbon nanotubes. Reversible capacities of 220 mA h g$^{-1}$ (at a rate of C/18) have also been found after using flash oxidation in air to generate TiO$_2$ particles on the surface of composite Ti$_3$C$_2$ powder electrodes. In the latter case, the capacity was attributed to the lithiumation and delithiation of the obtained TiO$_2$ anatase. These varying results, obtained with different Ti$_3$C$_2$T$_x$ electrodes, suggest that the capacity may depend not only on the structure of the electrode but also on the oxidation state of the MXene material.

The results presented in the literature clearly show that the capacities of electrodes composed of Ti$_3$C$_2$T$_x$ can differ significantly depending on how the electrodes were made and/or pretreated. In this context, it should be mentioned that Ti$_3$C$_2$T$_x$ colloidal solutions are known to undergo spontaneous oxidation to finally yield TiO$_2$ and carbon upon exposure to air. This indicates that oxidized titanium species, including TiO$_2$ or Ti$_2$O$_3$, may be present on the surface of a synthesized Ti$_3$C$_2$T$_x$ powder even if care is taken to minimize its exposure to air. This is interesting as the results discussed above suggest that the Ti$_3$C$_2$T$_x$ capacity can be increased by oxidizing the Ti$_3$C$_2$T$_x$ material. As was recently demonstrated, the approach used to prepare the MXene from the MAX phase can also affect the electrochemical performance of Ti$_3$C$_2$T$_x$. Etching the MAX phase with a Lewis acid molten salt, followed by an oxidative treatment with ammonium persulfate solution resulted in a capacity of 205 mA h g$^{-1}$ for a composite electrode containing 80 wt % MXene powder and 15 wt % carbon black. This capacity, which was obtained when cycling between 3 and 0.2 V versus Li$^+$/Li at a scan rate of 0.5 mV s$^{-1}$, was ascribed to redox reactions involving titanium.

In addition to the experimental work discussed above, studies have also focused on the calculation of the theoretical capacity and reduction potential of Ti$_3$C$_2$T$_x$ when used as a negative electrode material in lithium-ion batteries. For Ti$_3$C$_2$T$_x$, the results of density functional theory calculations indicated that a theoretical capacity of 320 mA h g$^{-1}$ should be obtained based on the redox reaction Ti$_3$C$_2^+$ + 2e$^- + 2$ Li$^+$ = Ti$_3$C$_2$Li$_x$, which was calculated to have a standard potential of about 0.62 V versus Li$^+$/Li. The same authors also found that surface functionalization of Ti$_3$C$_2$ yielding Ti$_3$C$_2$F$_2$ or Ti$_3$C$_2$(OH)$_2$ should result in lower theoretical capacities, that is, 130 and 67 mA h g$^{-1}$, respectively, as well as lower standard potentials, that is, 0.56 and 0.14 V versus Li$^+$/Li, respectively. Due to the lower capacities, it was concluded that surface modifications of Ti$_3$C$_2$ should be avoided as much as possible when using Ti$_3$C$_2$ as a negative electrode material in lithium-ion batteries. This recommendation is, however, not in agreement with the experimental results discussed above, indicating that the oxidation of Ti$_3$C$_2$T$_x$ electrodes can give significantly increased capacities. Moreover, the experimental data also show that the main part of the capacity stemmed from redox reactions taking place at potentials significantly higher than 0.62 V versus Li$^+$/Li. These findings indicate that the capacities obtained during the cycling of Ti$_3$C$_2$T$_x$ electrodes are unlikely to stem from the reduction of Ti$_3$C$_2$T$_x$ yielding Ti$_3$C$_2$T$_x$Li$_x$, as assumed in the abovementioned theoretical study. This raises questions regarding the origin of the capacity seen when cycling Ti$_3$C$_2$T$_x$ MXene electrodes in lithium-ion batteries. In addition to this and the abovementioned issues concerning the significantly different capacities reported for different Ti$_3$C$_2$T$_x$ electrodes, the origin of the large irreversible capacity, often seen on the first cycles, is still to be properly explained. Although the irreversible capacity typically is ascribed to the formation of a solid electrolyte interphase (SEI) layer on the electrode (mainly at potentials below 1 V vs Li$^+$/Li), the experimental results clearly show that the irreversible capacity also stems from, at least one, unidentified reduction taking place at higher potentials.

The main aim of the present work is to identify the redox reactions responsible for the reversible and irreversible capacities obtained for freestanding Ti$_3$C$_2$T$_x$ MXene electrodes, by employing a combination of chronopotentiometry, cyclic voltammetry, X-ray photoelectron spectroscopy (XPS), hard X-ray photoelectron spectroscopy (HAXPES), and X-ray absorption spectroscopy (XAS) data. The effect of spontaneous oxidation of Ti$_3$C$_2$T$_x$ in air on the capacities of the electrodes is evaluated and compared with the changes seen in the XPS, HAXPES, and XAS data. Experiments are also conducted with Ti$_3$C$_2$T$_x$ electrodes, prior to and after different drying steps, to evaluate the influence of the water content in the electrodes on their cycling performances. It is shown that the reversible capacities of the Ti$_3$C$_2$T$_x$ electrodes mainly stem from redox reactions involving the Ti-$\text{C}$ titanium species situated on the surfaces of the MXene flakes, whereas the Ti-$\text{C}$ titanium present within the flakes remains electrochemically inactive.

**EXPERIMENTAL SECTION**

**Synthesis.** The Ti$_3$C$_2$T$_x$ MXene, which was received in the form of a suspension, was synthesized as previously
Electrodes were assembled, each containing a Celgard 2325 separator impregnated with 100 µL of 1 M LiPF₆ in 1:1 (v/v) EC/DEC (LP40) electrolyte (Gotion, H₂O < 14 ppm). The cells were assembled and sealed in an argon-filled glovebox (H₂O, O₂ < 1 ppm) using two copper strips as the current collectors.

The coin cells (CR2032) containing electrodes composed of Ti₃C₂Tx that had been in contact with air for different times in an open vial (as described above) also contained Li–metal disks with a diameter of 13 mm as combined reference and counter electrodes, as well as Celgard 2400 separators and LP40 electrolyte. These cells were assembled and sealed in an argon-filled glovebox (H₂O, O₂ < 1 ppm).

The cyclic voltammetry (CV) experiments, which were performed with a Biologic MPG2 instrument, were conducted by scanning the potential of the freestanding Ti₃C₂Tx electrode from 3.0 to 0 V versus Li⁺/Li and then back to 3.0 V at a scan rate of 0.1 mV s⁻¹, if not stated otherwise.

Galvanostatic cycling (i.e., constant current cycling, CC) was performed with an Arbin battery tester using a current density of 10 mA g⁻¹ and cutoff voltages of 0 and 3.0 V versus Li⁺/Li, respectively, unless stated otherwise.

The ac impedance experiments were performed with a Ti₃C₂Tx/Li cell using a Biologic MPG2 instrument. The ac impedance was first measured at the OCV (~3 V vs Li⁺/Li) and then after scanning the potential (at a scan rate of 0.1 mV s⁻¹) to 1.9 V versus Li⁺/Li and 0.3 V versus Li⁺/Li and subsequently to 2.3 V versus Li⁺/Li and 3.0 V versus Li⁺/Li. The employed frequency range was 5 mHz to 20 kHz (seven points per decade were recorded), and the amplitude of the ac signal was 10 mV. The cell was held at each of the abovementioned potentials for 30 min prior to the ac measurement.

Spectroscopy Measurements. The in-house XPS measurements were performed with a PHI 5500 X-ray photoelectron spectrometer using an Al source with Kα radiation (1486.6 eV) and an electron emission angle of 45°, a pass energy of 23.5 eV, a step size of 0.1 eV, and time per step of 100 ms. The energy calibration was performed by referencing all spectra to the C 1s peak originating from the Ti–C peak located at 282.0 eV. To study the species found on the surface of the Ti₃C₂Tx MXene freestanding electrodes after lithiation (reduction) and delithiation (oxidation), respectively, the electrodes were subjected to a CV experiment (described above), followed by ex situ XPS and HAXPES analyses. A pristine electrode, dried at 120 °C for 16 h in vacuum, and an electrode left in contact with the electrolyte under open-circuit conditions were also studied for comparison. The cycled cells were stopped either at 0.3 V vs Li⁺/Li on the lithiation (i.e., reduction) step, or at 2.3 V versus Li⁺/Li on the delithiation (i.e., oxidation) step, of the first cycle. After finishing the cycling, the cells were transferred to an argon-filled glovebox (H₂O, O₂ < 1 ppm), in which the electrodes were extracted and washed with dimethyl carbonate (DMC; ≥99%, Sigma-Aldrich). The electrodes were then transferred from the glovebox into the XPS machine (or HAXPES end-station) without exposure to air using an argon-filled load-lock.

The HAXPES experiments (with an X-ray beam energy of 2.35 keV) and surface-sensitive XAS measurements with a total electron yield (TEY) detector were performed at the 109 beamline, Diamond Light Source Ltd, UK. The bulk-sensitive XAS data was collected in the transmission mode at the BALDER beamline, MAX IV Laboratory, Lund, Sweden. In
the XAS measurements, electrodes with a thickness of between 8 and 10 μm and a mass loading of approximately 3.5 mg cm$^{-2}$ were employed. The latter electrodes had been dried at 300 °C under vacuum for 16 h prior to cell assembly. A titanium foil and a pellet of TiO$_2$ anatase powder (Sigma-Aldrich, powder 99.8% trace metal basis) were used as references. Prior to the XAS measurements, the Ti$_x$C$_2$T$_a$ electrodes were hermetically sealed in Kapton tape and pouch material in a glovebox to enable their inert transfer to the beamline.

**RESULTS AND DISCUSSION**

To focus on the electrochemical performance of the Ti$_x$C$_2$T$_a$ MXene (i.e., Ti$_x$C$_2$ featuring different surface groups, T$_a$), the present study was conducted with freestanding, binder-free, and conductive additive-free electrodes. As the electrodes obtained via the filtering of Ti$_x$C$_2$T$_a$ MXene suspensions only contained Ti$_x$C$_2$T$_a$ flakes, the electrochemical behavior of the electrodes should therefore be determined by the electrochemical properties of the Ti$_x$C$_2$T$_a$ flakes. The obtained capacities should, however, also be affected by the degree of restacking of the Ti$_x$C$_2$T$_a$ flakes via a change of the electrochemically active surface area of the electrodes. The electrodes were first cycled between 3.0 and 0 V versus Li$^+$/Li in half-cells containing lithium–metal electrodes, employing either a constant current of 10 mA g$^{-1}$ or cyclic voltammetry at a scan rate of 0.1 mV s$^{-1}$. As seen in Figure 1a, the 5–7 μm thick freestanding electrode was found to exhibit a lithiation capacity of about 105 mA h g$^{-1}$ on the first constant current cycle, whereas the corresponding value was about 64 mA h g$^{-1}$ on the second cycle (see Table S1 in the Supporting Information). From the third cycle onward, the lithiation capacity generally increased to reach a value of about 68 mA h g$^{-1}$ after 27 cycles. The cycling curves are shown in Figure S2 in the Supporting Information. The initial capacity loss and the first-cycle Coulombic efficiency of less than 50% clearly indicate the presence of significant irreversible capacity. The first-cycle voltammetric lithiation capacity (see Figures 1b and S3) was also about 2.4 times larger than the corresponding delithiation capacity. In the voltammetric cycling, the first- and second-cycle lithiation capacities were about 75 and 65 mA h g$^{-1}$, respectively. In analogy with the constant current results, the voltammetric lithiation and delithiation capacities increased after the third cycle (see Figure S3), yielding a lithiation capacity of about 73 mA h g$^{-1}$ after 15 cycles.

The experimental results hence show that the specific capacities for the Ti$_x$C$_2$T$_a$ electrodes were significantly lower than that of graphite (i.e., 372 mA h g$^{-1}$), which typically is used as the negative electrode material in lithium-ion batteries. As is explained in the Supporting Information, the capacities were, however, too high to be compatible with the Ti$_x$C$_2$T$_a$ MXene double-layer capacity, assuming a nitrogen BET surface area of about 20 m$^2$ g$^{-1}$. This indicates that the main part of the capacity stemmed from, at least, one redox couple. This hypothesis is further supported by the shapes of the voltammograms in Figure 1b which indicate that the capacity stemmed from a broad lithiation (i.e., reduction) peak at about 1.6 V versus Li$^+$/Li and a broad delithiation (i.e., oxidation) peak at about 2.2 V versus Li$^+$/Li. One possibility could then be a reduction corresponding to those previously suggested for Ti$_x$C$_2$, Ti$_x$C$_3$F$_y$, and Ti$_x$C$_2$OH$_2$ (yielding Ti$_x$C$_2$F$_{2y}$, Ti$_x$C$_3$F$_{2y}$, and Ti$_x$C$_2$OH$_{2y}$, respectively). The standard potential and capacity for the reaction Ti$_x$C$_2$ + 2e$^-$ + 2 Li$^+$ = Ti$_x$C$_2$Li$_2$ have been estimated to be 0.62 V versus Li$^+$/Li and 320 mA h g$^{-1}$, respectively, whereas the corresponding values for the analogous reductions of Ti$_x$C$_2$F$_y$ and Ti$_x$C$_2$OH$_2$ were reported to be 0.56 V versus Li$^+$/Li and 130 mA h g$^{-1}$ and 0.14 V vs Li$^+$/Li and 67 mA h g$^{-1}$, respectively. These reactions are, however, not compatible with the second and subsequent cycle voltammograms (see Figure 1b), all featuring a lithiation peak at about 1.6 V versus Li$^+$/Li and a delithiation peak at about 2.2 V versus Li$^+$/Li. The experimental results consequently give rise to several questions: What were the reversible capacities due to? Why were the reversible capacities so relatively low? What was causing the initial irreversible capacity loss?
To answer the first two questions, one should first consider the redox reactions that may take place in the studied potential region. These redox reactions should either involve the carbon or titanium in the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene flakes. The hypothesis that the lithiation peaks seen at about 1.6 V versus Li\textsuperscript{+}/Li were due to the reduction of the carbon in the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene can, however, be rejected as the carbon should be reduced at significantly lower potentials. The standard potential for the (carbon reduction) reaction \(2C + 2\text{e}^- + 2\text{Li}^+ = \text{Li}_2C_2\) should be about 0.3 V versus Li\textsuperscript{+}/Li (see the Supporting Information). This, incidentally, also indicates that it is the carbon that is reduced in the abovementioned reductions of Ti\textsubscript{3}C\textsubscript{2}F\textsubscript{2} and Ti\textsubscript{3}C\textsubscript{2}OH\textsubscript{2}. Due to the low carbon reduction potential, carbon can clearly not oxidize titanium (as carbon is a very weak oxidizing agent). Both the carbon and titanium present in Ti\textsubscript{3}C\textsubscript{2} must, therefore, be elemental (see the discussion in the Supporting Information), which is why Ti\textsubscript{3}C\textsubscript{2} should be electrochemically inactive, at least at potentials above about 0.62 V versus Li\textsuperscript{+}/Li.

At this point, it should, however, be recalled that the employed freestanding electrodes contained Ti\textsubscript{i}C\textsubscript{3}T\textsubscript{x} (rather than Ti\textsubscript{3}C\textsubscript{2}) flakes as the Ti\textsubscript{i}C\textsubscript{3} flakes produced in the Ti\textsubscript{i}C\textsubscript{3}T\textsubscript{x} manufacturing process should undergo a spontaneous reaction with water and/or oxygen.\textsuperscript{2} As this reaction in fact involves an oxidation of the titanium at the surface of each Ti\textsubscript{i}C\textsubscript{3} flake, the obtained Ti\textsubscript{i}C\textsubscript{3}T\textsubscript{x} flake will then contain two types of titanium species, the \(T_x\text{−}Ti\text{−}C\) titanium species situated on the surfaces of the flakes and the Ti−C present at the center of the flakes, as is schematically illustrated in Figure 2. While the titanium in \(T_x\text{−}Ti\text{−}C\) bonds both to carbon and the \(T_x\) surface group, the titanium in Ti−C thus only bonds to carbon. In the discussion below, these two titanium species will therefore be referred to as \(T_x\text{−}Ti\text{−}C\) and Ti−C, respectively. Whereas the oxidation state of the titanium in \(T_x\text{−}Ti\text{−}C\) should be higher than zero, Ti−C titanium should remain elemental. The fact that Ti\textsubscript{i}C\textsubscript{3} flakes should undergo spontaneous oxidation upon exposure to air and/or water should not come as a surprise as it is well-known that titanium carbides undergo an oxidation, finally yielding titanium dioxide and carbon\textsuperscript{15,18,21} when exposed to oxygen and/or water (see the Supporting Information). As it is very difficult to completely avoid such exposure of the Ti\textsubscript{i}C\textsubscript{3} flakes, it is reasonable to assume that the observed lithiation capacity could stem from reductions involving \(T_x\text{−}Ti\text{−}C\) titanium species. This hypothesis is further supported by the fact that the activation of MXenes using surface oxidation has been found to enhance their reversible capacities.\textsuperscript{16} With respect to the relative low capacities seen in Figure 1, it is, however, also important to recall that the Ti\textsubscript{i}C\textsubscript{3}T\textsubscript{x} MXene flakes used in the present electrodes had been protected as much as possible from contact with both air and water during the synthesis, electrode manufacturing, and battery assembly. It could therefore be expected that the average oxidation state of the \(T_x\text{−}Ti\text{−}C\) titanium species was relatively low for the electrodes investigated here.

**Figure 2.** Schematic illustrations depicting a freestanding Ti\textsubscript{i}C\textsubscript{3}T\textsubscript{x} electrode (top left), a magnification of the Ti\textsubscript{i}C\textsubscript{3}T\textsubscript{x} flakes within the bulk of the electrode (bottom) as well as the structure of an individual Ti\textsubscript{i}C\textsubscript{3}T\textsubscript{x} MXene flake (top right). Ti\textsubscript{1} denotes the titanium in the Ti−C layer, whereas Ti\textsubscript{2} denotes the titanium in a \(T_x\text{−}Ti\text{−}C\) layer.
To investigate if the obtained capacities stemmed from redox reactions involving the \( T_x^- \text{Ti}^- \text{C} \) titanium species, experiments with bulk sensitive X-ray absorption spectroscopy (XAS) as well as surface sensitive X-ray photoelectron spectroscopy were performed. To minimize the change in the surface concentrations prior to the measurements (due to, e.g., self-discharge), the electrodes were transferred into the XPS instrument (or HAXPES end-station) without exposure to air using an argon-filled load-lock. The evaluation of the data was also based on the comparisons of the changes seen in the XPS results and in the electrochemical data for the different electrodes discussed below. As the same approach was used for all the different electrodes, comparisons of the results for the electrodes could still be used even though there may have been some changes in the oxidation states of the \( T_x^- \text{Ti}^- \text{C} \) titanium species prior to the XPS measurements. It should also be noted that the rate of self-discharge would be expected to be lower for a delithiated (i.e., oxidized) electrode than that for a lithiated electrode as the concentration of species able to undergo oxidation at potentials up to about 3 V versus Li\(^+\)/Li should be low in the electrolyte. To study the change in the titanium oxidation state within the electrode material, ex situ XAS of the Ti K-edge was performed in the transmission mode on pristine and cycled freestanding Ti\(_3\)C\(_2\)T\(_x\) electrodes. The XAS data (which should be less sensitive to self-discharge effects as XAS is a more bulk sensitive technique compared to XPS) for the pristine MXene are shown in Figure 3, together with the reference spectra for a titanium metal foil (for which the Ti oxidation state should be zero) and TiO\(_2\) anatase powder (for which the Ti oxidation state should be +IV). The titanium metal foil was used as a reference as the oxidation state of the Ti–C titanium present in the center of the MXene flakes also should be zero (see the Supporting Information). TiO\(_2\) was used as the other reference as the oxidation of the Ti\(_3\)C\(_2\)T\(_x\) MXene flakes by oxygen and/or water eventually should yield TiO\(_2\) and carbon (see the Supporting Information).\(^{15,18,21}\) As the oxidation of titanium to TiO\(_2\) is a four-electron oxidation reaction, one would, however, also expect to see intermediate titanium oxidation states such as Ti(II) and Ti(III) for the \( T_x^- \text{Ti}^- \text{C} \) titanium present on the surfaces of the Ti\(_3\)C\(_2\)T\(_x\) flakes. In Figure 3, it is seen that the XAS spectrum of the pristine Ti\(_3\)C\(_2\)T\(_x\) electrode differed substantially from both reference spectra. In the pristine Ti\(_3\)C\(_2\)T\(_x\) XAS spectrum, it was thus not possible to identify any contributions from the three characteristic pre-edge peaks seen in the TiO\(_2\) XAS spectrum. Moreover, the positions of the edges were also substantially different for the reference spectra and the pristine Ti\(_3\)C\(_2\)T\(_x\) electrode. As the energy position of the XAS edge generally is correlated to the oxidation state of the element, the Ti K-edge positions for the Ti\(_3\)C\(_2\)T\(_x\) electrodes were determined from the maximum of the first derivative of normalized intensity with respect to incident energy (see Table S2). This indicated that the (average) oxidation state of the titanium in the Ti\(_3\)C\(_2\)T\(_x\) MXene electrodes was higher than zero (i.e., higher than that for the titanium foil) but lower than +IV (i.e., lower than that for the TiO\(_2\) reference sample). As the position of the Ti K-edge was similar for all samples (i.e., the pristine and the cycled electrodes), it can also be concluded that there was no significant change in the (average) Ti oxidation state during the electrochemical cycling. The only sample that showed a considerable Ti K-edge shift (of +1.5 eV compared to that for the pristine Ti\(_3\)C\(_2\)T\(_x\) electrode) was a freestanding electrode that had been left in a stirred open beaker containing deionized water for 24 h at room temperature.

The XAS results hence indicate that the (average) titanium oxidation state in the pristine Ti\(_3\)C\(_2\)T\(_x\) electrode was higher than zero but lower than +IV and that the main part of titanium was redox-inactive during the cycling of the electrodes. This is in good agreement with the low capacities seen during the cycling of the pristine MXene-based electrodes (see Figure 1). As is discussed in more detail in the Supporting Information, these findings support the hypothesis that the \( T_x^- \text{Ti}^- \text{C} \) surface species on the MXene flakes in the pristine electrode contained oxidized titanium (e.g. Ti(II), Ti(III), and/or Ti(IV)). The XAS data also indicate that the pristine electrode did not contain substantial amounts of TiO\(_2\), that is, the expected surface oxidation to TiO\(_2\) and carbon was far from complete. The latter could be explained by the actions taken to minimize the exposure of the pristine sample to air and water, as well as the difficulties associated with the oxidation of each individual flake, particularly when there is restacking of the flakes. This slow oxidation hypothesis is further supported by the positive shift in the Ti K-edge (indicating an increase in the Ti oxidation state) seen for the electrode exposed to water and air for 24 h.

The surfaces of the Ti\(_3\)C\(_2\)T\(_x\) pristine and cycled electrodes were also studied using XPS and HAXPES, as can be seen in Figures 4 and S4, respectively. The Ti 2p XPS spectra for the electrodes were deconvoluted (see Tables S3 and S4 in the Supporting Information) based on the reference data for Ti MXene species (i.e., Ti–C and Ti bonded to the surface termination groups such as \(-\text{OH}, \text{=O}, \text{and } \text{F}\) as well as TiO\(_2\) surface oxide.\(^{19,22}\) All Ti 2p spectra showed asymmetric peak shapes, indicating that the metallic type of bond was predominant. For each sample, the peaks assigned to the Ti–C titanium surface species had higher relative intensities than those for the Ti–C component in the XPS spectra.
compared to that in the HAXPES spectra (compare Figures 4 and S4). This is not surprising as the spectra measured with lower photon energies (i.e., XPS) generally show relatively more of the surface components compared to measurements using higher photon energies (i.e., HAXPES). The results, hence, indicate that the Ti species containing Ti(II), Ti(III), and Ti(IV) were located closer to the surface than the Ti–C species. The surface species therefore most likely included titanium surface species such as C−Ti−O, C−Ti−OH, and C−Ti−F despite the fact that these Ti 2p peaks have been assigned to the Ti−C environment in some publications.15,19,24

The O 1s spectra were deconvoluted using seven different peaks. Going from lower to higher binding energies, the three first O 1s peaks were assigned to two C−Ti−O species, denoted C−Ti−O(I) and C−Ti−O(II)/LiOH as well as the TiO2 and TiO2−xFx peaks.23,25 These peaks are followed by the C−Ti−OH peak at ~532.1 eV and the peaks assigned to organic species: C−O, C−O, and O−C=O, adsorbed on the surface or as a part of the organic SEI. Lastly, the two peaks at even higher binding energies could be explained by the presence of weakly adsorbed water on the surface as well as inorganic fluorinated SEI components, for example, Li2POF2.26,27

By comparing the relative intensities of the Tn−Ti−C surface species to those of the Ti−C peak (see Table S3 in the Supporting Information), it is clear that the relative intensity of the Tn−Ti−C surface species (containing Ti(II), Ti(III), and Ti(IV)) decreased when the electrode was lithiated (i.e., reduced). This indicates that the lithiation resulted in a reduction of the Tn−Ti−C titanium surface species. Note also that the relative intensities of the Tn−Ti−C surface species increased during the subsequent delithiation (i.e., oxidation) step. These changes in the spectra support the hypothesis that the observed capacity (see Figure 1) stemmed from redox reactions involving Tn−Ti−C titanium surface species. In the carbon spectra, the bulk carbon peak (due to Ti−C) was found at the lowest binding energy. At higher binding energies, carbon bonded to oxygen was found, indicating the presence of oxidized carbon species. Such species are, however, commonly found in battery electrodes and battery electrolytes.28

The main differences between the spectra for the electrodes cycled to different potentials included (i) a change in the Ti 2p intensity ratio between the Tn−Ti−C surface species and Ti−C (see Table S3 in the Supporting Information), (ii) a change in the C 1s intensity ratio between the bulk Ti−C component and the surface components, and (iii) a change in the O 1s intensity ratio between the C−Ti−O(I) peak and the surface oxygen peak components. The changes in the C 1s and O 1s spectra (see the peak fitting results in Tables S5 and S6 in the Supporting Information) were mainly ascribed to the reduction of the electrolyte during the lithiation, resulting in the formation of a SEI layer on the electrode surface. This layer was to a large extent lost upon subsequent delithiation, most likely due to SEI dissolution.29,30

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Figure 4. Ex situ XPS Ti 2p (left), O 1s (middle), and C 1s (right) spectra for a pristine Ti3C2Tx MXene electrode, an electrode exposed to the electrolyte under open-circuit conditions, an electrode lithiated (i.e., reduced) to 0.3 V vs Li+/Li on the first cycle as well as an electrode delithiated (i.e., oxidized) to 2.3 V vs Li+/Li on the first cycle, respectively.

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formed on the MXene electrodes, additional SEI was consequently formed on each cycle. An estimation of the current due to the SEI formation process (see the Supporting Information), however, suggested that this current should have been of minor importance compared to that due to the reduction of the oxidized titanium surface species. The changes observed in the Ti 2p spectra, on the other hand, indicated the presence of redox reactions involving the $\text{Ti}^{\text{II}}$-$\text{Ti}^{\text{III}}$-$\text{Ti}^{\text{IV}}$ surface species (containing Ti(II), Ti(III), and Ti(IV)). The relative ratios between the main peaks in Ti 2p, O 1s, and C 1s are summarized in Table S3 in the Supporting Information. The C-$\text{Ti}$-$\text{O}(\text{I})$ [$\text{O 1s}$]/Ti-$\text{C}$ [Ti 2p] ratios were equal to 0.67, <0.01, and 0.76 for the soaked pristine, reduced (i.e., lithiated), and oxidized (i.e., delithiated) electrode, respectively. As a higher ratio was found for the delithiated (i.e., oxidized) electrode compared to both the soaked pristine and the reduced electrode, it is reasonable to assume that the $\text{T}_x$-$\text{Ti}$-$\text{C}$ surface species on the MXene flakes were redox-active, whereas Ti-$\text{C}$ in the center of the flakes should have remained electro-inactive.

Influence of the Degree of Surface Oxidation on the Electrochemical Performance. It is well known that the exposure of $\text{Ti}_3\text{C}_2\text{T}_x$ to oxygen and/or water results in the oxidation of titanium, eventually yielding TiO$_2$ anatase and carbon.$^{15,18,21}$ The surfaces of the generated carbon can then also be oxidized by oxygen to give oxygen-containing surface groups (i.e., oxidized carbon surface species). While the exposure of the $\text{Ti}_3\text{C}_2\text{T}_x$ material to air and water generally is minimized to prevent this oxidative degradation of the material, the results discussed above indicate that higher capacities should in fact be obtained when the $\text{T}_x$-$\text{Ti}$-$\text{C}$ surface species have been formed on the surface of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes. As the oxidation of Ti to TiO$_2$ is a four-

![Figure 5](https://doi.org/10.1021/acsomega.2c05785)
Figure 6. (a) Lithiation (i.e., reduction) and delithiation (i.e., oxidation) capacities, as well as the (b) associated Coulombic efficiencies, as a function of the cycle number. These values were evaluated from the voltammograms in Figure 5 for a pristine electrode and the electrodes prepared from a suspension of Ti$_3$C$_2$T$_x$ in deionized water maintained in an open vial (i.e., in contact with air) for 7, 14, and 28 days, respectively.

electron process, the $T_x$−Ti−C species may then include a mixture of Ti(II), Ti(III), and Ti(IV) species depending on the oxidation conditions. For a sufficiently long oxidation time, TiO$_2$ should, however, mainly be seen. This means that the capacity of the electrode should depend on the degree of oxidation of the $T_x$−Ti−C species present on the surfaces of the MXene flakes. The highest capacity should then be obtained with Ti(IV) species such as TiO$_2$ present on the surfaces of the MXene flakes. Experiments were therefore designed to assess this hypothesis.

To investigate the influence of the degree of oxidation of the Ti$_3$C$_2$T$_x$ electrodes on their capacities, a suspension of the Ti$_3$C$_2$T$_x$ MXene in water was kept in an open vial (i.e., in contact with air) during a period of 28 days. On the 7th, 14th, and 28th days of the experiment, 5 mL of the suspension with a concentration of between 3 and 4 mg/mL was taken from the vial with a syringe and vacuum-filtrated to obtain a freestanding film electrode which was then subjected to voltammetric cycling (see Figure 5). In addition to the abovementioned electrodes, a pristine electrode was also studied. Unlike that in Figure 1, a low cutoff limit of 0.8 V versus Li$^+$/Li was used to avoid complications due to the potential conversion reaction involving any TiO$_2$ formed on the surface of the electrode (i.e., TiO$_2$ + 4Li$^+$ + 4e$^-$ = Ti + 2Li$_2$O). As explained in the Supporting Information, this conversion reaction would be expected to have a standard potential of about 0.6 V versus Li$^+$/Li. As seen in Figure 5, all the obtained voltammograms featured a lithiation (i.e., reduction) peak at about 1.7 V versus Li$^+$/Li and a delithiation (i.e., oxidation) peak at about 2 V versus Li$^+$/Li. As this is in very good agreement with the results seen in Figure 1b, it is reasonable to assume that there was no significant influence of the abovementioned conversion reaction on the electrochemical performance of the electrode. More importantly, the results in Figure 5 clearly show that the lithiation (i.e., reduction) and delithiation (i.e., oxidation) peak currents increased with the number of days during which the Ti$_3$C$_2$T$_x$ material was exposed to water and air in the open vial. The capacity of the Ti$_3$C$_2$T$_x$ electrode thus increased when the surfaces of the Ti$_3$C$_2$T$_x$ flakes were oxidized. Here, it should also be noted that the potentials of the reduction and oxidation peaks are in good agreement with those generally seen for the lithiation and delithiation of TiO$_2$.\textsuperscript{31,32} It is therefore reasonable to assume that the increasing electrode capacity seen in Figure 5 was due to an increasing concentration of more oxidized titanium species, such as TiO$_2$, on the surfaces of the Ti$_3$C$_2$T$_x$ flakes.

The trends seen in the voltammetric data can be more clearly seen in the obtained specific capacities and Coulombic efficiencies, presented in Figure 6. The average capacity thus increased with the time the Ti$_3$C$_2$T$_x$ suspension was exposed to water and air. For the pristine electrode and the electrode based on the Ti$_3$C$_2$T$_x$ suspension exposed to water and air for 7 days, the capacities remained relatively constant, yielding about 21 and 50 mA h g$^{-1}$ after 25 cycles, respectively. In the pristine electrode case, the lithiation and delithiation capacities, however, increased somewhat during the cycling, whereas the lithiation and delithiation capacities for the 7 day electrode reached a maximum (i.e., 60 and 57 mA h g$^{-1}$, respectively) on the fourth cycle. The lithiation capacities for the 14 and 28 day electrodes, on the other hand, decreased from 89 mA h g$^{-1}$ on the first cycle to 68 mA h g$^{-1}$ after 25 cycles for the 14 day electrode. The corresponding values for the 28 day electrode were 106 and 74 mA h g$^{-1}$. These results thus indicate that the electrochemical performances of the Ti$_3$C$_2$T$_x$ electrodes depended not only on their exposure to air and water but also on their cycling history. Still, when comparing the obtained capacities with that of about 165 mA h g$^{-1}$ for the lithiation of anatase TiO$_2$ to Li$_x$TiO$_2$, assuming $x = 0.5$,\textsuperscript{33} it is immediately clear that only a fraction of the MXene flakes could have been oxidized to TiO$_2$. As it is reasonable to assume that there was some restacking of the Ti$_3$C$_2$T$_x$ flakes after their manufacturing or during the manufacturing of the electrodes, this could have slowed down the oxidation rate of the MXene flakes to yield a lower electrode capacity. This could also explain why relatively long times (i.e., up to 28 days) were needed to oxidize the Ti$_3$C$_2$T$_x$ suspension despite the fact that the suspension was in contact with both oxygen and water. The results hence indicate that while the surfaces of the Ti$_3$C$_2$T$_x$ flakes underwent oxidation involving the formation of $T_x$−Ti−...
C species containing oxidized titanium, for example, TiO$_2$, the electrode still contained significant amounts of electro-inactive material even after an exposure to water and air for 28 days.

The surfaces of the electrodes used in the abovementioned oxidation experiment were also studied using XPS (see Figure 7). In this case, there should not have been any significant self-

Figure 7. Ti 2p XPS spectra for a pristine freestanding Ti$_3$C$_2$T$_x$ film as well as films prepared from an aqueous Ti$_3$C$_2$T$_x$ suspension exposed to air for 7, 14, and 28 days, respectively. The corresponding C 1s and O 1s spectra are shown in Figure S5.

However, important to note that the XPS data confirm that the pristine Ti$_3$C$_2$T$_x$ contained very little TiO$_2$ and TiO$_2$-F$_x$, most likely as particular care was taken not to expose the Ti$_3$C$_2$T$_x$ MXene to air (i.e., oxygen). The results hence indicate that the capacity of a pristine Ti$_3$C$_2$T$_x$ MXene electrode should be too low to be of practical importance for use as a negative electrode in lithium-ion batteries.

Influence of Water on the Irreversible Capacity. As can be seen in Figure 1, the first lithiation (i.e., reduction) capacity was much larger than both the corresponding oxidation capacity and the subsequent reduction capacities. This clearly indicates the presence of a significant irreversible capacity. What could this irreversible capacity be due to? There are at least two effects that should be considered here, that is, reduction of adsorbed water and SEI formation. While SEI formation should be seen at potentials below about 1 V versus Li$^+/\text{Li}$, the onset of the reduction of adsorbed water should be seen at higher potentials, for example, 1.6 V versus Li$^+/\text{Li}$. Water confinement between the MXene flakes is in fact a known phenomenon. It is also well known that the reduction of adsorbed water can give rise to large irreversible capacities for TiO$_2$ electrodes and that it can be difficult to remove water completely (see Discussion in the Supporting Information). As there should be oxygen on the surfaces of the Ti$_3$C$_2$T$_x$ flakes, it is reasonable to expect a similar behavior for the Ti$_3$C$_2$T$_x$ electrodes used here. Experiments were therefore conducted involving constant current and voltammetric cycling of Ti$_3$C$_2$T$_x$ electrodes, which either had been dried at 300 °C for 16 h in a vacuum or not at all (see Figures 8 and 9). While the irreversible capacity due to SEI formation (i.e., the reduction of the electrolyte), in principle, should be the same in both cases, a lower irreversible capacity due to the reduction of water should clearly be expected for the electrode dried at 300 °C (see also the Supporting Information).

A comparison of the voltammograms in Figure 9 clearly shows that a larger irreversible capacity was seen for the nondried electrode. It can also be seen that only a relatively
small part of the irreversible capacity was due to reduction below 1 V versus Li+/Li (Figure 9). The latter suggests that the main part of the irreversible capacity was due to the reduction of adsorbed water. It should also be noted that all the voltammograms in Figures 8 and 9 except the first cycles feature a broad reduction peak at about 1.5–1.6 V vs Li+/Li as well as a broad oxidation peak at about 2 V versus Li+/Li in analogy with the voltammograms seen in Figures 1 and 5.

Figure 9. Cyclic voltammograms recorded between 0.3 and 3 V vs Li+/Li at a scan rate of 0.1 mV s⁻¹ for a (a) freestanding Ti₃C₂Tx electrode heat-treated for 16 h at 300 °C under vacuum and a (b) nondried freestanding Ti₃C₂Tx electrode.

Figure 10. Ti 2p (left), O 1s (middle), and C 1s (right) XPS spectra for Ti₃C₂Tx electrodes dried at 300 °C for 16 h in a vacuum. The top spectra were obtained with a pristine sample, while the spectra below were obtained with a sample soaked in the electrolyte at the OCP. The two lower sets of spectra were obtained with an electrode that was first lithiated to 0.3 V vs Li+/Li and then delithiated to 2.3 V vs Li+/Li, respectively, on the first cycle.
The performance of the electrode dried at 300 °C for 16 h (see Figures 8 and 9) can also be compared with that seen in Figure 1 for an electrode dried at 120 °C for 16 h, although it should be noted that different cycling windows were used in these two experiments. The lower first-cycle lithiation capacity seen for the electrode dried at 300 °C can be explained by a smaller contribution from the reduction of adsorbed water. The Coulombic efficiencies were also generally higher for the smaller contribution from the reduction of adsorbed water.

The lower first-cycle lithiation capacity was smaller for the more extensively dried electrode. While the irreversible capacity on the first cycles could be due to both the reduction of adsorbed water and that of the electrolyte giving rise to an SEI layer, the results indicate that the largest effect was due to adsorbed water.

To further study the effect of the drying step on the electrodes, XPS studies were made on three Ti₃C₂Tₓ electrodes dried at 300 °C for 16 h, where one electrode remained pristine, one was merely soaked in the electrolyte, while the third electrode was subjected to first-cycle lithiation (i.e., reduction) and delithiation (i.e., oxidation) to 0.3 and 2.3 V versus Li⁺/Li, respectively. The results for the pristine electrode (see Figure 10) show that the drying of the electrode at 300 °C only resulted in minor changes in the Ti 2p spectrum, seen as an increase in Ti−C surface species relative to the Ti−C peak (compare Figures 4 and 10). Larger changes were, on the other hand, observed in the O 1s and C 1s regions. In the O 1s spectrum, the relative intensities of the C−Ti−OH and C=O, O−C=O, and O=C=O peaks were substantially increased, while the H₂O (ads) intensity decreased compared to the C−Ti−O(1) peak. This indicates that the drying at 300 °C resulted in a Ti₃C₂Tₓ termination group rearrangement, loss of water, and buildup of oxygen-rich surface species. At the same time, the C 1s spectrum showed a large increase of the C=O species and a small decrease of C−O−C and C−OH relative to the C 1s Ti−C peak as well as a probable depression of the C−F peak. It is therefore reasonable to assume that during the drying process at 300 °C under vacuum, water adsorbed on the surface of the Ti₃C₂Tₓ electrode reacted to yield titanium oxides as well as oxidized carbon and oxygen-containing species on the surface of the electrode. This is not unexpected as this reaction also should take place at room temperature, albeit at a lower rate.

For the soaked electrode (Figure 10), no major changes were seen in the Ti 2p spectrum compared to that for the pristine electrode. There was, however, a relative increase in C=O and O−C=O peaks in the O 1s spectrum and C=O peak in the C 1s spectrum. These changes were most likely caused by the adsorption of electrolyte degradation products present in the electrolyte due to the reaction of the electrolyte with the lithium metal electrode.

After lithiation (i.e., reduction) to 0.3 V versus Li⁺/Li on the first cycle, lower intensities were seen for the Ti−C surface species (i.e., the Ti(II), Ti(III), and Ti(IV) species) compared to that for the pristine electrode, while the intensity of the Ti−C peak remained approximately the same. As decreased intensities likewise were seen for titanium containing oxygen and carbon species, the results demonstrate that the lithiation involved a reduction of Ti−C species. From the O 1s and C 1s spectra, it can further be concluded that the lithiation step resulted in a thicker overlayer composed of C−O−C− and C−OH− containing species due to the formation of an SEI layer.

After the subsequent delithiation (i.e., oxidation) to 2.3 V versus Li⁺/Li, the relative intensity of the Ti−C surface species generally increased relative to that of the Ti−C peak in the Ti 2p region. A corresponding increase in the intensities for the Ti−C species was seen in the O 1s region. An increase in the intensity of the TiO₂ and TiO₂−F, peaks in the Ti 2p spectrum was, however, not seen. This indicates that the extent of oxidation of titanium to Ti(IV) was limited during the delithiation step, most likely due to the formation of a surface layer of titanium species with lower oxidation states acting as a passivating layer. An analogous effect was previously described for SnO₂ electrodes where a complete reformation of the initial SnO₂ was very difficult to obtain during the delithiation step. Such problems yield lithiation (i.e., reduction) capacities which are significantly larger than the corresponding delithiation (i.e., oxidation) capacities during the initial part of cycling, in good agreement with the results presented above.

As is shown in Figure S7, XAS experiments were also conducted on the soaked, lithiated, and delithiated electrodes, complementary to the XPS experiments discussed above. The XAS results indicated that there was a small change in the e₉/t₉ ratio. This suggests a small change in the titanium oxidation state at the surface (i.e., within a depth of a few nanometers) of the electrodes during the first cycle, in good agreement with the XPS results discussed above.

**What Determines the Reversible and Irreversible Capacity of the Ti₃C₂Tₓ Electrodes?** The results discussed above demonstrate that the Ti−C species present on the surfaces of the Ti₃C₂Tₓ flakes give rise to the observed reversible capacity. These Ti−C species contain oxidized titanium (i.e., Ti(II), Ti(III), and/or Ti(IV) species) that can undergo reduction during the lithiation step and oxidation during the subsequent delithiation step. The shapes of the cyclic voltammograms and chronopotentiograms, as well as the Nyquist plots shown in Figure S8, further indicate that the different redox reactions overlapped during the reduction and oxidation steps. Redox-active Ti−C surface species should in fact have been formed already during the manufacturing of the MXene flakes as a result of the following redox reaction: Ti₃C₂ + 2H₂O = Ti₃C₂(OH)₂ + H₂. In this reaction, water is clearly reduced to yield hydrogen. This means that there must be an accompanying oxidation involving either Ti or C. As Ti is easier to oxidize than carbon, Ti(II), Ti(III), and/or Ti(IV)−containing Ti−C species are formed on the surface of the MXene flakes, while the center of the flakes still contains titanium only bonded to carbon (i.e., the Ti−C titanium). The titanium bonded to Cl, F, and O on the surface of the MXene flakes should thus have an oxidation state higher than zero, whereas the titanium present in Ti₃Cₓ should, as in Ti−C in the center of the Ti₃Cₓ flakes, be elemental. The oxidation state of the titanium in the Ti−C surface species should, however, also depend on the time the MXene flakes are exposed to oxygen, water, or other oxidizing species. This explains the increase in the capacity seen when exposing the Ti₃C₂Tₓ flakes to water and oxygen for increasing times discussed above. The fact that the Ti−C surface species would be oxidized to different degrees during the manufacturing and electrode preparation procedures is most likely one important reason for the large variation in the reversible capacities reported when Ti₃C₂Tₓ is used as a negative electrode material for lithium-ion batteries.

The capacities of Ti₃C₂Tₓ MXene electrodes will clearly also depend on the extent of restacking of the MXene flakes, as this
will hinder the oxidation of the surfaces of the MXene flakes. When using Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} as a negative electrode material for lithium-ion batteries, it is, therefore, essential to make sure that all MXene flakes remain in contact with the electrolyte. To obtain a high degree of oxidation of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} material, the surface area of the material clearly needs to be maintained as large as possible. The ideal Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrode should therefore contain a large number of individual Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene flakes, where each flake should have a Ti−C core coated with T\textsubscript{3}−Ti−C surface species, according to the schematic illustration in Figure 2. In this context, it should also be pointed out that it would be more appropriate to refer to the redox reactions involving the T\textsubscript{3}−Ti−C surface species as surface-confined redox reactions rather than conventional intercalation reactions.

The results further suggest that the previously predicted reduction of the elemental carbon present in Ti\textsubscript{3}C\textsubscript{2}F\textsubscript{2}\textsubscript{r} or Ti\textsubscript{3}C\textsubscript{2}(OH\textsubscript{2}) to yield Ti\textsubscript{3}C\textsubscript{2}Li\textsubscript{2}, Ti\textsubscript{3}C\textsubscript{2}FeLi\textsubscript{2}, or Ti\textsubscript{3}C\textsubscript{2}(OH\textsubscript{2})Li\textsubscript{2} (e.g., Ti\textsubscript{3}C\textsubscript{2}(OH\textsubscript{2}) + 2e\textsuperscript{−} + 2Li\textsuperscript{+} = Ti\textsubscript{3}C\textsubscript{2}(OH\textsubscript{2})Li\textsubscript{2}) do not appear to take place at potentials above 0 V versus Li\textsuperscript{+}/Li\textsuperscript{−}, despite the fact that their standard potentials have been calculated\textsuperscript{13} to be 0.62, 0.56, and 0.14 V versus Li\textsuperscript{+}/Li\textsuperscript{−}, respectively. As the titanium in Ti\textsubscript{3}C\textsubscript{2} is elemental, this means that Ti\textsubscript{3}C\textsubscript{2} should be electrochemically inactive (see the discussion in the Supporting Information) during the lithiation step. It is therefore inappropriate to use the theoretical capacities (i.e., 320, 130, and 67 mA h g\textsuperscript{−1}, respectively) for the abovementioned reactions in conjunction with the use of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} as a negative lithium-ion electrode material.

Even though the capacity of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes mainly stems from the presence of oxidized T\textsubscript{3}−Ti−C species, it is still very difficult to fully identify the redox reactions involved. The reason for this is that there can be many different oxidized titanium species yielding overlapping redox reactions (see the list of possible redox reactions in the Supporting Information). Some examples of possible redox reactions can be found in the Supporting Information. It is, however, clear that the full oxidation of the T\textsubscript{3}−Ti−C surface species should result in the formation of TiO\textsubscript{2} and carbon. This means that the capacities of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes should approach those of the corresponding TiO\textsubscript{2} electrodes. Here, it should be noted that the capacity for a TiO\textsubscript{2} electrode is typically measured between about 1.2 and 3 V versus Li\textsuperscript{+}/Li\textsuperscript{−} rather than between 0 and 3 V versus Li\textsuperscript{+}/Li\textsuperscript{−}. As the redox reaction is only assumed to involve a reduction of Ti(IV) to Ti(III) according to TiO\textsubscript{2} + xe\textsuperscript{−} + xLi\textsuperscript{+} = Li\textsubscript{x}TiO\textsubscript{2}. As x typically is equal to about 0.5, the attainable capacity for a TiO\textsubscript{2} electrode is then typically around 170 mA h/g.\textsuperscript{31,32} Higher capacities should, however, be seen when cycling to lower potentials than 1.2 V versus Li\textsuperscript{+}/Li\textsuperscript{−}. The capacity contribution due to the presence of oxidized carbon surface species is more difficult to estimate as these typically yield a pseudocapacitive behavior rather than peaks that can be seen in the voltammograms. The present results, nevertheless, indicate that the main capacity of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes stemmed from redox reactions involving oxidized titanium surface species. While this is in good agreement with the findings for oxidized Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes,\textsuperscript{35,16,18} the general recommendation, however, still appears to be to avoid the oxidation of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes as much as possible. One reason for the latter recommendation is that the full oxidation to TiO\textsubscript{2} and carbon typically results in the disintegration of the electrode material.\textsuperscript{18,58}

A large part of the irreversible capacity seen on the initial cycles most likely stemmed from the reduction of water adsorbed on the surface of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} material, in analogy with the findings for TiO\textsubscript{2} electrodes.\textsuperscript{31} As the present results show that it is very difficult to remove this water, great care should be taken when drying the material prior to its use in nonaqueous batteries. The fact that adsorbed water most likely will contribute to the lithiation capacity during the initial part of the cycling should naturally be considered when reporting the capacities for the material. The present results indicate that the irreversible capacity contribution from the formation of the SEI typically is less important than that due to the reduction of the adsorbed water. While an incomplete oxidation to TiO\textsubscript{2} during the delithiation (i.e., oxidation) step likewise can contribute to the irreversible capacity as indicated by the XPS results, it is difficult to quantify this effect mainly due to the large influence from the reduction of the adsorbed water.

### CONCLUSIONS

The present results demonstrate that the reversible capacity seen for freestanding Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene films, when used as negative electrodes in lithium-ion batteries, mainly stems from the presence of oxidized titanium and carbon species on the surfaces of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene flakes. Spontaneous oxidation of the flakes due to contact with air and/or water was demonstrated to result in an increased concentration of oxidized surface species, yielding an increased reversible capacity. The previously suggested reduction of the elemental carbon in Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} predicted to take place below about 0.6 V versus Li\textsuperscript{+}/Li\textsuperscript{−}, could not be verified experimentally. As the Ti−C titanium, present in the center of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes, should be elemental, this titanium would not be expected to contribute to the lithiation (i.e., reduction) capacity at potentials between 3 and 0 V versus Li\textsuperscript{+}/Li\textsuperscript{−}. This is in excellent agreement with the obtained electrochemical, XPS, HAXPES, and XAS results. As a result, pristine Ti\textsubscript{3}C\textsubscript{2} is consequently not a promising negative electrode material for lithium-ion batteries. The capacity of electrodes composed of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene flakes hence depends on the oxidation state of the titanium present in the T\textsubscript{3}−Ti−C surface species. In contrast to the general recommendations to minimize the contact between the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene and oxygen and water, the attainment of a high degree of oxidation of the T\textsubscript{3}−Ti−C surface species is essential when using Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene-based negative electrodes for lithium-ion batteries.

The significant irreversible capacity seen for the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene electrodes during the initial cycles can mainly be ascribed to the reduction of adsorbed water, although there should also be contributions from SEI formation and the inability to fully reform the oxidized titanium surface species on the delithiation (i.e., oxidation) steps. To eliminate the influence of the residual water, more attention should be paid to drying the electrodes prior to their use in lithium-ion batteries. The present results show that water was still present in the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes even after drying for 16 h at 300 °C in a vacuum.

As oxidized titanium and carbon surface species will be formed gradually on the surface of the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes when these are exposed to air and/or water, the reversible capacity of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} electrodes should depend on the exposure time and the experimental conditions employed. Since the Ti−C, situated underneath the T\textsubscript{3}−Ti−C surface layer, is electrochemically inactive (see the discussion in the Supporting Information), it is expected that the irreversible capacity is mainly due to the oxidation of the Ti−C species resulting in the formation of TiO\textsubscript{2}.
The capacity of Ti$_3$C$_2$T$_x$ electrodes should depend on the degree of oxidation of the T$_x$–Ti–C surface layer, the porosity of the electrode, as well as the degree of restacking of the Ti$_3$C$_2$T$_x$ MXene flakes in the electrode. This means that the capacity of Ti$_3$C$_2$T$_x$ MXene-based electrodes should depend on the procedures used to manufacture, wash, store, and dry the obtained material prior to its use as a negative electrode material in lithium-ion batteries. This can explain the significant variation in the reversible capacities seen in the literature. As the full oxidation of the titanium in Ti$_3$C$_2$T$_x$ should result in the formation of TiO$_2$ (and carbon), the reversible capacities for such Ti$_3$C$_2$T$_x$ electrodes should be comparable to those obtained for TiO$_2$ electrodes. When using Ti$_3$C$_2$T$_x$ as a negative electrode material in lithium-ion batteries, Ti$_3$C$_2$T$_x$ should consequently be subjected to a pretreatment step, resulting in the formation of Ti(II), Ti(III), and Ti(IV) surface species.

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